ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS

Noelia Ramírez González

Dipòsit Legal: T-1454-2011

ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS

Noelia Ramírez González

DOCTORAL THESIS

Supervised by

Dr. Francesc Borrull and Dra. Rosa Maria Marcé

Departament de Química Analítica i Química Orgànica

UNIVERSITAT ROVIRA I VIRGILI

Tarragona
2011

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

UNIVERSITAT ROVIRA I VIRGILI
Departament de Química Analítica
i Química Orgànica

El Dr. FRANCESC BORRULL i BALLARIN, Catedràtic del Departament de Química Analítica i Química Orgànica de la Facultat de Química de la Universitat Rovira i Virgili, i

La Dra. ROSA MARIA MARCÉ i RECASENS, Catedràtica del Departament de Química Analítica i Química Orgànica de la Facultat de Química de la Universitat Rovira i Virgili,

FEM CONSTAR:
Que la present Tesi Doctoral, que porta per títol: "ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS", presentada per NOELIA RAMÍREZ GONZÁLEZ per optar al grau de Doctor per la Universitat Rovira i Virgili, ha estat realitzada sota la nostra direcció, a l'Àrea de Química Analítica del Departament de Química Analítica i Química Orgànica d'aquesta universitat, i que tots els resultats presentats són fruit d'experiències realitzades per l'esmentada doctoranda.

I, per a que consti, expedim aquest certificat a Tarragona, 25 de maig de 2011.

Dr. Francesc Borrull i Ballarín

Dra. Rosa Maria Marcé i Recasens

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

En la vida arriba un moment on tot és conegut i tot sembla definit. Quan arriba aquest moment dues són les possibles opcions: o continuar gaudint d'aquest estatus al que tant ens ha costat arribar, o plantejar-nos nous reptes. Aquesta segona opció és la que jo vaig decidir prendre fa quatre anys i en aquest nou camí desconegut moltes són les persones que m'han ajudat i a les que en aquestes línies vull agrair el seu recolzament.

En primer lloc vull donar el meu més sincer agraïment als meus directors de Tesi, el Dr. Francesc Borrull i la Dra. Rosa Maria Marcé. Gràcies per donar-me l'oportunitat de formar part del vostre grup d'investigació i, gràcies per la vostra dedicació, els valuosos consells i el suport durant aquests anys. Gràcies per fer possible aquest somni. Li dec un especial agraïment al Siscu, perquè la confiança que va dipositar en mi em va obrir aquesta possibilitat que pensava que estava ja tancada.

Vull agrair l'atenció, l'ajuda i els consells de les Dres. Carme Aguilar, Eva Pocurull, Marta Calull, Núria Fontanals i Sandra Peñalver. També vull donar les gràcies al personal del Departament: Avelina, Eulàlia, Olga i Tere que tant m'han ajudat amb el dia a dia, i al Dr. Joan Ferré pels ànims que em va donar per fer aquest pas i la seva valuosa ajuda durant aquests anys.

En aquest temps he tingut la sort també de tenir els millors companys de viatge, per això vull agrair els bons moments passats amb els meus companys de laboratori, tant els ja hi éreu abans que jo i em vau acollir i ajudar en els primers moments, com els que vàreu arribar després. Especialment vull donar les gràcies a aquells amb els que he passat més temps. Gràcies Antonio, Blanca, Jasper, Jordi, Judith, Laura Mata, Laura Vallecillos, Maria, Marta Pedrouzo, Mireia, Montse, Núria Gilart, Paula, Pol, Sílvia Echevarría i Toni. Especialment voldria agrair a la Rosa la seva paciència i dedicació durant els primers mesos, a l'Anna i la Dominika, amb les que he compartit alguna cosa més que ciència, a la Laura Ferreres, la Marta Palomo i la Sílvia Mariné pel recolzament en els últims temps. I com no, als que ja no puc anomenar companys sinó amics: Igor, Irene i Vero... gràcies per totes les estones que hem viscut junts i les que viurem en el futur.

Una part important d'aquest tesi s'ha realitzat en col·laboració amb l'Observatori de la Salut i Medi Ambient de la Generalitat de Catalunya. Vull agrair la col·laboració del seu Director, l'Enric Rovira, i especialment de l'Anna Cuadras per tota la seva dedicació i les hores que hem passat juntes analitzant dades i fent i refent articles. També vull donar les gràcies al Ferran i al Joan del Departament de Medi Ambient per la seva inestimable ajuda amb els mostrejos de contaminants atmosfèrics.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

I would like to thank Professor Ally C. Lewis and Dr. Jacqui Hamilton of the University of York for giving me the opportunity to take part of their research group and for their guidance and kind attention during my stay. I am especially grateful to Dr. Mustafa Özel for his valuable help during and after the stay. Thank you very much for your everyday help and for your friendship. I would also want to thank all the members of the Atmospheric research group for their kind help and for all the good moments that we have shared together. I would also not forget the good moments that I have spent with the people that I met in York, especially with Ana, Barbara, Eva, Javi, Olga and Pedro. But the most important person during my stay was my "landlady" Rose. I cannot find the words to say how happy I have been living with you.

Per acabar vull agrair als meus amics totes les trucades i els missatges de suport i el saber perdonar els pocs moments que els he pogut dedicar durant l'elaboració d'aquesta tesi. Amor, Dani, Isa, Joan, Núria i Pin gràcies a vosaltres i a les vostres famílies per fer-me costat en tot moment. Y a Elisa y Manolo por su apoyo isleño a "larga distancia", las llamaditas animosas de los domingos por la mañana y todas las aventuras vividas juntos por el mundo.

Però de tots els que d'alguna manera han format part d'aquest projecte, aquesta tesi la vull dedicar a les persones que porto més dins del cor:

A les meves "nenes" la Sara i la Laura, per estimar-me sense recances i ser una part tan important de la meva vida.

A mis padres, Ana y Pedro, por todo su cariño y su ayuda incondicional.

I sobretot al Carles perquè, aquesta tesi és també fruit del seu esforç i sacrifici personal. Pels caps de setmana sense sortir de casa, les nits en vetlla i totes les hores que l'he deixat sol. En paraules del poeta Virgili "qui amant ipsi sibi somnia fingunt" i aquest somni no s'hagués forjat mai sense ell al meu costat.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

Felix qui potuit rerum
cognoscere causas
Vergilius, s. I b.C.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

INDEX

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

1. INTRODUCTION

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

The World Health Organization (WHO) estimates that approximately a quarter of current human diseases occur because of prolonged exposure to environmental pollution [1]. Therefore, over the last three decades, there has been increasing global concern about the sources, sinks, distribution and pathways which release environmental contaminants into the global environment. Among these environmental contaminants, organic contaminants are of major interest because of their ubiquitous presence in the environment and their adverse effects on human health and the environment, even at very low levels. Some of these organic contaminants can occur naturally in the environment, such as isoprene and terpenes emitted from vegetation [2] or polycyclic aromatic hydrocarbons (PAHs) emitted during volcanic eruptions [3]. Although anthropogenic emissions are nowadays controlled by different legislation in most countries, and emissions of some contaminants have been banned or reduced, the major source of organic contaminants is through daily anthropogenic activities. The main pathway of anthropogenic organic contaminants into the environment is through emissions into atmospheric and aquatic environments.

The atmosphere is a complex mixture of gases, liquids and solids and organic contaminants can be distributed in all of the different phases. In recent decades, air quality has become a major concern as studies have shown the great impact of atmospheric pollution on environmental health [4]. Clean air is considered to be a basic requirement of human health and well-being. However, air pollution still constitutes a significant threat to health worldwide [5]. Globally, ca. 2.4 million people die each year from causes directly attributable to air pollution, with 1.5 million of these deaths attributed to indoor air pollution [6]. Therefore, exposure to air contaminants requires action by public authorities at national, regional and even international levels.

Anthropogenic emissions into the atmosphere include emissions related to fuel production, industrial and domestic combustion (fossil fuel and biofuel), transportation, waste disposal, industrial processes, solvent production and use and agriculture, among others. The main contaminants in outdoor atmospheres are ozone and aerosol precursors: nitrogen oxides (NO_x), carbon monoxide (CO), methane (CH_4), volatile organic compounds (VOCs), sulphur dioxide (SO_2), ammonia (NH_3) and particulate matter (PM) [4]. Although atmospheric emissions are controlled by current legislation and have decreased in recent years, other factors such as climate change can influence the occurrence and toxicity of atmospheric contaminants. For instance, increases in temperature may enhance the toxicity of contaminants and increase concentrations of tropospheric ozone regionally, but also increase rates of chemical degradation. While further research is needed, climate change coupled with air contaminant exposures may have potentially serious adverse consequences for human health in urban and polluted regions [7]. Furthermore, the atmosphere is considered the main long-range transport

medium of persistent organic pollutants (POPs), resulting in their widespread distribution, even in remote non-anthropogenic regions [8].

Indoor air quality has also been of great concern for many years because most people in developed countries spend up to 90% or their time indoors. Taking into account that each person inhales about 22 m^3 of air per day, inhalation of indoor air is potentially the biggest way in which humans are exposed to many different kinds of contaminants. VOCs are commonly-present in indoor air because they are emitted from a wide range of products used indoors such as paints, cosmetic products and building materials. VOCs are related to sick building syndrome and their concentration indoors is 2-5 times higher than outdoors [9]. Semi-volatile organic compounds (SVOCs) are also a major class of indoor contaminants, which mainly come from indoor sources, such as environmental tobacco smoke, cooking, cleaning or the use of personal care products [10]. However, indoor pollution can also be highly influenced by the outdoor levels of contaminants and, therefore, typical industrial organic contaminants can be also found in indoor environments [9-11].

Because of their nature, some VOCs and SVOCs can be present in indoor air and dust. Indoor dust is a complex mixture of inorganic and organic materials, such as skin tissues, hair fibres, mites and particulate matter that acts as a sink and repository of SVOCs. The study of the composition of indoor dust is of major concern because numerous contaminants have been found in this matrix in high concentrations and with a higher degree of persistence than in outdoor environments [12]. The organic contaminants bound onto house dust may enter the human body by inhalation of suspended particles, through non dietary ingestion, through ingestion of particles adhered to food, as well as by absorption through the skin [13]. Therefore, house dust is an important route of toxicant exposure, especially for children, who are estimated to ingest about 100 mg of indoor dust per day [14]. Determinations of compounds in house dust are not only a measure of indoor contamination, but may also provide valuable information for the assessment of human indoor exposure.

As well as clean air, free access to clean water is a fundamental human right. In most countries, the direct emissions of organic contaminants into environmental waters are controlled by water pollution policies. However, one of the most important sources of anthropogenic emissions to environmental waters is through industrial and municipal waste waters. The use of waste water treatment plants (WWTPs) has drastically reduced the discharges of contaminants. After the use or intake by humans, thousands of organic chemicals are flushed down drains and into sewer systems before arriving at the WWTPs. They are then dispersed through rivers and seas to other environmental waters, including aquifers, estuaries and marine systems. Therefore, the efficiency with

which WWTPs can remove the organic contaminants is very important. However, common waste water treatment methods are not efficient at removing some organic contaminants. These contaminants are released through WWTP effluents into the aquatic environment [15]. Therefore, WWTPs are a major pathway of organic contaminants into environmental waters [16]. In order to improve the removal, some advanced tertiary treatments can be applied including advanced oxidation processes, membrane processes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis), or adsorption into sorbents, such as granular activated carbon.

Besides the partial removal of some organic contaminants, degradation products more oxidized and sometimes more toxic than their respective precursors can be formed during WWTP abiotic and biotic processes and released into the environment through WWTP effluents [17]. Additionally, a major pathway of removal of the more apolar contaminants is through their adsorption into sewage sludge [15]. Sewage sludge can also be reused, for instance as manure in agriculture, creating another pathway to re-introduce organic contaminants into the environment.

Scarcity of freshwater is one of the most serious environmental problems and many strategies will have to be implemented in order to deal with water shortage. One of these strategies is the reuse of waste water effluents for the irrigation of crops [18]. These practices, in addition to landfill leachate of the products dumped at landfill sites, are a possible source point contamination of ground waters and surface waters. Since surface waters are the main sources of drinking water, there is a clear potential risk of drinking water contamination involving organic contaminants. Furthermore, the technologies used in some drinking water treatment plants are not able to reduce the levels of trace organic contaminants and can even produce some disinfection by-products (DBPs) as a result of processes such as chlorination [19]. In addition, the more persistent contaminants can accumulate through the food chain in aquatic biota tissues, creating an important route of human exposure to some organic chemicals [8].

Taking into consideration the impact of the organic contaminants in environmental atmospheres and waters commented on before, the control of the occurrence of organic contaminants in these matrices is of major importance. In this sense, analytical chemistry plays an important role in developing analytical methods for the reliable determination of these contaminants in different environmental matrices. Since most of the target organic contaminants are present at trace levels, highly sensitive analytical methods are required. Furthermore, the complexity of some environmental matrices, such as indoor settled dust or waste water, also demands methods with high selectivity. Current trends in analytical chemistry focus on the development of high throughput analytical methods with a reduction of the consumption of organic solvents during the

whole process. To that end, sample preparation methods for air and water contaminants based on sorption into sorbents followed by thermal desorption are especially useful because they provide high sensitivity and selectivity and avoid the use of organic solvents [20]. Among them, the enrichment into solid sorbents, both by passive or active sampling, has been widely used for determining air contaminants, whereas several methods based on solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE) can be found in the literature for determining water contaminants. Furthermore, other strategies that reduce the amount of solvents have been used for the extraction of solid samples such as airborne particulate matter and house dust, including pressurised liquid extraction (PLE) and microwave assisted extraction (MAE). So far, the most widely-used determination methods reported in the literature for environmental organic contaminants are based on gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry. Despite the fact that in the last few years some studies have focused on the development of high throughput environmentally friendly analytical methods, more studies are needed to cover the wide range of organic contaminants.

In light of the above, the introduction of this Thesis highlights some of the most important organic contaminants and the most widely-used analytical methods applied to their determination in environmental atmospheres and waters. First, the main characteristics of these contaminants, as well as their occurrence and main environmental and health effects, are reviewed. This is followed by an overview of current analytical techniques. After the introduction, the main objectives of this Doctoral Thesis are laid out. The third chapter presents the results and discussion of the studies derived from the experimental research included in paper format. Finally, the main conclusions that can be drawn from the studies are presented.

1.1. Environmental organic contaminants

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

Currently, a wide variety of organic contaminants have been identified in environmental atmospheric and water samples. As previously mentioned, some of these contaminants are regulated by current legislation. As an example of the increasing interest in the regulation of contaminants, the European Union constituted the REACH program (Registration, Evaluation, Authorisation and Restriction of Chemical substances). Through the EC 1907/2006 law [21], the European Union intends to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. At the same time, REACH aims to enhance innovation and competitiveness of the EU chemical industry.

Some environmental organic contaminants are active compound that can react with other chemicals in the different environmental matrices causing their degradation or the formation of new compounds. These are, for instance, volatile organic compounds (VOCs), which take part in most atmospheric photochemical reactions [22]. The degradation of VOCs can lead to a more active volatile species and also produces ozone. Furthermore, the more volatile compounds formed from the degradation of some VOCs can migrate to the condensed phase, forming secondary organic aerosols (SOAs), which can modify the global climate [23].

However, some other groups of organic contaminants remain intact for long periods of time as they resist photolytic, chemical and biological degradation. These are called persistent organic pollutants (POPs) and are highly toxic chemicals that can accumulate and pass from one species to the next through the food chain. As POPs are semi-volatile compounds, they can be transported over long distances in the atmosphere or by the movement of both fresh and marine waters [8]. Consequently, POPs are globally distributed, including regions where they have never been used, such as the Antarctic [24]. In fact, Polar Regions are the final sink of some POP compounds that arrive there through atmospheric or oceanic transport. To address this global concern, the United Nations Environmental Protection Stockholm Convention [25,26] and the United Nations Economic Commission for Europe Aarhus Protocol on POPs [27] regulates or eliminates the production, use and release of some POPs, such as organochlorine pesticides (OCPs, including aldrin, chlordanes, DDT, dieldrin, endrin, heptachlor, mirex, and toxaphene); industrial chemicals (polychlorinated biphenyls – PCBs - and hexachlorobenzene, which is also used as a pesticide); flame retardants such as polybrominated diphenyl ethers (PBDEs); and unintentional by-products such as dioxins, furans and polycyclic aromatic hydrocarbons (PAHs).

In recent years, the scientific community has shown a growing interest in new kinds of organic contaminants. These are called emerging organic contaminants (EOCs) and are compounds which can be persistent or not in different environmental matrices. They

are characterized by their continuous introduction into the environment because of their widespread usage or formation in anthropogenic processes. An organic pollutant can be called “emerging” because of a new route of human exposure or new analytical methods which enable scientists to detect them, among other reasons [28]. Because of the definition of EOCs mentioned above, the list of these compounds is continuously increasing [19]. Table 1.1 summarizes the main studied families of EOCs and some examples of each family.

Table 1.1. Main studied families of EOCs and some examples of each group.

Group of EOC	**Examples**
Pharmaceuticals	Analgesics, antibiotics, psychoactive drugs
Hormones	17 β-estradiol, estriol, norethindrone
Brominated flame retardants (BFRs)	Polybrominated diphenyl ethers (PBDEs), Polybrominated biphenyls (PBBs),
Perfluorinated compounds (PFCs)	Perfluorooctane sulfonates (PFOSs), perfluorooctanoic acids (PFOAs)
Drinking water disinfection by products (DBPs)	Halogenated DBPs, N-nitrosamines
Personal care products (PCPs)	Synthetic musks, UV filters, parabens
Pesticides (new and transformation products)	Triazines and their degradation products
Phthalate esters	Diethylphthalate, dibutylphthalte, benzylbutylphthalte, bis(2-ethylhexyl)*phthalate*
Organophosphate esters	tri-n-butyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP) and tris(2-chloropropyl) phosphate (TCPP)
Illicit drugs	Heroin, cannabinoids
Phenolic Endocrine Disrupting Chemicals	Bisphenol A, phenylphenol
Benzotriazoles	Tolyltriazole, benzotriazole, benzosulfamides, benzothiazoles
Solvent stabilizers	1,4- dioxane
Siloxanes	Cyclic and linear siloxanes
Naphthenic acids	n-butylcyclohexylbutanoic acid 4-methylcyclohexaneacetic acid

Data concerning the occurrence, ecotoxicity and risk assessment for most of these emerging contaminants is scarce, so it is difficult to predict their effects on the environment and health. Therefore, most of these EOCs are currently unregulated, but may be candidates for future regulation depending on future research on their potential effects on health [29].

Although there is a lack of regulation for most EOCs, some of them are considered to be priority pollutants. In this sense, the USEPA Contaminant Candidate List-3 (CCL-3) [30] includes drinking priority contaminants, which can occur in drinking water systems and will be considered for potential regulation. This list includes three pharmaceuticals, eight hormones, several disinfection by-products (including five nitrosamines), pesticides and pesticide degradation products among other organic, inorganic and microbial contaminants. Some EOCs are emerging POPs, such as the polybrominated diphenyl ethers (PBDEs) used worldwide as flame retardants, which have been considered in recent POP regulations because of their impact on the environment and their increasing contamination at high latitudes of the northern hemisphere [26].

In this section, an overview of some of the most detected environmental contaminants is provided. These contaminants have been selected as the focus of this Thesis because of their occurrence in environmental atmospheres and waters, and their adverse effect on the environment and health. These selected contaminants are volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and some groups of emerging organic contaminants (EOCs), such as personal care products (PCPs), especially synthetic musk fragrances, parabens and insecticides, and nitrosamines including N-nitrosamines and tobacco-specific nitrosamines (TSNAs).

1.1.1. Volatile Organic Compounds

Volatile organic compounds (VOCs) consist of thousands of organic compounds (i.e. paraffinic, olefinic and aromatic hydrocarbons, and various oxygen-, nitrogen-, sulphur-, and halogen- containing molecules) and are characterized by their low boiling points, large vapour pressures and atmospheric photochemical reactivity [2,31,32]. Since VOCs are naturally emitted and widely-used as ingredients in paints, adhesives, solvents, fragrances and in other processes and consumer products, they are ubiquitously present in the environment. VOCs can be found in environmental waters and solids. However, because of their high volatility, they are especially present in the atmosphere.

Every day, large quantities of VOCs are released into the atmosphere from both anthropogenic and natural sources. The global emission of anthropogenic VOCs in the year 2000 was estimated to be 186 Tg y^{-1} [33]. Figure 1.1 shows, on a global average,

the most important sources of these anthropogenic VOC emissions [33]. The major anthropogenic source of VOCs is from the use and production of fossil fuels, predominately due to road transport and oil production, followed by biomass and biofuel combustion (mainly from the transport sector). Industrial processes contribute 16% of all anthropogenic VOC emissions.

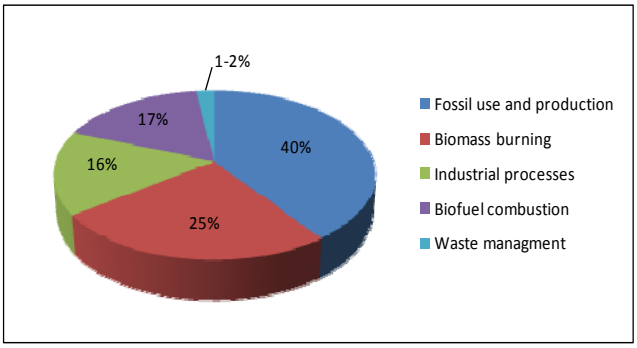


Figure 1.1. Major sources of anthropogenic VOC emissions [33].

However, the majority of VOCs in the atmosphere are related to biogenic emissions, with estimated global emissions up to 1150 TgC y^{-1} [34]. These originate almost exclusively from vegetation with smaller contributions coming from oceans and soils. Although globally VOCs biogenic sources dominate, in urban and industrial areas the majority of VOCs come from anthropogenic sources [22].

Some VOCs are controlled by air quality legislation. For instance, most compounds listed in the US EPA Clean Air Act list of Hazardous Air Pollutants (HAPs) are VOCs [35]. In Europe, VOC emissions into the atmosphere are controlled by several Council Directives, such as Directive 94/63/EC which controls the VOC emissions from the storage of petrol and its distribution from terminals to service stations [36]; the 1999/13/EC, which limits the emissions of VOCs from the use of organic solvents [32]; and the 2008/50/EC, which recommends the monitoring of ozone precursor VOCs [37]. However, only the ambient concentration of benzene is regulated by the Directive 2008/50/EC [37] and limited to an annual average of 5 µg m^{-3} since 2010.

Although VOCs are usually in low concentrations in the atmosphere (from µg L^{-1} to pg L^{-1} levels), these contaminants have a major impact on atmospheric chemistry. Figure 1.2 summarises the tropospheric chemistry of VOCs including direct emissions, chemical transformations, transport and deposition.

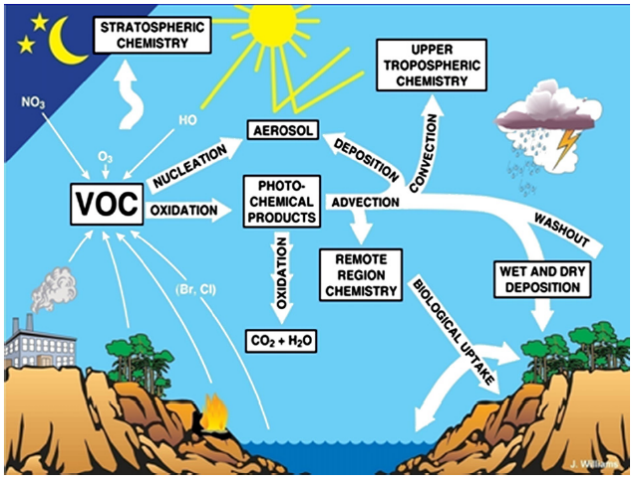


Figure 1.2. Tropospheric chemistry of VOCs [2]

In the troposphere, VOCs can be chemically transformed by photolysis, reaction with the hydroxyl radical ($HO^{\cdot}$, typically during daylight hours), reaction with the nitrate ($NO_3^{\cdot}$) radical (especially during evening and night-time hours), reaction with O_3, and in coastal and marine areas, reaction with chlorine atoms during daylight hours [38]. These chemical reactions can cause the degradation of VOCs or the formation of new VOC compounds. Depending on the atmospheric conditions and the reactivity of the compound, the lifetime of VOCs in the atmosphere can range from hours to thousands of years [22].

Among the environmental effects of VOCs, the most relevant is the formation of tropospheric ozone and secondary organic aerosols. The photochemical ozone formation is probably the most important environmental effect of atmospheric VOCs. Tropospheric ozone can be formed by the oxidation of organic compounds in the presence of NO_x and sunlight [38]. Ozone is toxic to humans and plants and can become a major air quality problem in cities and larger areas such as the Mediterranean. Furthermore, tropospheric ozone is considered the main cause of photochemical smog formation. The potential of the different VOC compounds to form ozone depends on the spatial and temporal pattern of emissions, the photochemical reaction rates, and the molecule-dependent potential for producing ozone. According to their ozone production ability, VOCs can be ranked using the Photochemical Ozone Creation Potential (POCP) [39,40] or the Maximum Incremental Reactivity scale (MIR, [41]). Table 1.2 shows the list of the VOC precursors recommended for measuring by the European Council Directive 2008/50/EC [37]. Most of the VOCs listed are paraffinic, olefinic hydrocarbons with at least 8 carbons in their structures, and some aromatic hydrocarbons.

Table 1.2. Ozone precursor VOCs recommended for ambient air measuring by the directive 2008/50/EC [37].

Ethane	trans-2-Butene	n-Hexane	m-Xylene
Ethylene	cis-2-Butene	i-Hexane	p-Xylene
Acetylene	1,3-Butadiene	n-Heptane	o-Xylene
Propane	n-Pentane	n-Octane	1,2,4-Trymethylbenzene
Propene	i-Pentane	i-Octane	1,2,3-Trymethylbenzene
n-Butane	1-Pentene	Benzene	1,3,5-Trymethylbenzene
i-Butane	2-Pentene	Toluene	Formaldehyde
1-Butene	Isoprene	Ethylbenzene	Total non-methane hydrocarbons

Another relevant VOC environmental effect is the formation of secondary organic aerosols (SOAs). SOAs are airborne particulate matter formed by the chemical transformation of atmospheric organic compounds. The most important mechanism of SOA formation is the oxidation of VOCs, forming products of lower volatility that migrate to the condensed phase [42]. SOAs are a major component of the total aerosol mass and can contribute to the modification of the radiative balance of the atmosphere induced by particulate matters and, therefore, to the global climate [23].

Because of their low boiling points, the main exposure route to most VOCs is through inhalation, with indoor environments being the most relevant source of exposure [43,44]. Some relevant indoor sources of VOCs are environmental tobacco smoke, organic solvents from paints, cleaning and cosmetic products, office equipment and building materials and furnishings [9,45]. However, several studies have demonstrated that one of the main sources of indoor VOCs is the infiltration of outdoor pollution into buildings [46,47]. Besides atmospheric VOC exposition, VOCs can be also ingested through drinking water, especially chlorinated drinking water, or adsorbed through the skin [14].

As mentioned previously, the term VOCs comprises a broad range of compounds, which consequently involves a broad range of possible health effects. These health effects can be mainly classified as carcinogenic and non-carcinogenic. According to a study of the US Environmental Protection Agency (USEPA), ambient VOCs are responsible for between 35% and 55% of the outdoor air cancer risk in the US [48]. Besides lung cancer, the ambient VOC emissions also correlated with the incidence of cancers affecting the brain, nervous system, endocrine system and skin [49]. The International Agency for Research on Cancer (IARC) [50] classified several VOCs as carcinogenic to humans, and the World Health Organization (WHO) has associated a lifetime unit risk (UR) for exposure to 1 μg m^{-3} for some of them [51]. Table 1.3 shows the IARC classification and

WHO UR values for some VOCs typically found in urban and industrial areas. Included in the IARC Group 1 are VOCs considered carcinogenic to humans, such as benzene or formaldehyde; Group 2A includes those probably carcinogenic to humans (those that have shown strong evidence to cause cancer in humans, such as tri- or tetrachloroethene); and in Group 2B are those possibly carcinogenic to humans (those that presented some evidence to cause cancer in humans, such as ethylbenzene or styrene) [50].

Table 1.3. Health data of some typical VOCs: cancer classification by IARC [50], lifetime unit risk levels (UR) by WHO [51] or IRIS [52] and non-cancer reference values by IRIS [52] or ASTDR [53].

VOCs	Group IARC	Unit risk $(\mu g\ m^{-3})^{-1}$	RfC $(\mu g\ m^{-3})$
Benzene	1	6.0×10^{-6}	9.6
1,3-Butadiene	1	2.8×10^{-4}	2
Formaldehyde	1	1.3×10^{-5}	n.g.
o-Toluidine	1	n.g.	n.g.
2-Naphtylamine	1	n.g.	n.g.
Vinyl chloride	1	8.8×10^{-6}	1
1,2-Dibromoethane	2A	6.0×10^{-4}	9
Tetrachloroethene	2A	5.9×10^{-6}	271
Trichloroethene	2A	4.3×10^{-7}	600
1,2,3-Trichloropropane	2A	n.g.	0.3
Acrylonitrile	2B	1.7×10^{-5}	2
Chloroform	2B	2.3×10^{-5}	98
1,2-Dichloroethane	2B	2.6×10^{-5}	2430
Dichloromethane	2B	n.g.	n.g.
Carbon tetrachloride	2B	6.0×10^{-6}	100
1,4-Dioxane	2B	7.7×10^{-6}	3600
1,3-Dichloropropene	2B	4.0×10^{-6}	31.8
Ethylbenzene	2B	2.5×10^{-6}	1300
Styrene	2B	n.g.	852
1,4-Dichlorobenzene	2B	1.1×10^{-5}	60
Hexachloroethane	2B	4.0×10^{-6}	n.g.
1,2-Dibromo-3-chloropropane	2B	2.0×10^{-3}	0.2
Naphtalene	2B	8.7×10^{-5}	3.7

n.g.: data not given

VOCs can also exhibit non-carcinogenic effects, such as acute irritation (eye, nose, and throat), sensory problems (headaches, loss of coordination, nausea); chronic damage to

liver, kidney, and central nervous system; and chronic respiratory effects, such as asthma, and negative impacts on the reproductive system and birth defects [43,51,54]. Risk assessment of human exposure to these non-carcinogenic effects is calculated comparing the VOC ambient concentration with a concentration (Reference Concentration, RfC) considered to be at the minimum risk level, established by the Agency for Toxic Substances and Disease Registry (ATSDR) [53] or the USEPA Integrated Risk Information System (IRIS) [52]. Table 1.3 shows the RfCs of some VOCs given by these international agencies.

Recently, some studies have estimated the cancer risk by inhalation of VOCs in several outdoor and indoor environments. For instance, lifetime cancer risks (LCRs) for benzene found in industrial and urban indoor and outdoor environments of La Plata, Argentina, were higher than 1 case per million people (1×10^{-6}) [55], which is the benchmark recommended by the USEPA [56]. In New York City and Los Angeles, VOC LCRs of 666 and 486 cases per 1 million, respectively, were found in an exposure study of teenagers living in the inner city [57]. Furthermore, higher risks have been found in industrial workplaces. For instance, global LCRs for inhalation of 7 VOCs emitted from the facilities of a steel plant in Taiwan ranged from 3.7 to 30×10^{-3} cases [58].

There is an extensive bibliography focused on the presence of atmospheric VOCs in urban, suburban and industrial outdoor locations, as well as indoor environments such as private houses, schools and offices. Below, the results of some recent studies are discussed.

The spatial and temporal distribution of VOCs in the atmosphere depends on the location of their sources, their reactivities and regional and global transport phenomena [2]. In urban atmospheres, VOCs exhibit certain recurrent patterns due to the time-dependent contribution of different sources. For instance, in most cities, VOCs are emitted predominantly by vehicular traffic, and therefore the highest concentrations of atmospheric VOCs correlate with the episodes of major traffic intensity [2]. As an example, this pattern was found in the air of Tarragona (Spain) when a previous study by our group showed total VOC concentrations ranging from 306 μg m^{-3} in high intensity traffic hours to 87 μg m^{-3} in low intensity hours [59]. In general, the most determined VOCs are the BTEX (benzene, toluene, ethylbenzene and xylenes) because they are the most abundant compounds in urban environments. These compounds are mainly emitted in the combustion of fossil fuels and, therefore, can be used as indicators of traffic sources. Table 1.4 shows an overview of some VOC measurements in big urban areas in different parts of the world.

Table 1.4. VOC concentrations in urban areas from different cities of the world, expressed in μg m^{-3}.

VOCs	Houston USA [60]	London UK [61]	Athens Greece [62,63]	43 cities China [64]	Rio de Janeiro Brazil [65]	Karachi Pakistan [66]
n-Pentane	2.26	0.7-1.0	1.7-14.2	0.2-7.7	-	13.4
n-Hexane	0.86	0.2-0.4	0.6-4.1	0.1-3.6	-	7.5
1,3-Butadiene	0.08	0.2-0.4	-	0.02-2.5	-	0.8
cis/trans-Pentene	0.11	0.3-0.4	-	0.04-14.7	-	0.4
Benzene	0.42	1.2-1.9	2.5-11.7	0.7-10.4	1.1	5.2
Toluene	0.5	2.7-3.6	6.7-21.2	0.4-11.2	4.8	7.1
Ethylbenzene	0.08	0.5-0.7	1.3-4.0	0.1-2.7	3.6	1.1
m,p-Xylene	0.28	1.5-2.1	3.2-11.1	0.4-15.3	10.4	2.1
o-Xylene	0.09	0.7-0.8	1.5-5.5	0.1-6.0	3.0	1
Formaldehyde	2.44	-	10.7-17.2	-	151	-

As seen in the table, in general VOC concentrations found in developing country megacities are higher than those found in Western Europe and North America. Toluene was in general the most abundant urban BTEX with average concentrations ranging from 0.5 μg m^{-3} in Houston to 21.2 μg m^{-3} in Athens. In most cities, average concentrations of benzene did not exceed the European threshold of 5 μg m^{-3} , except for locations in Athens, some Chinese cities and Karachi. It is also worth mentioning the high levels of formaldehyde found in some cities, such as the average concentration of 151 μg m^{-3} found in Rio de Janeiro (Brazil). As previously shown in Table 1.3, formaldehyde is considered carcinogenic for humans by the IARC with an attributable UR of 1.3×10^{-5} for exposure to 1 μg m^{-3}, therefore the control of formaldehyde emissions is of major concern for human health. The worldwide regulations of VOC emissions have led to a reduction of urban VOCs in recent years. For instance, a comparative study of VOC concentrations in Zurich for the years 1993-1994 and 2005-2006 [67] suggested that the contribution of most VOC sources decreased by a factor of about 2 to 3. The air quality control restrictions implemented for the Olympic games of 2008 in Beijing also led to a reduction of 35% of non-methane VOC concentrations [68].

Several studies have also determined VOC concentrations in industrial atmospheres. For instance, Cetin et al. [69] demonstrated that VOC concentrations around a chemical complex and a refinery in Izmir (Turkey) were 4 to 20 times higher than those found in a suburban area of the same city. Massolo et al. [55] found total industrial VOC concentrations were anything from 3.5 to 5.6 times higher in industrial areas than in urban and semi-rural areas of Argentina. Jobson et al. [70] observed that the abundance of ethene, propene, 1-butene, C_2-C_4 alkanes, hexane, cyclohexane, methylcyclohexane, isopropylbenzene, and styrene at Houston were systematically affected by

petrochemical industry emissions. Other sources of anthropogenic VOC emissions are industrial and urban waste water treatment plants (WWTPs). Industrial WWTPs can be an important source of industrial-related VOCs such as acrylonitrile [71-73], whereas urban WWTPs can be an important emission source of chlorinated VOCs [74,75]. However, few studies have focused on the determination VOC emissions from WWTPs and their contribution to the global concentration of VOCs is often underestimated.

Humans are predominantly exposed to VOCs in indoor environments, thus VOC concentrations are usually higher in indoor environments than in outdoor air [9]. Several studies have evaluated the different ways that outdoor, indoor and personal environments can contribute to exposure to VOCs. These studies have found that indoor concentrations (especially from homes, offices and vehicles) had the largest influence on personal exposure [45,76]. Some important sources of indoor VOCs are environmental tobacco smoke, cooking, building materials and furnishing, and the use of consumer products such as cleaning and personal care products [9,45]. However, the infiltration of outdoor pollution is also an important source of indoor VOCs [76]. As an example of indoor VOC concentrations, Esplugues at al. [46] recently found average BTEX concentrations in Valencia (Spain) of 17.6 μg m^{-3} indoors, whereas concentrations of 8.0 μg m^{-3} were found outdoors. In a study in Rio de Janeiro [77], indoor office samples presented total VOC concentrations ranging from 304 to 1680 μg m^{-3}, whereas outdoor samples ranged from 22 to 643 μg m^{-3}. A review of indoor VOCs by Barro et al. [9] reported total indoor VOC concentrations from 0.005 up to 2496 μg m^{-3} in homes and from 0.01 up to 4600 μg m^{-3} in offices.

Because of their ubiquitous presence in the atmosphere and all the environmental and health effects mentioned above, VOC concentrations are considered an essential parameter for assessing the air quality in indoor and outdoor environments. Although BTEX have been the most determined VOCs, the study of the presence of a wide range of VOC compounds in different atmospheric samples is of major interest for a more accurate evaluation of air quality and the health effects related to these compounds.

1.1.2. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic contaminants which are characterized by the presence of at least two fused aromatic rings. These compounds come mainly from pyrolytic processes and the incomplete combustion of organic matter at high temperatures [3]. The presence of PAHs is ubiquitous in the environment and they have been found in all kinds of environmental matrices (air, water, soils and sediments, and biota), as well as in various consumer products, such as

food [78]. PAHs are classified as priority pollutants by both the Unites States Environmental Agency (USEPA) [35] and the European Environment Agency [79]. Although European Directive 2004/107/EC only establishes a limit of 1 ng m^{-3} of Benzo[a]pyrene (BaP) in airborne particulate matter ≤ 10 μm (PM_{10}), it also recommends the monitoring of at least benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), indeno[1,2,3-cd]pyrene (Ind), and dibenzo[a,h]anthracene (DahA) [80]. Figure 1.3 shows the structures of the 16 PAHs considered to be priority pollutants by the USEPA. Some of them are also included in the European rules.

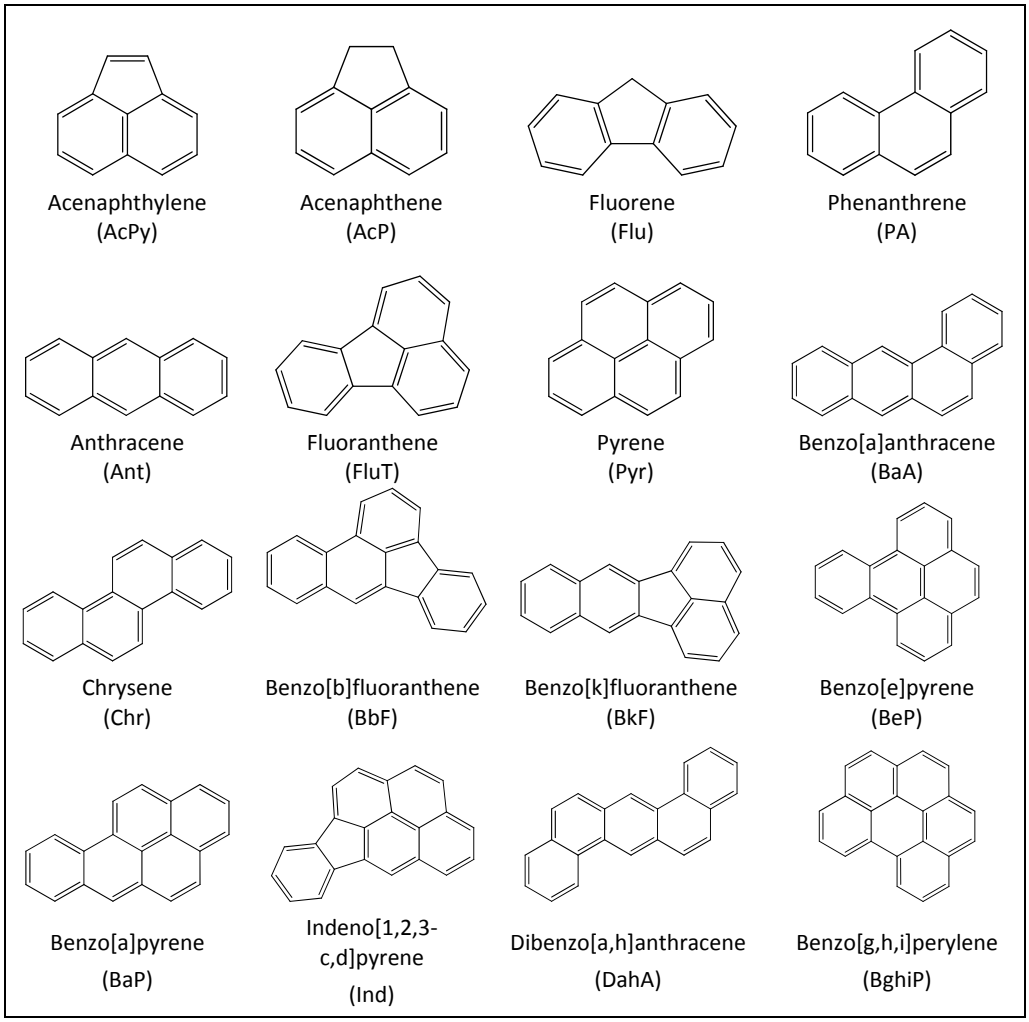


Figure 1.3. Chemical structures of the 16 USEPA priority PAHs.

PAH concentrations are also regulated in other matrices besides airborne particulate matter. For instance, the European Directive 98/83/EC [81] limits the content of BaP to 0.01 µg L^{-1} and the sum of four PAH concentrations (BbF, BkF, BghiP and Ind) to 0.10 µg L^{-1} in drinking water. PAHs are also regulated in extender oils and tyres by the European Directive 2005/69/EC [82], which limits the content of PAHs to less than 3% of the mass of these materials, the content of BaP to less than 1 mg kg^{-1}, and the sum of the ten listed PAHs of the Directive to less than 10 mg kg^{-1}.

PAHs can occur naturally in the environment, essentially from non-anthropogenic forest fires and volcanic eruptions [83]. However, anthropogenic activities are the main source of PAHs in the environment, mainly from the incomplete combustion of fossil fuels or wood and as by-products from some industrial processes [3,83]. The global atmospheric emissions of the 16 priority PAHs in 2004 were estimated to be 520 Gg y^{-1} [84]. Figure 1.4 shows the relative contribution of various combustion sources to the atmospheric emission of the 16 priority PAHs. Globally, biomass burning is the major emission source of PAHs (56.7 % from biofuel combustion and 17 % from wildfire). Other PAH sources are the use of consumer products, traffic oil and domestic coal combustion and coke production. The major industrial activities contributed less than 10 % of the global PAH emissions.

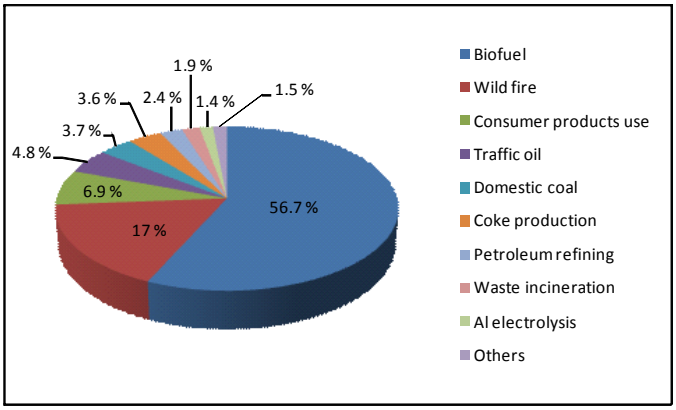


Figure 1.4. Relative contributions of various sources to PAH 16 [84].

PAHs are high lipophilic contaminants which are ubiquitously present in the environment [78]. Because of their low biodegradation, their bioaccumulation in the adipose tissues of organisms, and their biomagnification through the food chain, PAHs are considered persistent organic pollutants (POPs) [85]. The major pathway of these compounds into the environment is through atmospheric emissions with the soil acting as the ultimate deposit for them. Atmospheric PAHs can be distributed in the gas and the particulate phase depending on their vapour pressure, the atmospheric

temperature, the PAH concentration, the affinity of the PAH for the atmospheric suspended particles (determined by the partitioning coefficients K_{oc}) and the nature and concentration of the particles [86]. In general, the most volatile PAHs (the 2-3 ring PAHs) are mainly associated with the gas phase and the less volatile (the 4-6 ring PAHs) to the particle fraction [3,78]. However, recent studies have also demonstrated the presence of the most lipophilic PAHs in the atmospheric gas phase [87]. It has been estimated that 10–80% of PAH inputs to the world's oceans is from atmospheric sources [88]. However, higher PAH concentrations have been found in urban and industrial areas rather than in remote non-anthropogenic areas. For instance, in the seawater of the western Mediterranean, higher levels of PAH content were found in the off-shore of Barcelona (1.8 ng L^{-1}) and in the Ebro river plume (2.17 ng L^{-1}) than in remote stations where concentrations were lower (0.4-0.9 ng L^{-1}) [89]. Additionally, the soil system seems to be the important long-term repository for PAHs and is considered to be a certain indicator of the state of environmental pollution. Accumulation of PAHs in soils may lead to further potential contamination of vegetables and food chains, and then cause direct or indirect exposure to humans. Moreover, leaching, evaporation and migration are possible sources of atmospheric or surface and groundwater contamination by PAHs.

The most important transformation processes of these compounds in the environment are the gas and heterogeneous phase reactions induced by atmospheric oxidants such as hydroxyl, ozone or nitrogen oxides, to form nitro- and oxy-PAH derivatives [78]. These derivatives are of particular interest because they have higher potential carcinogenic properties than their related parent PAHs [90,91].

Humans can be exposed to PAHs mainly through three pathways [92]: inhalation (of PAH-containing air or particulate matter, such as cigarette smoke, vehicle exhaust, or air containing industrial or domestic PAH emissions); ingestion (of PAH-containing foodstuffs, such as fried and charcoal-grilled meat); and skin adsorption by contact with PAH containing products. Ingestion is quantitatively the main route for human exposure to PAH for humans non-occupationally exposed to PAHs [88]. PAHs can be found in non-refined oils, fish, milk, roasted cereals and beverages, such as coffee and tea, among other foodstuffs [93].

PAH health effects have been widely studied, primarily because of their potential carcinogenic and mutagenic properties. Several organs are believed to be susceptible to tumour formation after PAH exposure. These include lungs (in particular the bronchi), skin, oesophagus and colon, pancreas, bladder, and women's breast tissue [78]. In general, the carcinogenic properties of PAHs increase with the number of aromatic rings. The IARC classified BaP as carcinogenic to humans (Group 1), other PAHs, such as

DahA, as probably carcinogenic to humans (Group 2A), and some others – such as naphthalene (Nap), BaA, Chr, BbF, benzo[j]fluoranthene (BjF) and Ind – as possibly carcinogenic to humans (Group 2B) [50].

Carcinogenic effects of BaP are the most studied and, therefore, this PAH is used as a marker for the carcinogenic risk of the other PAHs. The WHO has established a unit risk of 8.7×10^{-5} for people exposed to a chronic inhalation of 1 ng m^{-3} of BaP [51]. For risk assessment calculations of PAH mixtures, each PAH is ranked according to their carcinogenic potency relative to BaP using Toxic Equivalence Factors (TEFs) [94,95]. Table 1.5 shows the most widely-used TEFs for the 16 USEPA priority PAHs. By multiplying the individual PAH concentration for the corresponding TEF, it is possible to express the concentration of the mixture in Benzo[a]pyrene equivalents (BaP-eq) and then calculate the risk using BaP UR. DahA is considered more carcinogenic than BaP (TEF value 1.1). The rest of USEPA 16 PAHs are considered 10 times less carcinogenic than BaP, such as BbF, to 2000 times less carcinogenic, such as Flu, PA or Ant.

Table 1.5. The most widely-used TEFs for the 16 USEPA priority PAHs. TEFs for acenaphthene and acenapthylene are from Nisbet and Lagoy [94], all others are from Larsen and Larsen [95].

PAH	TEF
Acenaphthylene (AcPy)	0.001
Acenaphthene (AcP)	0.001
Fluorene (Flu)	0.0005
Phenanthrene (PA)	0.0005
Anthracene (Ant)	0.0005
Fluoranthene (FluT)	0.05
Pyrene (Pyr)	0.001
Benzo[a]anthracene (BaA)	0.005
Chrysene (Chr)	0.03
Benzo[b]fluoranthene (BbF)	0.1
Benzo[k]fluoranthene (BkF)	0.05
Benzo[e]pyrene (BeP)	0.002
Benzo[a]pyrene (BaP)	1
Indeno[1,2,3-c,d]pyrene (Ind)	0.1
Dibenzo[a,h]anthracene (DahA)	1.1
Benzo[g,h,i]perylene (BghiP)	0.02

Some studies have estimated the risk related to PAH inhalation. For instance, Kameda et al. [96] found average LCRs of 1.7×10^{-4} for 22 PAHs in the airborne particulate matter of the Yokohama (Japan) residential area. In the western Balkans, a study of 16 PAHs found LCRs for gas phase PAHs ranged from 1.11×10^{-8} to 2.85×10^{-7} and from 1.36×10^{-8} to 5.46×10^{-6} for the particle phase PAHs [97]. However, occupational exposure can lead to a higher risk of PAH inhalation. As an example, Liu et al. [98] found LCRs of 9.6×10^{-4} and 1.09×10^{-3} in two foundries in Taiwan.

Besides the carcinogenic effects, studies of PAH health effects have demonstrated their influence on the development of arteriosclerosis [51], reproductive defects, such as intrauterine growth retardation [99,100], and adverse effects on children's neurological development [101].

As previously mentioned, the major pathway of PAHs into the environment is through atmospheric emissions. Therefore, some recent studies of atmospheric PAH concentrations are discussed in this section. Table 1.6 presents a summary of total PAH and BaP concentrations in recent studies in Spain and Europe, as well as a road tunnel in Hong Kong. The main PAH compounds and the kind of sample in which PAHs have been determined (total suspended particles (TSP), particles ≤10 μm (PM_{10}) or gaseous phase (air)) are also indicated.

European cities showed total PAH concentrations ranging from 1.6 ng m^{-3} to 137 ng m^{-3} depending on the activities of the different locations, whereas those reported in the road tunnel increased to 252 ng m^{-3}. Comparing the results obtained in the European cities, it can be seen that the highest total PAH concentrations have been found in industrial locations, with maximum concentrations recorded in Flanders, Belgium (from 90 to 137 ng m^{-3}). For instance, total PAH values in industrial areas of Sevilla and Tarragona (Spain) were 1.5 to more than 2 times higher than those found in other urban locations in the same area. In Flanders, Ravindra et al. [87] found that total PAH values in industrial locations were almost 14 times higher than in rural areas and 4 times higher than in urban and suburban locations.

Furthermore, traffic also makes a large contribution to urban atmospheric PAHs and PAH concentrations in high traffic areas have been reported at almost 2 times the levels of those found in low traffic areas. For instance, the average total PAH concentration in high traffic locations in Toulouse (France) was 19.7 ng m^{-3} whereas in the city centre it was 12.3 ng m^{-3}. As regards BaP, average concentrations in European cities do not normally exceed the European legal benchmark (1 ng m^{-3}), except for isolated incidents, such as the 1.77 ng m^{-3} found in suburban locations of Flanders, 1.10 ng m^{-3} in Duisburg (Germany) and 3.15 ng m^{-3} in Prague (Czech Republic).

Table 1.6. Overview of some recent studies on PAH concentrations.

Location	Matrix	Kind of location	Total PAH (ng m^{-3})	BaP (ng m^{-3})	Main PAHs	Ref.
Errenteria (Spain)	TSP	Urban	10.7	0.5	Flu, Pyr, Chr, BbF, BjF, BkF, BeP, BaP, Ind, BghiP	[102]
Sevilla (Spain)	TSP	High traffic	8.6-14.6	0.5-0.9	Pyr, BaA, Chr,BbF, BkF, BaP, Ind, BghiP	[103]
		Low traffic	2.1-5.4	0.1-0.29	Chry, BbF, Ind, BghiP	
		Industrial	12.4	0.98	Pyr, BaA, Chr, BbF, BaP, Ind, BghiP	
Tarragona (Spain)	TSP + air	High traffic	9.7-14.3	n.d.-0.04	Nap, AcPy, Flu, PA, Pyr	[104]
		Low traffic	4.2-9.6	n.d.	Nap, Flu, PA, Pyr	
		Industrial	4.2-22.5	n.q.	Nap, AcPy, Flu, PA, FluT, Pyr	
Zaragoza (Spain)	TSP	urban	8.77	0.59	Ind, BghiP	[105]
Toulouse (France)	PM_{10} + air	High traffic	19.7	0.17	AcPy, PA, FluT, Pyr	[106]
		Urban centre	12.3	0.13	AcPy, AcP, Flu, PA, FluT, Pyr	
		Industrial	21.6	0.81	AcPy, AcP, Flu, Pyr	
6 European cities[1]	PM_{10}	Urban	26-55	0.05-3.15	PA, FluT, Pyr, Chry, BbF, BjF, BkF, BeP, BaP	[107]
Menen (Belgium)	TSP	Urban	6.7	0.6	Nap, PA, FluT, Chr, BbF, Ind, BghiP	[108]
Flanders (Belgium)	TSP + air	Urban	9.0-35	0.9-1.5	Nap, AcPy, Flu, PA, FluT, Pyr	[87]
		Suburban	4.1-40.2	0.02-1.77	AcPy, flu, PA, FluT, BaP, Ind, BghiP	
		Rural	7.0-10.0	n.d.-0.07	Nap, PA, FluT	
		Industrial	90-137	0.08-0.24	Nap, Flu, PA, FluT, Pyr	
Shing Mun Tunnel (Hong Kong)	TSP + air	High traffic	79.5-252	2.1-11.9	Nap, Ace, AcPy (gas phase); Flu, Pyr (particle phase)	[109]

[1] European cities in this study: Duisburg (Germany), Prague (Czech Republic), Amsterdam (The Netherlands), Helsinki (Finland), Barcelona (Spain) and Athens (Greece).
n.d., values under the limit of detection
n.q., values under the limit of quantification

These high BaP values were reported during the winter. As a curiosity, concentrations of BaP found in the road tunnel were up to 12 ng m^{-3}. As regards concentrations of other PAHs, studies have shown that the less volatile PAHs were, as expected, the most abundant in particulate matter. For instance, Ind and BghiP were reported to be the most abundant in TSP in Zaragoza (Spain) and PA, FluT, Pyr, Chry, BbF, BjF, BkF, BeP, BaP were the most abundant in other European cities. However, in samples of air and particulate matter, high and mid-volatility PAHs are the most abundant because of their high presence in the gas phase. The distribution of PAHs also depends on the PAH sources and therefore will vary according to the sampling location, as can be seen in Table 1.6. Therefore, the use of ratios of some PAH characteristics or certain sources can help in some cases to assess PAH emission sources [3].

Atmospheric PAH concentrations can also have seasonal patterns. Temperature appears to have a big impact on the concentration of PAHs in the atmosphere. In general, higher PAH concentrations have been reported in cold seasons than in warm seasons. This tendency can be in part explained by the increase of fuel consumption in winter in urban locations. For instance, concentrations of total PAHs in the city of Menen (Belgium) were 5-7 times higher in January, February and December, compared to May, June and August [108]. Finally, PAHs in the gas phase were generally shown to have the highest values of all PAHs, especially the most volatile ones. Gas phase PAHs were 10 times higher than those in the particle phase in Flanders (Belgium) [87] and 15 times higher in the road tunnel in Hong Kong [109].

Because of their severe health effects and their ubiquitous presence in environmental matrices, PAHs are one of the most studied contaminants. However, as mentioned previously, concentrations of airborne PAHs are only regulated in PM_{10} and the contribution of the atmospheric gas phase PAHs is often underestimated. Therefore, more studies on PAH concentrations in the gas phase and their influence on human health should be a major concern in the future.

1.1.3. Emerging Organic Contaminants

As mentioned in the introduction to this section, emerging organic contaminants (EOCs) are compounds continuously introduced in the environment because of their widespread use in anthropogenic processes. Although most EOCs are currently unregulated, some of them exhibit adverse effects on the environment and human health which make them potential candidates for regulation in the future.

Therefore, some of the studies presented in the experimental part of this thesis have focused on the determination of some groups of EOCs in different environmental

samples. These EOCs have been chosen because of their ubiquitous presence in the environment and their recognised effects on health. The studied contaminants include three families of personal care products (synthetic musk fragrances, parabens and insect repellents), which are used daily in several consumer products, and volatile N-nitrosamines, which are by products of drinking water disinfection and considered to be EOCs. In this section we have also included tobacco-specific nitrosamines (TSNAs). Although TSNAs are not yet considered to be EOCs, major interest in future research is being shown because of their potential indirect pathway to human exposure, such as the oral ingestion of drinking water containing these carcinogens [110].

In this section, a description of these EOCs is provided, including their main characteristics, health effects and main environmental sources, occurrence and fate.

1.1.3.1 Personal care products

The active ingredients of personal care products (PCPs) are a broad range of organic compounds currently used as additives in cosmetic, household, food and pharmaceutical products, among others. Because of their widespread use, PCPs are one of the groups of EOCs most commonly detected in environmental matrices. PCPs have been found in matrices such as water, biota, sediments, sludge, and outdoor and indoor air, particulate matter and settled dust [111].

The interest in the determination of PCPs in the environment has been growing over the last two decades. Some PCPs belong to the list of high production volume chemicals and are produced in thousands of tonnes every year [112]. Since PCPs are included in many different consumer products, they can be absorbed by the body, where they are metabolized and excreted, or washed off after application. As a consequence, the main route of exposure of PCPs into the environment is through waste water effluents. Nevertheless, PCPs can also be introduced directly into the environment via the direct release into surface waters from the skin (e.g. sunscreen filters, parabens) or volatilized into the air (e.g. via synthetic musk fragrances and insect repellents) [113], among other pathways.

PCPs can be transformed in the human body, biota, and surface waters or during WWTP processes to create intermediate metabolites and degradation products. Data on the ecotoxicity of the PCP degradation products is scarce, and it is possible that these products produce environmental and health effects which have not been yet evaluated [17].

The most commonly-studied PCPs are: fragrances (e.g., synthetic musks), antimicrobials (e.g., triclosan), UV filters (e.g., benzophenones), insect repellents (e.g., DEET), preservatives (e.g., parabens) and siloxanes (e.g., decamethylcyclopentasiloxane). Because of their ubiquitous presence in the environment, their high volatility, and their effects on the environment and public health, this thesis is focused on the determination of synthetic musk fragrances, parabens, and insect repellents.

Synthetic musk fragrances

Synthetic musk fragrances are added in high quantities to scent a wide range of consumer products, such as detergents and cosmetics. These fragrances, synthesized to replace expensive natural musks, include a broad range of different compounds, which can be divided in three groups according to their chemical structures: nitro, polycyclic and macrocyclic musk fragrances [114]. Figure 1.5 shows the structures of a representative synthetic musk from each group.

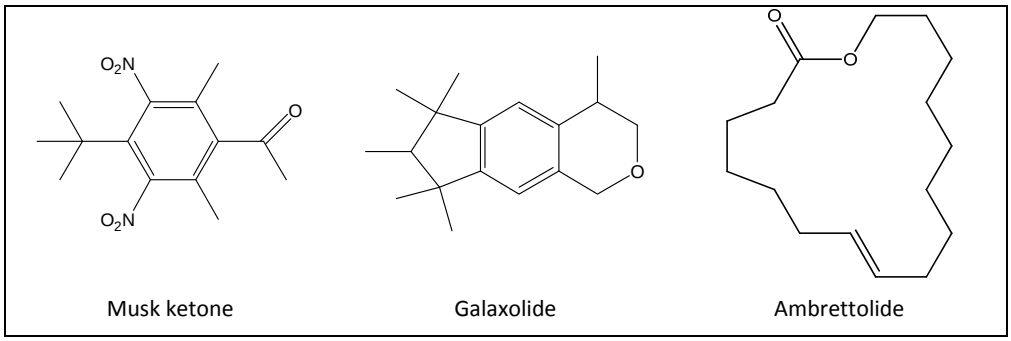


Figure 1.5. Representative structures of three synthetic musk fragrances: musk ketone (nitromusk), galaxolide (polycyclic musk), and ambrettolide (macrocyclic musk).

The nitromusk fragrances are two or three-fold nitrate benzene derivatives with additional alkyl, keto or methoxy groups. These musks were the first to be produced but their use has been drastically reduced in recent decades due to their accumulation in environmental matrices and their potential carcinogenic effects [114]. In this sense, the 1998 amendment of the European Directive 76/768/EEC relating to cosmetic products prohibits the use of musk ambrette, moskene and tibetene in cosmetics and limits the contents of musk xylene (MX) to 1 % in fine fragrances, 0.4 % in eau de toilette and 0.03 % in other products. Musk ketone (MK) is limited to 1.4 %, 0.56 % and 0.042 % respectively [115]. Furthermore, nitromusks can be transformed in WWTPs - as well as in biota - into amino metabolites [116], which show higher toxicity [117] and higher hormone disrupting potential [118].

The polycyclic musk compounds are the most widely-used nowadays. These musks were first synthesized in the 1950s and can be indane, tetraline or cumarin derivatives and tricyclic compounds. Compared with the nitromusks, the polycyclic have better properties such as a higher resistance to light and alkali [114]. The most representative polycyclic musks are the commercially named: galaxolide (HHCB), tonalide (AHTN), cashmeran (DPMI), celestolide (ADBI), phantolide (AHMI), and traseolide (ATII). Among these, galaxolide and tonalide represents 95% of the commercially-used polycyclic musks [119]. However, polycyclic musks have also been found in environmental matrices [111] and, therefore, limits have been set regarding the amounts that can be used in cosmetic products. For instance, the maximum authorized concentration in a finished cosmetic product for tonalide is 0.1 % for leave-on products and 0.2 % for rinse-off products [120].

The macrocyclic musks are 15 or 17-membered ring systems, which can be found in nature or synthesized, and are mainly divided in two groups: ketones (from animals) and lactones (from plants). These compounds have stability to light and alkalis, high fixation and quality odours, and seem to be more easily degradable in the environment [121]. Although macrocyclic musks have these outstanding properties, they are not used often because of their relatively high production costs. However, they are expected to be of increasing interest in the future [114].

As mentioned above, polycyclic and nitromusks do not occur in nature and are structurally and chemically very different from natural musk compounds. These synthetic musks are more lipophilic and persistent chemicals, and therefore can accumulate in sediments, sludge and biota and are able to biomagnify throughout the food chain [116,122-124]. Furthermore, they are only partially biodegradable and, therefore, are not completely eliminated in WWTPs. Removal of approximately 50 to more than 90 % have been reported in literature, mainly caused by their sorption into sludge [125,126]. As an example of their low biodegradation, Bester et al. [127] found average HHCB concentrations of ca. 1900 ng L^{-1} in influents, 700 ng L^{-1} in effluents and 3000 ng g^{-1} in sludge in an urban WWTP in Germany. Hence, the main pathway of synthetic musks into the environment is through waste water effluents [128]. Moreover, the digested sludge applied as fertilizer to soils is considered to be an important source of these compounds to terrestrial ecosystems [129]. Additionally, some degradation products of the synthetic musks can be produced during the waste water treatment, such as the amino metabolites of the nitromusk (mentioned above) or the galaxolidone (HHCB-lactone), which is more oxidised and hydrophilic than the precursor polycyclic musk (HHCB) [126].

The most widely-found synthetic musks in environmental samples are HHCB and AHTN and the degradation product HHCB-lactone. Concentrations of these compounds in urban WWTP effluents have been reported up to 7000 ng L^{-1} for HHCB, up to 2000 ng L^{-1} for AHTN [130] and up to 400 ng L^{-1} for HHCB-lactone [127]. These compounds have been also found in natural waters but at lower concentrations, such as 5-30 ng L^{-1} for HHCB and 3-15 ng L^{-1} for AHTN in the Tamar and Plym Estuaries in the UK [131]. The other musks are generally less frequently detected in natural waters. The nitromusk compounds MX and MK have also been detected in environmental waters but usually at lower concentrations. As an example, Sumner et al. [131] found concentrations of 4-7 ng L^{-1} of MX and 10-30 ng L^{-1} of MK in final effluents samples from WWTPs in UK.

Because of the low vapour pressure of most synthetic musks, another important route of exposure is also their vaporization into the air. For instance, synthetic musks have been detected in urban and rural air in Iowa and the Great Lakes at concentrations of up to 0.8 ng m^{-3} for HHCB, 0.33 ng m^{-3} for AHTN and 0.022 ng m^{-3} for MX [132]. However, most of the determinations of musks in air have focused on indoor air and dust where musk concentrations are much higher [133-137]. For instance, Kallenborn et al. [138,139] detected concentrations in indoor environments of up to 44.3 ng m^{-3} for HHCB, 13.4 ng m^{-3} for AHTN and 1.0 ng m^{-3} for MX, which were 10 times higher than those detected outdoors.

The long-range transport and persistence of synthetic musks, as well as their exchange between air and water matrices, has caused them to be found in remote non-anthropogenic areas such as the Great Lakes [132,140] and Arctic waters [141]. Their presence has been also reported in biota, such as fish, mussels, crustaceans [124,142], birds and mammals [143]. Due to their widespread use and the detection of these fragrances in environmental matrices, several authors have suggested the use of polycyclic musks as chemical markers of anthropogenic pollution [144,145].

Synthetic musks have also been found in several human tissues: blood plasma [146,147], adipose tissue [148,149] and breast milk [149-151]. The information about the health effects of musk is scant and currently there is a debate about the estrogenic or anti-androgenic endocrine disrupting activity of polycyclic musks [129,147]. Polycyclic and nitromusks inhibit the activity of multidrug efflux transporters responsible for multixenobiotic resistance in muscle, among other effects [152]. Although polycyclic musks have not shown mutagenic potential in different tests, general data on their toxicological effects on humans are scarce [148].

Parabens

Parabens (p-hydroxybenzoic esters) are the most commonly-used preservatives and antimicrobial agents used in personal care, pharmaceutical and food products. Figure 1.6 shows the general structure of parabens. The most widely used are methyl and propyl parabens, because of the synergistic effect when using both compounds together [111]. Other parabens commonly-used are ethyl, isopropyl, butyl, isobutyl and benzyl parabens. The widespread use of parabens as preservatives comes from their high antimicrobial activity, inertness, worldwide regulatory acceptance, biodegradability, low cost and stability to pH (effective between pH 4.5-7.5) and temperature [153].

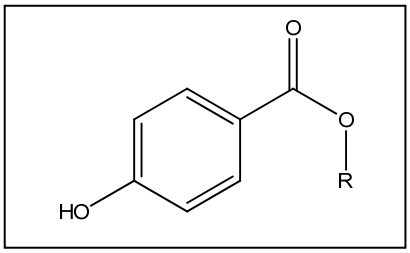


Figure 1.6. General structure of parabens.

The European Union permits the use of parabens in cosmetic products with a maximum concentration of each one of 0.4 % and a total maximum concentration of 0.8 % [120]. The US Food and Drug Administration regulations limit paraben concentrations in food to 0.1% [154], while paraben concentrations in pharmaceuticals do not exceed 1%.

Parabens can occur naturally in plants. For instance, methyl paraben (MeP) has been reported as a constituent of cloudberry, yellow passion fruit juice and white wine, and n-propyl paraben (PrP) has been detected in the aerial part of the plant Stocksia brahuica [155]. However, their major fate in the environment occurs because of their anthropogenic use. As mentioned before, parabens are used as preservatives in cosmetics, pharmaceuticals and food products. Because of their daily use, these PCPs are continuously released into the environment through urban and industrial waste water. They have been detected in water samples at concentrations ranging from ng L^{-1} to mg L^{-1}. Parabens can be effectively removed during conventional waste water treatments [121,156,157] and therefore their levels in WWTP influents are usually much higher than those found in WWTP effluents and, therefore, those in surface waters. For instance, González-Mariño et al. [158] found MeP and PrP in influents of a WWTP in the surroundings of Santiago de Compostela (Spain) at 5138 ng L^{-1} and 1147 ng L^{-1}, respectively, whereas the concentrations in the effluents were under the limit of

quantification. Concentrations of these parabens in the rivers of the area were up to 6.8 ng L^{-1} for MeP and 5.9 for PrP. Parabens have been also found in sewage sludge at concentrations up to 202 µg kg^{-1} for MeP and 10 µg kg^{-1} for PrP [159].

Few studies have determined parabens in air and indoor dust [160,161]. Rudel et al. [162] studied their occurrence in 120 homes in Cape Cod (USA). The most detected paraben was MeP with a median indoor concentration of 2.9 ng m^{-3}. More recently, the same group of researchers detected MeP up to 17 ng m^{-3} in an indoor environment, but all the studied parabens were under limit of detection in outdoor samples [163]. Reported concentrations of parabens were higher with values of up to 1640 ng g^{-1} for MeP and 1050 ng g^{-1} for PrP in homes in the north of Spain [160,164] and up to 10600 ng g^{-1} for MeP and 10800 ng g^{-1} for PrP in Canadian homes [165].

Parabens present some health effects and influence several molecular pathways within cells. As endocrine disrupting chemicals, the most extensively described activity is their ability to bind to human estrogen receptors (ER) and then to act via ER-mediated mechanisms to regulate gene expression and cell growth in estrogen-responsive cells [166,167]. Parabens act also as androgen receptor (AR) antagonists or as inhibitors of sulfotransferase enzymes [168]. On wider cellular functions, they can disrupt lysosomal and mitochondrial functions [169], can cause DNA damage [170] and can cause UVB-induced damage through the production of reactive oxygen compounds and nitric oxide [171]. Furthermore, parabens have been detected in human breast tissue and tumours [172] and, therefore, their estrogenic activity may influence the growth of estrogen responsive breast cancers [173].

The main human exposure route of parabens is through the skin and gastrointestinal tract [153]. However, there is little information regarding their presence in air or their toxicity and their absorption into the human body through the skin or the respiratory system [174].

Current concentrations found in human samples for single parabens (in the range 10-80 nM) are 2 to 4 orders of magnitude lower than effective concentrations in *in vitro* systems such as cell proliferation and aromatase inhibition in placental microsomes [175]. However, information of synergistic effects of parabens together with other cosmetic chemicals is unknown and should be a matter of future research [173].

Insect repellents

Insect repellents are substances applied to skin, clothing or other surfaces which prevent humans and animals from being bitten by insects. They also prevent the risk of infectious diseases being spread worldwide by insects. Insect repellents can be obtained from a natural origin or based on synthetically-produced active agents. Among the synthetic insect repellents, DEET (N,N-diethyl-m-toluamide or N,N-diethyl-3-methylbenzamide) is the most commonly-used insect repellent because it can repel a broad spectrum of insects. Recently, however, a new active agent – 1-piperidinecarboxylic acid 2-(2-hydroxyethyl) 1-methylpropyl ester (called icaridin, KBR 3023 or Bayrepel) – was introduced as a DEET substitute in some products. Both compounds and the main degradation product of Bayrepel, the Bayrepel-acid (1-[(1-methylpropoxy)carbonyl]-2-piperidineacetic acid), are the main insect repellents determined in environmental matrices. Among these, DEET is the most studied. Figure 1.7 shows the chemical structure of DEET. DEET is classified by the USEPA as an indoor, residential-use pesticide and, therefore, ecological risk assessments are not required [176]. DEET is not regulated by any European legislation, but has been voluntarily replaced by the main producers as a result of public concern.

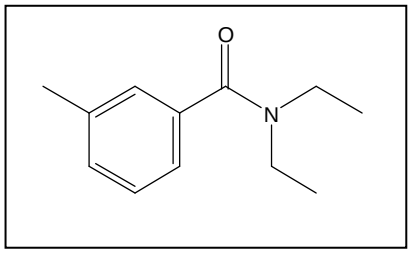


Figure 1.7. Chemical structure of DEET.

DEET has been widely detected in aquatic systems, including ground, surface and drinking water [177-179]. Recent reviews of the worldwide occurrence of DEET in the aquatic environment have reported concentrations ranging from 40 ng L^{-1} in fresh water samples to 13000 ng L^{-1} in some ground water samples [179,180]. However the processes controlling the environmental effects of DEET have not been studied in detail and further investigation on the effects of DEET and its metabolites in aquatic ecosystems is required. Furthermore, there is little information about its presence in atmospheric samples.

Information about DEET toxicity is also scarce but there is evidence that it is slightly toxic to aquatic invertebrates, fish and birds but practically nontoxic to mammals [176]. The main route of exposure for humans is skin absorption. A few toxic side effects in

humans have been reported when used excessively [179], most of them due to antagonistic interactions of DEET with cholinesterase, an enzyme required for the proper functioning of the nervous system. Research has also shown that DEET has potential carcinogenic properties in human nasal mucosal cells [181].

1.1.3.2 Nitrosamines

Nitrosamine is the general term used to designate a vast group of N-nitroso compounds (NOCs). Among these NOCs, N-nitrosamines are of special interest because of their occurrence and effects on health. In this section, we overview first the N-nitrosamines most commonly found in the environment and next the tobacco-specific nitrosamines, which are potent carcinogens formed by oxidation of nicotine.

N-nitrosamines

N-nitrosamines are genotoxic organic contaminants widely-distributed in the environment. The main route of formation of N-nitrosamines is by nitrosation reactions that take place between a nitrosating agent (like nitrite (NO_2^-) in an acidic environment, nitrous acid (HNO_2), nitrogen oxides (NO_x), nitrosyl chloride (NOCl) and a nitrosable agent such as a secondary amine. Nitrosation reactions occur in some foods such as vegetables, fish, and especially meat products cured with nitrite. In the atmosphere, N-nitrosamines are formed because of the presence of nitrogen-containing compounds originated from combustion processes. The main industrial sources are those which manufacture amines, herbicides, pesticides, pharmaceuticals and rubber. Moreover, fertilization of arable lands and grassland soils with mineral nitrogen encourages the formation of nitrosamines in soils. They can also be formed because of the biotransformation of some pesticides and other precursors [182]. A source of particular interest is the formation of N-dimethylamine (NDMA) and other N-nitrosamines as disinfection by-products (DBPs) during the chlorination of drinking water supplies [183]. These N-nitrosamines are included in the EOC group [184]. Recently it was recorded that the presence of other nitrogen-organic compounds present in waste waters, such as some PCPs, can also act as NDMA precursors [185]. Figure 1.8 shows the structures of the N-nitrosamines most commonly found in the environment.

Little current legislation regulates the concentration of N-nitrosamines in the environment. For instance, European legislation only regulates the release of N-nitrosamines and N-nitrosable substances from elastomer or rubber to a limit of 10 µg kg^{-1} for total N-nitrosamines and of 200 µg kg^{-1} for nitrosable materials such as secondary amines [186]. N-nitrosamines in the atmosphere are only regulated by

German legislation, which limits the airborne N-nitrosamine concentrations to 2.5 µg m^{-3} around manufacturing and storage areas and up to 1 µg m^{-3} in other atmospheric environments [187].

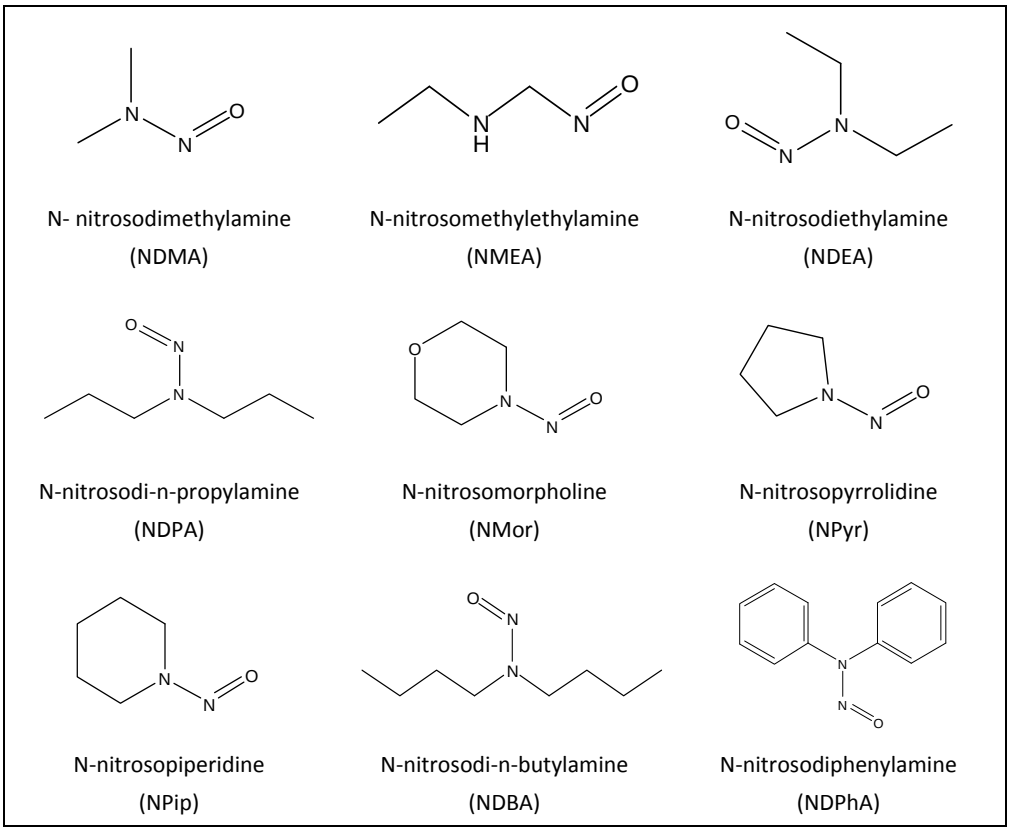


Figure 1.8. Chemical structures of the N-nitrosamines most commonly found in the environment.

Regarding levels in water, five N-nitrosamines have been included in the USEPA New Contaminant Candidate List-3 (CCL-3) of water contaminants [30]. Although there is a lack of directives for the maximum allowable amounts of NDMA and other nitrosamines, a current limit of 10 ng L^{-1} for notification is internationally accepted. Recently, the state of California published limit levels of NDMA of 3 ng L^{-1} [188] and the USEPA recommends that levels of NDMA in lakes and rivers should be limited to 1.4 ng L^{-1}, to prevent possible health effects from drinking water or eating contaminated fish [189].

As mentioned previously, N-nitrosamines are widely-distributed in the environment and have been detected in air, water, sediments, as well as in food and consumer products. In a study of drinking water in Canada, levels of 108 ng L^{-1} for NDMA, 71 ng L^{-1} of NPyr

and 2 ng L^{-1} of NPip were found [190]. In a recent study of our research group by Llop et al. [191] N-nitrosamines were found in the urban drinking water of Tarragona with concentrations of 10.3 ng L^{-1} for NDMA, 28.8 ng L^{-1} for NMEA, 66.6 ng L^{-1} for NPyr and 51.1 for NMor. The highest atmospheric concentrations have been detected in the rubber industry, with values of airborne NDMA of 0.3 µg m^{-3} and of NMor of 0.23 µg m^{-3} in a German rubber factory [192].

The main route of exposure of N-nitrosamines is through the ingestion of food and waters containing these contaminants [183,193]. Moreover, human endogenous formation of N-nitrosamines can occur in the acidic stomach through nitrosation reactions of amines in the presence of nitrite and nitrate. This formation increases the risk of gastric, esophageal, nasopharyngeal, and bladder cancer [182].

N-nitrosamines are environmental toxins that can be metabolized into potent genotoxic agents. There are an extensive number of studies of their genotoxicity [183]. NDMA is a model compound of this class, which is genotoxic in a wide array of systems *in vitro* and *in vivo*. It induces gene and chromosomal mutations as well as DNA damage. Furthermore, it is activated into a mutagen by various enzymes. IRIS identified 4 nitrosamines as probable human carcinogens (group B2) [52] and IARC found sufficient evidence in animals for the carcinogenicity of NDMA, NPyr, NMor and NPip [50]. According to the IRIS database, 7 ng L^{-1} in drinking water represents a 10^{-5} lifetime cancer risk for the average adult.

Nicotine and tobacco-specific nitrosamines

Of special concern are the so-called tobacco-specific nitrosamines (TSNAs), which are among the most abundant carcinogens identified in tobacco and its smoke. TSNAs are non-volatile nitrosamines formed by nitrosation of nicotine and other related tobacco alkaloid precursors with nitrogen oxides, during the tobacco curing, ageing or fermentation processes and during its combustion [194]. The structures of nicotine and of the most commonly-related TSNAs are shown in Figure 1.9.

Because of their origin, the presence of TSNAs is especially important in indoor environments. Nicotine is the most abundant organic compound emitted during smoking and deposits almost entirely on indoor surfaces. This nicotine can also react with atmospheric compounds (ozone, nitrous acid and nitrogen oxides) to produce TSNAs. Given the low volatility of TSNAs and the high levels of nicotine typically found in environments contaminated with tobacco, TSNAs can persist for weeks to months [195].

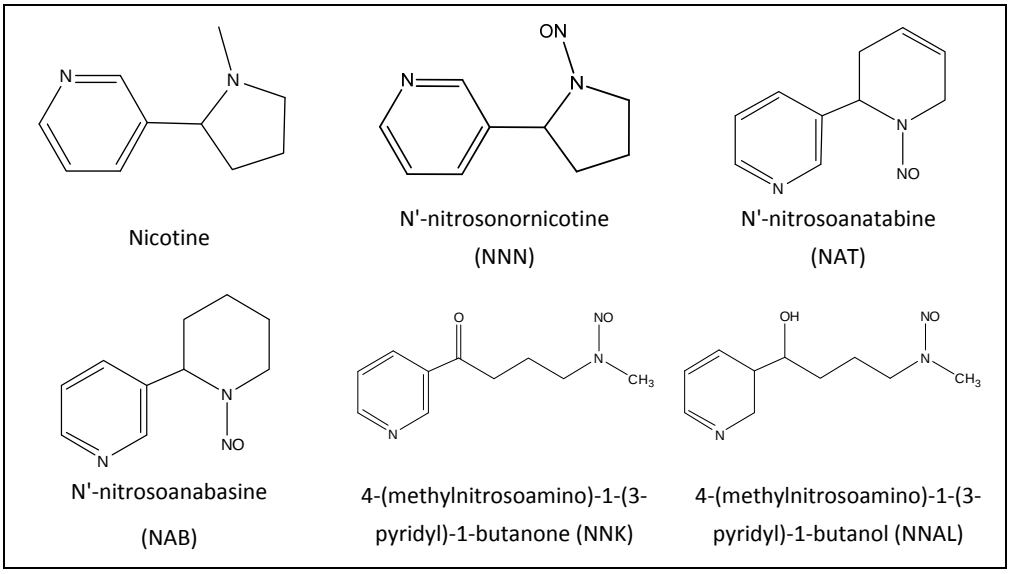


Figure 1.9. Chemical structures of nicotine and the most common tobacco-specific nitrosamines.

Furthermore, several experiments have suggested that airborne NNK concentrations in sidestream cigarette smoke can increase by 50% to 200% per hour during the first 6 hours after cigarettes are extinguished [196].

The main route of exposure to TSNAs is through inhalation of environmental tobacco smoke. The environmental tobacco smoke, most commonly called second hand tobacco smoke (SHS), consists of diluted and dispersed sidestream tobacco smoke that is emitted by smouldering cigarettes. SHS contains many mutagenic and carcinogenic chemicals, and of these TSNAs are among the most potent carcinogens [194]. Whereas direct inhalation of SHS is an exposure pathway of concern, non smokers, especially infants, are at risk through contact with surfaces and dust contaminated with residual smoke gases and particles [197] (called thirdhand smoke (THS)) [198]. THS has been overlooked as a source of long-term exposure to TSNAs [195]. Several studies have detected nicotine in indoor dust and on surfaces. Kim et al. [199] analysed 7 dust samples of non-smoking homes and 30 of smoking homes and found that the average concentration of nicotine in smoking homes was 43.4 ng mg^{-1}, 3 times higher than in non-smoking homes. Similarly, Matt el al. [197] found nicotine levels 5-7 times higher in the households of smokers, with concentrations of up to 4.43 µg per m^2 found on surfaces. Rumchew et al. [200] determined nicotine concentrations of PM_{10} in 92 homes in Australia. The average nicotine concentrations in smoking homes were 0.75 µg m^{-3}, whereas concentrations in non-smoking were < 0.5 µg m^{-3}. TSNAs have been determined in tobacco leaves, in cigarette smoke and in SHS. However, there is no information about their presence in house dust. Concentrations of TSNAs in SHS have

been reported to be 4.36 ng m^{-3} for NNN and 1.95 ng m^{-3} for NNK [201]. Average concentrations of TSNAs in tobacco smoke per cigarette are 159 ng of NNN, 115 ng of NAT, 13 ng of NAB and 135 ng of NNK [202].

According to IARC, TSNAs are a leading class of carcinogens in tobacco products [203]. Of all TSNAs identified, NNK and NNN are the most prevalent and strongest carcinogens in tobacco products [194] and so IARC classified them as the only TSNAs carcinogenic to humans (Group 1) [203]. NAB and NAT are considered to be not as classifiable regarding its carcinogenicity to humans (Group 3 IARC). TSNAs have been linked to acute leukaemia [204] and lung cancer [205].

Because of the adverse health effects related to tobacco smoke, several countries have prohibited smoking in indoor public places. This prohibition has reduced the exposure of non-smokers to nicotine and TSNAs dramatically. However, exposure to these contaminants is still present in private homes and cars. Hence, further investigation on the presence of nicotine and TSNAs in indoor surfaces and dust and their implications for human health should be carried out in the future.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

1.2. Determination techniques

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

As previously commented, organic contaminants can be found at very low concentrations in environmental atmospheres and waters. Therefore, efficient and highly sensitive detection techniques that allow low limits of detection (LODs) are required for their reliable determination. Liquid and gas chromatography continue to be the predominant techniques for the identification and quantification of organic contaminants, their metabolites and transformation products in the environment. They are also the techniques which are recommended in most of the standard methods. Gas chromatography (GC) is the preferred analytical technique for determining volatile compounds but it is also used for the determination of some semi-volatile contaminants. However, for the determination of more polar and less volatile organic contaminants, a derivatization step is often needed prior to GC analysis. Hence, liquid chromatography (LC) is the preferred technique for determining these contaminants. Both GC and LC can be used in combination with several detection techniques. Mass spectrometry (MS) is currently the most widely-used because of its high sensitivity and selectivity.

Other analytical techniques, such as capillary electrophoresis (CE), have also been used. Recent advances in CE coupled with MS detection make this hyphenated technique more competitive in the analysis of environmental samples [206]. However, for the determination of atmospheric contaminants, few applications in CE have been published. As an example, Van Pinxteren et al. developed a capillary electrophoresis/electrospray ionization mass spectrometry (CE/ESI-MS) for the determination of 38 organic acids in atmospheric particles and cloud water [207]. The preconcentration of the analytes in a solid-phase extraction cartridge and the coupling of CE with time-of-flight (TOF) spectrometry allowed limits of detection (LODs) in the low pg m^{-3} range. More applications can be found for the determination of organic contaminants in waters. As an example, non-aqueous CE has been used for determining parabens and synthetic musks in waters [208], allowing LODs of low ng L^{-1} comparable with those found with other GC-MS methods. DEET has also been quantified by field-amplified concentration with micellar electrokinetic chromatography (FAC/MEKC) and spectrophotometric detection [209].

Currently, the development of more selective and environmentally-friendly techniques is an issue of major concern. Increasing interest is being shown in immunochemical methods [210] as techniques for trace determination of organic contaminants. These techniques require only a little preparation, exhibit high sensitivity, and may be less expensive in comparison with instrumental analysis based on chromatography and mass spectrometry. Furthermore, fully automated immunosensor systems can be applied for the routine analysis of real samples. Currently, however, there are few applications being used to determine organic contaminants in environmental samples. One

application by Tschmelak et al. [211] used an optical biosensor for the determination of pharmaceuticals, antibiotics, hormones, endocrine disrupting chemicals and pesticides in water and it showed LODs below 0.2 ng L^{-1}.

Real-time determination of organic contaminants is also becoming increasingly important because of growing concerns over toxicity and the increase in environmental legislation. Real-time determinations are especially useful to study variations in the levels of atmospheric contaminants and for the detection of occasional high levels that can be produced in the atmosphere. In general, spectroscopic techniques are ideal for on-line process monitoring because of their short analysis times. Fourier-transform infrared spectrometry (FTIR), X-ray fluorescence spectrometry (XRF) and MS are examples which are used for continuous, on-line monitoring.

Direct air sampling-MS (DS-MS) is the most widely-used method for continuous air sampling and monitoring of VOCs in ambient air [212]. In DS-MS, an inlet system extracts and transfers the analytes from the atmospheric pressure to the high vacuum inside the MS, while an auxiliary pump is used to draw the air sample continuously into the inlet system. The most commonly-used inlets are capillary restrictors and polymeric membranes.

The most widely-used DS-MS techniques for the determination of atmospheric contaminants, their times of analysis, LODs, advantages and disadvantages and some examples of analytes are summarised in Table 1.7. Differential optical absorption spectroscopy (DOAS) shows a fast response time and low LODs. DOAS is based on the different light absorption of different organic molecules and gives specific differential absorption spectra that allow their identification. DOAS instruments permit continuous, moderately sensitive determination of VOCs in ambient air, but the presence of oxygen, ozone and several hydrocarbons with similar spectra gives rise to severe interference effects. Moreover, the sensitivity of the DOAS technique was shown to be reduced under low-visibility conditions.

Low pressure and atmospheric chemical ionization combined with tandem MS systems (LPCI-tandem MS and APCI-tandem MS) are sensitive and permit real-time continuous determination of VOCs in ambient air. LPCI-tandem MS gives low background levels and lower method LODs than APCI-tandem MS. However, LPCI-tandem MS instruments are expensive and are not yet able to achieve very low LODs, so they are not very conclusive for measuring VOCs, particularly BTEX, in ambient air at the low-µg m^{-3} concentrations of regulatory levels widely set by authorities in environmental and occupational health areas. In this sense, proton-transfer reaction MS (PTR-MS) provides rapid, sensitive measurement of VOCs in ambient air with very low LODs. However, the main drawback

of this technique is that isomeric and isobaric compounds are not separated and measured individually by PTR-MS instruments.

Table 1.7. Most representative real-time techniques for determining atmospheric organic contaminants [212-214].

Real-time technique	Time of analysis	LODs ($\mu g\ m^{-3}$)	Analytes	Advantages	Disadvantages
DOAS	30-60 s	1-2.6	BTEX Formalde-hyde	High time resolution. Real time-data. No chemical interferences. Multi-component. Sensitive determination of a wide range of VOCs.	Interferences caused by the presence of oxygen and hydrocarbons with similar spectra. Reduction of sensitivity under low-visibility conditions. High cost.
APCI-tandem MS	< 5 s	38	BTEX PAHs	High ionization efficiency. High sensitivity. Direct sampling.	Not recommended for measuring BTEX at low concentration. Formation of water clusters. High cost.
LPCI-tandem MS	5 s	2.0	BTEX PAHs	Simplicity. On-site determination of wide range of VOCs.	Expensive. Presence of dilution of H_3O^+ reagent ions.
PTR-MS	1 s	0.3; 0.03-0.4 for BTEX	BTEX Alcohols Terpenes Isoprene Aceto-nitrile THF	High sensitivity. Low LODs. Short time analysis.	Isobaric interferences on hydrocarbon measurements. Reaction time of H_3O^+ ions and flow-drift tube pressure limitations from the electrical field.

Since GC and LC are the most widely-applied separation techniques for the determination of organic contaminants in environmental samples, this section is dedicated to reviewing the current GC and LC methods.

1.2.1. Gas Chromatography

As mentioned before, GC is a versatile technique suitable for the determination of thermally stable volatile and semi-volatile organic contaminants. One of the main advantages of GC is that it is compatible with sample preparation techniques that require the subsequent liquid desorption (LD) or thermal desorption (TD) of the analytes and therefore can be used in combination with a wide range of sample preparation techniques. For instance, GC analysis is the preferred technique for determining synthetic musk fragrances because these compounds have high thermal stability and lipophilicity [122]. Furthermore, for the determination of more polar analytes, such as amines, carbonyls, phenolic contaminants or polar degradation products of PCPs, a derivatization step prior to the GC analysis can be used. The main objective of derivatization is to block the polar functional groups, leading to an increase in volatility and reduction in polarity. This enhances GC peak shape and leads to higher sensitivity. For instance, silylating reagents like N-methyl-N-(trimethylsilyl) trifloroacetamide (MSTFA) or N-methyl-N-tert-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) have been successfully applied for the derivatization of compounds containing hydroxyl groups, such as UV filters, antimicrobials [215] and preservatives [216].

The most commonly-used injection system is the split/splitless. However, the use of large volume injection (LVI) techniques is one of the strategies used currently to improve sensitivity. The most widely-used LVI techniques are on-column (OC) and programmed temperature vaporizer (PTV) injection, but also newer applications, such as direct sample introduction, at-column injection, and through oven transfer adsorption-desorption interfaces, can be found in the literature [206]. While split/splitless injectors are usually limited to about 4 µL of injection volume, 50 µL can be injected to PTV and OC injectors. However, because of the large volumes that can be injected in OC and PTV injectors, the chromatographic system can easily become polluted and give unreliable results, thus are only recommended when very clean samples are used [122].

One of the most common capillary columns used for the determination of organic contaminants are those coated with a film of 5% diphenyl polydimethylsiloxane, with 0.25 mm or 0.32 mm i.d. and 30 m or 60 m of length. Although these columns allow the separation of a wide range of compounds, more selective GC phases are needed for the resolution of isomeric or enantiomeric compounds that usually coelute. For instance, more polar polydimethylsyloxane phases, such as a 50% diphenyl, have been successfully used for the enantiomeric separation of some PAHs, and 65% diphenyl phases have been used for the separation of high polar degradation intermediates of

PCPs [17]. However, liquid crystalline columns provide greater selectivity of 50% or 65% than diphenyl polydimethylsyloxane columns [217]. Liquid-crystalline columns can separate the three important pairs of PAHs that typically coelute on traditional 5% phenyl methylpolysiloxane columns (Chr and triphenylene; BbF and BjF; and dibenzo[a,c]-and DahA) [217]. Since these PAHs present different carcinogenic and mutagenic effects, their accurate separation is of major concern for health studies. The main limitations of liquid-crystalline columns are variation in selectivity, changes in the order of elution of PAHs among different columns, and a limited temperature range, which results in a limited mass range for the determination of organic contaminants. To overcome this, a 50% dimethyl 50% (mole fraction) liquid-crystalline polydimethylsiloxane phase has been developed to offer a greater operating temperature range. Currently the most efficient enantioselective GC phase is the (heptakis-(2,3-di-*O*-methyl-6-*O*-t-butyldimethyl-silyl)-β-cyclodextrin), which can separate the enantiomers of the polycyclic musks and their metabolites [122].

However, the complexity of environmental matrices can provide several problems with the identification and quantification of the target organic contaminants. The chromatographic peaks of these contaminants can sometimes be overlapped with other target compounds or matrix components and, therefore, cannot be resolved by one dimensional GC. To overcome this obstacle, comprehensive two-dimensional gas chromatography (GC×GC) has emerged over the last two decades as a powerful analytical technique. This is an excellent choice for the determination of organic contaminants in complex matrices. When the multidimensional GC approach based on heart-cutting type was used previously, only a few small fractions eluting from the first columns were selected for further separation on the second column and, therefore, its applicability was limited to determining known target analytes. In the comprehensive approach (GC×GC), the entire first dimension column eluate is further analysed in the second dimension column. GC×GC increases the separation space and improves the chromatographic resolution, allowing more confident analyte identification and quantification [218]. The LODs of GC×GC are usually three to five times lower, and the number of resolved peaks is up to 10 times greater than with one dimensional GC [218]. Equipment for GC×GC includes: an injector and a detector (as in the one dimension GC equipment); a first column (15-30 m length × 0.25-0.32 mm i.d., 0.1-1 µm film thickness); a modulator, usually a cryogenic one, which accumulates and traps the analytes that elute from the first column, and releases each fraction to the second column rapidly; and a much shorter, narrower and polar second dimension column (0.5-2 m × 0.1 mm i.d., 0.1 µm film thickness) [219]. Figure 1.10 shows the scheme of a GC×GC system with the second column held in a separate oven. This is the most widely-used approach these days because it enables more flexible temperature control. GC×GC

systems have largely been applied for the characterization of air and aerosol organic contaminants. One of the most relevant applications was the separation of more than 550 VOC species from urban air samples by Lewis et al. [220]. Amador-Muñoz et al. [221] used GC×GC for the determination of PAHs in urban dust, obtaining enhanced sensitivity with minimum sample treatment, compared with more traditional one dimensional techniques. Recently, Gómez et al. [222] used a GC×GC method for the automatic searching and evaluation of non-polar and semi-polar contaminants (13 PCPs, 15 PAHs and 27 pesticides) in waste water and river water, obtaining excellent separation efficiency and compound identification.

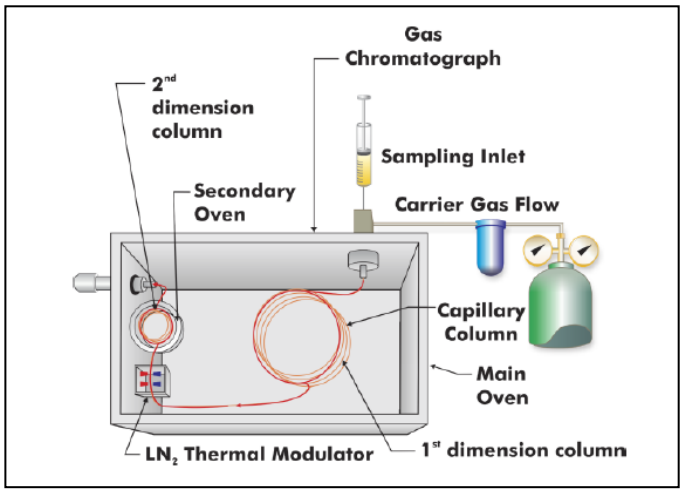


Figure 1.10. Scheme of a GC × GC system showing 1st dimension column, thermal modulator and 2nd dimension column located inside a secondary oven [223].

GC can be used in combination with a wide variety of detectors, such as classic detectors like flame ionization detector (FID). An alternative involves the use of specific GC detectors that provide higher selectivity in the determination of specific compounds, such as the electron capture detector (ECD), nitrogen-phosphorous detector (NPD) or the nitrogen chemiluminiscence detector (NCD). For instance, Özel et al. [224] recently demonstrated that GC×GC coupled with NCD, specific for organic nitrogen (ON) compounds, allows the detection of more ON species with higher sensitivity than when mass spectrometry detectors are used. However, the most commonly-used detection technique coupled with GC that is used nowadays is MS. In GC analysis, the full scan mode of MS is employed for identifying compound structures, whereas the selective ion monitoring (SIM) can be applied to achieve high sensitivity for quantification. The electron impact mode (EI) is the most appropriate if the analysis is focused on the

enforcement of maximum residue levels, simultaneous identification and quantification of a very large number of target analytes.

Chemical ionization (CI) is a softer ionization mode that provides information on the fragmentation pattern which is useful for structure identification of organic contaminants and their metabolites. Furthermore, CI mode can increase sensitivity of some compounds, such as nitromusk fragrances and their amino metabolites [111] and volatile amines and nitrosamines [191,225]. The negative CI (NCI) detection of these nitrogenated compounds increases sensitivity to achieve LODs comparables to ion trap MS (IT-MS) [226]. NCI with methane has also been shown to be highly sensitive and selective for some isomeric PAHs, such as the selective detection of the molecular ions of FluT over Pyr and of BaP over BeP [217].

Several MS analysers can be found in the literature. Single quadrupole MS has been successfully applied for determining a wide range of organic contaminants, such as VOCs [59], PAHs [227] and PCPs [122]. Other MS analysers, high resolution MS (magnetic or TOF), IT-MS or tandem MS allow the suppression of a matrix background to achieve higher selectivity and sensitivity [17]. For instance, Planas et al. [228] proposed an automated SPE method and isotope dilution GC with magnetic high resolution MS for the determination of nine nitrosamines in water samples, achieving LODs between 0.08-1.7 ng L^{-1}. These MS analysers can also be combined with LVI to provide higher sensitivity. Besides, TOF-MS permits full-scan screenings with high mass resolution, and mass accuracy. For instance, one useful application of TOF-MS is for the identification of unknown degradation intermediates of PCPs in environmental matrices [17]. The use of TOF-MS in combination with the high chromatographic resolution capability of GC×GC reduces the sampling pre-treatment steps, increasing the sample throughput. For instance, Matamoros et al. [229] developed a methodology based on a polymeric solid-phase extraction, followed by in GC-port methylation and GC×GC/TOF-MS determination for the simultaneous determination of 97 organic contaminants in river water, with LODs from 0.5 to 100 ng L^{-1}. More recently, Leda et al. [230] detected highly chlorinated PAHs in environmental samples for the first time using a GC×GC/TOF-MS method. One of the main drawbacks of this coupling is that GC×GC/TOF-MS chromatograms are very complex and the identification of a specific group of compounds is a very time-consuming process.

The tendencies in modern GC are towards the miniaturisation of instrumentation and the achieving of shorter separation times. GC is the most widely-used separation technique for the in-field determination of organic contaminants. To that end, portable and miniaturised GC equipments are being developed, such as GC-FID or GC-MS which are widely-used for determining VOCs in atmospheric samples [214]. One recent

example of GC miniaturisation is the development by Hallyday et al. [231] of a microfabricated GC×GC system (coupling the primary column to the secondary via a differential flow modulator). This is suitable for the separation of VOCs and sub-ng detection sensitivity to monoaromatics when coupled with a low power photoionization detector (PID).

One of the approaches that provides shorter times is low pressure GC (LPGC). A typical LPGC set-up involves the use of a short microbore column (typically 0.5–1 m × 0.10 mm internal diameter) at the injector side connected with a zero dead-volume connector to a short megabore column (typically 10 m × 0.53 mm) to be used with higher gas velocities. This set-up maintains atmospheric injection conditions, while the analytical column is operated under low-pressure conditions that are compatible with MS detectors [232]. Although the use of LPGC results in a loss of separation efficiency, it offers a 3–5-fold reduction in analysis time for organic compounds and thus increases sample throughput and enhances the signal-to-noise ratio, leading to improved detection limits. LPGC has been widely-used for determining pesticides in fruits and vegetables; however it has also been applied for determining other contaminants in environmental matrices. For instance, LPGC coupled with ITMS has been used for the analysis of gas and aerosol phase PAHs from ambient air samples [233]. 16 PAHs were separated in less than 13 minutes using LPGC-ITMS, whereas 40 minutes are needed when using a conventional GC-MS. LPGC-ITMS has also been applied for determining BTEX in environmental samples in 1 minute of analysis time [234].

Additionally, the so-called *fast GC* uses shorter, narrower columns and higher carrier gas velocity to achieve faster analysis times, in the order of minutes or even milliseconds. Fast GC is designed to minimise analysis time without compromising chromatographic resolution and it is usually accomplished by reducing the characteristic diameter of the GC column and the use of shorter columns. A major advantage is that peak width is small so the signal-to-noise ratio is larger. Analysis using fast GC can give peak widths at half height of 0.2-3 s and separation efficiencies equal to or greater than conventional GC but 5 to 30 times faster [235]. For instance, Jurado-Sánchez et al. [236] developed a fast GC method coupled with a NPD for the screening of N-nitrosamines in tap and swimming pool samples in 3 minutes. Recently, Pinto et al. [237] developed a fast GC method based on LVI-fast GC-MS for the determination of trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) and BTEX in soil samples. The separation of the analytes was carried out in less than 5.50 minutes with LODs in the range of 0.2 to 15 μg kg^{-1}. A disadvantage of fast GC is that the stationary phase may be substantially overloaded if the analytes are highly concentrated. The main limitation of fast GC is the speed of detector response, and therefore is limited to GC-FID, GC-ECD and GC-TOF-MS. The advantages of fast GC are: reduced time; greater

throughput; feasibility of more replicate analysis resulting in greater precision; lower carrier gas consumption; reduced cost; and applicability of field portable instruments [235].

1.2.2. Liquid Chromatography

In contrast with GC, liquid chromatography (LC) is the preferred technique for the determination of less-volatile, polar or thermolabile organic contaminants. For instance, LC has been used for the determination of apolar semi-volatile compounds such as PAHs, [217], less volatile PCPs such as UV filters [238], and some PCP degradation products which are more polar than their respective PCP precursors [17].

Reverse phase is the most typical LC mode, with C_{18} and C_8 columns being the most frequently-used [239]. However, the overall trend in LC is for fast-LC methods that use short, narrow bore columns, high mobile phase flow-rates and ultra-high pressures in order to reduce the analysis time (and therefore the solvent consumption) without compromising the peak resolution. One of the options to reduce run times is ultra-high performance LC (UHPLC), which uses columns packed with sub-2 μm particles. This enables elution of sample components in much narrower and more concentrated bands, resulting in better chromatographic resolution and increased peak capacity [240]. Pedrouzo et al. [238] developed a UHPLC method for determining 11 PCPs in environmental waters in only 9 minutes of chromatographic separation. However, the increase in pressure when using columns packed with small particles requires the use of specialized LC systems able to tolerate back-pressures of up to 15,000 psi. To overcome this, shell-core columns have recently been introduced. These shell-core particles are 2.7 μm in diameter, with a 1.7 μm solid core and a 0.5 μm porous outershell with 9 nm pores. This configuration allows very rapid separations at modest pressures. There are few reported applications of these columns in the determination of organic contaminants in environmental atmospheres or waters. Recently, it was used for determining drugs of abuse and their metabolites in waste and surface waters in 13 minutes of analysis [241].

Another recent trend in LC is the application of hydrophilic interaction chromatography (HILIC) for the separation of polar compounds. This involves a polar stationary phase (such as silica gel or aminopropyl HILIC columns) and an aqueous-organic mobile phase rich in organic solvents in which water is introduced to play the role of a stronger eluting solvent. HILIC increases sensitivity in MS detection compared to reverse phase LC. Because of this, applications of this technique to the determination of organic contaminants in environmental samples have increased in the last few years. For

instance, Esparza et al. [242] developed a HILIC method for determining diallyl-dimethylammonium chloride in water samples with LOD of 50 ng L^{-1}. The low detection limit achieved, in combination with the absence of matrix effects, allowed the direct analysis of samples without any pre-treatment, pre-concentration or clean-up step. The application of HILIC-tandem MS for determining drugs of abuse in waste water provided limits of quantification (LOQs) in the 1-2 ng L^{-1} range [243].

Several detectors can be used with LC such as diode array UV absorbance and fluorescence detection, among others. For instance Silva et al. [244] used LV-diode array detection to determine triclosan in biological and environmental matrices with an LOD of 100 ng L^{-1}. However, hypenation with MS detection is necessary for trace analysis in environmental complex matrices and for the identification of new compounds [210]. The use of tandem MS or TOF-MS rather than single-quadrupole is especially relevant when it is coupled with LC because of the lower chromatographic resolution of this technique and the often low fragmentation obtained. Since LC-tandem MS allows separation and detection of compounds having the same molecular mass but different product ions, even if they coelute, tandem MS detection is the preferred method because of its increased analytical sensitivity and selectivity in complex water matrices. Different tandem MS approaches are the triple quadrupole (QqQ), the IT and the hybrids quadrupole-ion trap (Qtrap) and quadrupole-TOF (Q-TOF). Among them the most commonly-used detection mode is QqQ because of its high sensitivity which allows the determination of organic contaminants at very low levels. For instance, Rodil et al. [245] applied a QqQ for the determination of emerging organic contaminants in water samples with LODs between 0.3 and 30 ng L^{-1}. Pedrouzo et al. [238] determined parabens, antimicrobials and UV filters using a QqQ with limits of detection in river waters in the range of 1-5 ng L^{-1}. In general, QqQ MS or Qtrap-MS are usually applied for structure elucidation and quantitative analysis, whereas TOF-MS is more useful for identification [246]. Another hybrid, the Q-TOF, permits the acquisition of full-scan product ion spectra, with the accurate mass of the product ions. Based on the product ion spectra, structure elucidation of unknown compounds, as well as identification of target compounds, can be obtained with a much higher degree of certainty [247]. For instance, Petrovich et al. [248] used Q-TOF for determining pharmaceuticals in water samples with LODs ranging 10 to 500 ng L^{-1}.

The most commonly-used LC-MS interfaces are atmospheric pressure ionization technologies, such as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). ESI is well-suited for the determination of polar compounds, whereas APCI is very effective in the determination of medium-polarity and low-polarity substances. For instance, an ESI interface was used by Negreira et al. [249] for determining six polar derivatives of 2-hydroxybenzophenone, a UV filter, in water

samples. Whereas both ESI and APCI are the most suitable for the detection of low-molecular mass molecules, the atmospheric pressure photoionization (APPI) interface is the best choice for the analysis of contaminants which are difficult to ionize [206]. Viglino et al. [250] used a LC-APPI-tandem MS method for determining natural and synthetic estrogenic endocrine disruptors in environmental waters achieving LODs of 5 ng L^{-1}. Matrix effects are one of the major drawbacks of the LC-MS coupling, particularly when working in the ESI mode. It can result in the suppression or, less frequently, the enhancement of analyte signals, leading to erroneous quantification [184]. The least time-consuming method to compensate for matrix effects is to use isotopically labelled standards as surrogate or internal standards. For instance, González-Mariño et al. [158] used analogous isotopically labelled compounds of methyl paraben, triclosan and tricarbam to compensate for matrix effects in (ESI)-tandem MS. Other strategies to compensate for matrix effects include the dilution of the samples or the calibration by standard additions in the sample matrix.

As seen from the information above, GC-MS, both single quadrupole and ion trap, are the most widely-used techniques for determining volatile and some semi-volatile organic contaminants in both atmospheric and water samples. Additionally, the current methodological trends for the determination of semi-volatile and non-volatile organic contaminants involve the use of LC-tandem MS, especially when a QqQ analyser is used. New trends in both techniques involve a combination of strategies which allow the fast analysis of samples without losses of sensitivity and selectivity.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

1.3. Sample preparation

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

As mentioned before, the major pathway of anthropogenic organic contaminants into the environment is through emissions into the atmosphere and aquatic systems. Therefore, the determination of organic contaminants in atmospheric and water samples is an issue of major concern because of the environmental and health effects of these contaminants. Analytical methods to determine these organic contaminants come up against two main challenges. Firstly, the environmental samples are heterogeneous mixtures with a large number of components that can interfere in the determination of the analytes. Secondly, the target organic contaminants are usually at very low concentrations, usually at ng L^{-1} or ng m^{-3}. Therefore, in most cases, both atmospheric and water samples cannot be analysed directly and require the use of extraction and pre-concentration methods prior to the chromatographic analysis. For all of the above mentioned, the selection of a suitable sampling and extraction technique is a decisive point in the analytical process. In this section, we provide an overview of the most widely-used sampling and extraction techniques for the determination of organic contaminants in environmental atmospheres and waters.

Because of the complexity and heterogeneity of atmospheric samples, sampling of atmospheric organic contaminants should also be drawn up carefully, so that the representativeness of the sample is assured. For air samples, whole-air collection methods show high representativeness and use time-integrated samples. However, most of the current sampling and extraction methods of organic contaminants in air are based on enrichment onto solid sorbents, either by passive or active sampling. The main advantage of this technique is that it allows the sampling and preconcentration of the target analytes in one step. The suitable sorbent or group of sorbents, sampling volume (for active methods) and sampling instrumentation are among the most important parameters that should be optimised. Organic contaminants can also be present in the airborne particulate phase and in settled dust. These matrices can be collected using filters or denuders or in vacuum cleaner bags.

After sampling, atmospheric contaminants can be extracted either by liquid or thermal desorption. Liquid desorption (LD) is the preferred technique for semi-volatile compounds trapped on solid sorbents or bounded to airborne particulate matter of indoor settled dust. LD can be done by classic techniques, including Soxhlet and ultra-sound extraction, or more environmentally friendly techniques, such as pressurised liquid extraction (PLE), microwave assisted extraction (MAE) or supercritical fluid extraction (SFE). However, thermal desorption (TD) is the most widely-used technique for volatile organic contaminants. Some recent applications of the thermal desorption of semi-volatile compounds are described below.

Several extraction techniques can be used for the extraction of organic contaminants from water samples. Among these techniques, solid-phase extraction (SPE) has been the most widely-used extraction and preconcentration technique for determining organic contaminants because of the wide range of sorbents developed that cover a broad variety of analytes. However, current trends in sample preparation include the use of more environmentally-friendly methods that avoid or reduce the use of organic solvents. Among these green techniques, solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) are most commonly-used techniques. After SPME and SBSE, analytes are usually desorbed directly by thermal desorption which avoids clean-up steps and therefore reduces the risk of external contamination. Section 1.3.2 reviews the most recent developments in extraction and preconcentration techniques for water samples, including the development of more selective sorbents, as well as the most recent microextraction methods.

1.3.1. Atmospheric Samples

The atmosphere is a heterogeneous complex matrix mainly composed of a mixture of gases and solid particles. Furthermore, the atmospheric composition is continuously changing, as it can be affected by meteorological conditions, diffusion processes, and the reactivity of the organic compounds into different compounds. Organic contaminants can either be associated with the atmospheric gas phase or the particle phase. Because of their low vapour pressures, the most volatile contaminants, such as VOCs, are usually associated with the gas phase. However, semi-volatile organic compounds (SVOCs) can be distributed between both gas particle phases. This portioning between both phases depends on the molecular weight of the organic compound, their heat of condensation and the aerosol surface area [251]. The association of the organic compounds with particles can be done through adsorption and through some combination of surface interactions involving van der Waals and Lewis acid/base forces, and absorption such as insertion into an organic or aqueous layer on a particle's surface [252]. Therefore, sample preparation techniques for contaminants associated with particles should be strong enough to extract the analyte from the particle.

As discussed in section 1.1, atmospheric organic contaminants are often at low concentrations ranging from μg m^{-3} for VOCs to pg m^{-3} for SVOCs such as PAHs or EOCs. Hence, it is usually necessary to concentrate, focus or trap the analytes of interest prior to the analysis to increase sensitivity. The choice of the right sample preparation technique depends on several parameters. The most important parameters are: the phase in which the organic pollutant is associated (mainly gas or particulate matter); the

type of compound (volatile or semi-volatile) and its concentration level; the aim of the measurement (emission, immission, deposition); the period of measurement (long or short term); and the desired information (qualitative screening, variability of the concentrations, etc.).

Because of the nature of the atmospheric samples, the sample collection step plays a crucial role in the analytical process, as it determines the representativeness of the sample. Furthermore, sampling and preconcentration can be done in one single step, such as in the methods based on enrichment into solid sorbents. New trends in the analysis of atmospheric samples are the development of more rapid, less expensive and environmentally-friendly methods. Below, an overview of the most widely-used techniques for the sampling, extraction and desorption of organic contaminants present in air, particulate matter and settled dust is provided.

1.3.1.1. Sampling and extraction of air

Volatile and some semi-volatile organic contaminants can be found in the gaseous atmospheric phase. Currently, the most widely-used techniques for the sampling and extraction of these organic contaminants in air are whole-air collection and enrichment into solid sorbents either by active or passive sampling. This section is dedicated to the overview of the advantages and disadvantages of these methods, as well as some recent developments and applications.

1.3.1.1.1. Whole-air sampling

Air can be collected in containers, such as canisters, glass bulbs, bags made from synthetic materials – such as Tedlar – and gas pipettes. Currently the most commonly-used containers are canisters and plastic bags [235]. Sampling can be at atmospheric or sub-atmospheric pressures. Depending on the concentrations of the target contaminants, the air samples can be analysed directly by GC or in combination with a preconcentration step prior to the analysis. Whole-air collection techniques present some advantages over sorbent enrichment methods. Some of the main advantages are: high representativeness of the sample; absence of breakthrough of the analytes; availability of multiple sample aliquots for replicate analysis; and time-integrated samples when using controlled-flow pumps to introduce the sample into the container [235]. Some of the disadvantages are: no exclusion of non-target compounds which may lead to sampling matrix effects or analytical interferences; water condensation; adsorption of target compounds onto particles collected on the pre-filter or on the walls of the container; and the bulkiness of the sample.

Canisters samplers are recommended in the USEPA methods TO-14A and TO-15, to determine 40 atmospheric non-polar VOCs [253,254]. However, canisters have shown more versatility and have been used to efficiently determine more than 150 polar and non-polar VOCs [255]. These containers are made from specially-modified stainless steel, which preserve the stability of the VOCs. To avoid wall adsorption of VOCs, the interior surface of canisters can be coated with a layer of chrome-nickel oxide (Summa canisters) or, more recently, with a thin layer of fused silica [255]. Additional advantages of passivated canisters include: no degradation of trapping materials; sample stability for weeks or months; greatly reduced contamination problems; easy cleaning; and consistent recoveries [255]. Canisters are recommended for the analysis of C_2-C_5 hydrocarbons but are not recommended for hydrocarbons with a larger number of carbons because of the possibility of the wall effect [235].

Plastic bags can be made of Tedlar (polyvinyl fluoride), Teflon (fluorinated ethylene and propylene copolymer) or Nalofan (polyterephthalic ester) according to EN 13725 of the European Committee for Standardization [256]. Plastic bags are cheaper, can be used with a wide range of volumes (0.5-100 L), and can be reused after purging repeatedly with pure nitrogen or ultra-pure air. However, the main disadvantages are: the instability of the retained compounds during 24-48 hours of storage; the limited sample volume; and the permeability of some bags to certain compounds and humidity [235,257].

The biggest challenge in whole-air sampling is the removal of the collected water prior to injection in a GC column. Among other adverse effects, water can interfere with the subsequent analytical techniques, the VOCs associated with condensed water can be lost, the blockage of cryogenic traps through the formation of ice, variability of GC retention time by overloading and damaging the stationary phase, and deterioration of the MS ion source due to ionization of water [214]. Basic techniques for removal of water vapour from gas streams include adsorption, desiccation, permeation drying, cryocondensation and cold trap dehydration. Nowadays, the most widely-used methods are cryocondensation and cold trap dehydratation, which results in the removal of more water without affecting VOC recovery [255].

Depending on the concentrations of the target organic contaminants in the air samples and on the sensitivity of the detector, enrichment into a sorbent or in a cryogenic trap may be necessary prior to analysis. Most recent standards and regulatory guidance relating to whole air monitoring methods favour the use of one or more sorbent focusing traps held at ambient or moderately cooled temperatures for subsequent analysis [254,258].

Recently, canister methods have been used to determine chlorinated VOCs with a cryofocusing trap injector device followed by GC-MS. This method developed by Zoccolillo et al. [259] allowed accuracy of less than 4% and LODs between 0.1 to 0.2 pptv. Doezema et al. [260] determined fifteen ambient hydrocarbons in Los Angeles using 2 L-canisters followed by cryotrapping and GC-FID with %RSD <6% RSD for all compounds. The variability of seven alkyl nitrates in coastal New England was monitored by Russo et al. [261] using 2 L-canisters followed by a Thompson Farm GC system, which consisted of dual stage cryotrapping (first stage at -20°C for water removal and second stage at -185°C for trapping the analytes), reaching LODs of 0.01 pptv and %RSD between 10-20%. The suitability of Tedlar bags for determining volatile siloxanes in landfill gas was recently demonstrated by Ajhar et al. [262]. The bags were connected to a PTFE injection loop and analysed in a GC-MS, obtaining %RSD < 4%, and storage stability up to 30 days.

1.3.1.1.2. Enrichment into solid sorbents

The adsorptive enrichment into solid sorbents, either by active or passive sampling, is currently a well-established sampling technique for airborne organic vapours. This technique allows the sampling and enrichment in one simple step, which provides low limits of detection. The main advantages of sorbent sampling are that it allows a larger volume of sample than with a canister to be collected, and is easier to handle [257]. However, it is not a real-time technique and the range of analytes that can be collected is limited to the type of sorbent. In this section, an overview of the currently available sorbents, as well as the main active and passive sampling methods, is provided.

The main decision with sorbent-based methods is the selection of the suitable sorbent or group of sorbents that ensure the complete retention of the analytes during sampling and the complete desorption and recovery prior to the analysis [263]. Selection of the sorbent basically depends on the kind of target contaminants to be collected (volatility, polarity, etc.), on the sample matrix, and the subsequent desorption, analysis and detection techniques. Table 1.8 shows the main characteristics of some common solid sorbents: strength, surface area (in $m^2\ g^{-1}$), desorption method (liquid of thermal desorption), thermal stability, and the most characteristic features.

During the selection of the appropriate sorbent, the main parameters that should be taken into account are: the strength of the sorbent to avoid breakthrough of the volatile analytes or excessive retention of the less volatile analytes; the degradation products of the sorbents that cancause artifacts that affect the analysis; the inertness to avoid side reactions with the analytes; and the water affinity (the more hydrophobic, the less undesirable the effects are on chromatographic analysis).

Table 1.8. Main properties of some selected solid sorbents commonly used for the sampling and extraction of organic compounds from air samples.

Type	Sorbent	Strength	Surface area ($m^2 g^{-1}$)	Desorption	Thermal stability	Features
Inorganic	Silica gel	Weak	300-800	Liquid	< 400 °C	Suitable for high polarity and low volatility contaminants, such as PCBs and pesticides. High water affinity.
	Molecular sieves	Very strong	500-800	Liquid/ Thermal	> 400 °C	High artifacts (ca. 10 ng) in TD. High hydrophilic.
	Aluminum oxides	Weak	ca. 300	Liquid	< 400 °C	Used for polar analytes. High water affinity.
	Florisil	Weak	ca. 300	Liquid	> 400 °C	Used for polar analytes. High water affinity.
Carbon based	Activated charcoal	Strong	800-1200	Liquid	> 400 °C	Medium polarity. Low-medium water affinity.
	Carbon molecular sieves	Very strong	400-1200	Liquid/ Thermal	> 400 °C	Low polarity. Low-medium water affinity. Carbosieve SIII has minimal artifacts (<0.1 ng). Inert-suitable for labile compounds.
	Graphitized carbon blacks	Medium-strong	12-100	Thermal	> 400 °C	Hydrophobic. Minimal artifacts (<0.1 ng). Friable.
Porous polymers	Styrene-divinilbenzene polymers or polyvinyl-pyrrolidone polymers (PoraPak, Chromosorb, XADs)	Medium	300-800	Liquid/ Thermal	< 250 °C	Hydrophobic. High inherent artefact levels (10-50 ng/component). Inert-suitable for labile components.

Table 1.8. (cont.)

Phenyl-phenylen-oxide polymers (Tenax)	Medium	20-35	Thermal	< 350 °C	Low polarity and low water affinity. Low inherent artifacts (< 1 ng). Inert-suitable for labile components.
Poly-urethane Foams	Weak	~ 15	Liquid	< 200 °C	Suitable for collection of non-volatile analytes.
Poly-dimethyl-siloxane	Medium		Liquid/ Thermal	< 320 °C	Good sorption material for semi-volatile organic compounds.

Inorganic sorbents, such as silica, aluminium oxides and florisil, are weak sorbents, whose main drawback is their high water affinity. They are therefore currently-used for determining very polar compounds such as methanol [264] and amines [265] or as a substrate for derivatizing agents. Similarly, molecular sieves are inorganic sorbents with high water affinity and which show high artifacts when used in combination with TD. Therefore, several applications can be found in the literature for organic contaminants. For instance, zeolite molecular sieves can be used in sampling 1,3-butadiene [266].

Carbon-based sorbents have been widely-used for the determination of air contaminants. Activated charcoal has been by far the most common sorbent used in combination with liquid desorption, especially in occupational samplings. It is the sorbent used in the majority of NIOSH and OSHA methods and is also recommended for the determination of benzene in air by the European method EN-14662-2 [267]. Activated charcoal is a strong sorbent with a high surface area and is suitable for medium polarity air contaminants. More recent carbon-based sorbents include carbon molecular sieves, which are compatible with TD, and graphitized carbon blacks, which show minimal artifacts and low water affinity [268].

Porous polymers are weak-medium sorbents which are useful for trapping semi-volatile airborne contaminants. XAD resins and polyurethane foams (PUFs) have been widely-used as sorbents for persistent contaminants such as PAHs [217] and pesticides [269]. Tenax is one of the sorbents most commonly-used with TD, because of its low water affinity, its low inherent artifacts and its inertness. This makes it suitable for the sampling of labile analytes [266]. Polydimethylsyloxane (PDMS) can be used in combination with LD and TD and has been used for trapping semi-volatile compounds, such as PAHs [270].

For non-volatile and strongly adsorbed compounds, sample recovery from the sorbent remains the limiting step, whilst very volatile compounds may cause breakthrough problems. Since one single sorbent is not usually appropriate for all of the target air organic contaminants, multi-bed sorbent tubes are the best option these days to determine compounds in a wide range of volatility. In these tubes, high-boiling compounds get trapped in the first zone of the adsorbent bed (often a porous polymer such as Tenax), and the more volatile are collected on a sorbent with greater activity. Several authors have used different combinations of multi-sorbent beds for trapping a wide range of VOCs, such as Tenax TA-Carbograph TD for monitoring 64 VOCs in industrial and urban air [59,271,272] or Carbotrap-Carbopack X- Carboxen-569 for determining a wide range of odour nuisance and air-quality VOCs [273].

When commercially-available sorbents are used, volatile polar atmospheric contaminants are difficult to trap and usually show poor sensitivity and peak shapes in GC analysis. For those kinds of compounds, a derivatizing agent is usually added to the sorbent. For instance, carbonyl compounds are usually collected by simultaneous sampling-derivatization processes. The most common derivatizing agent for those kinds of contaminants is 2,4-dinitrophenylhydrazine (2,4-DNPH) added to C_{18} cartridges, silica or XAD resins in active [274] or diffusive samplers [275]. Moreover, some new sorbents have been developed using different technologies, such as nanoparticles [276]; molecularly-imprinted polymers (MIPs) [277]; and carbon nanotubes (CNTs) [278]. Most of these new sorbents have not shown sufficient robustness and repeatability for widespread application. However, new kinds of CNTs have been developed recently that show better sampling precision than previous CNTs because of better air permeability. For instance, Wang et al. [279] developed a 3-amino-propylsilica gel-multi-walled CNT for determining 38 VOCs in indoor samples, including alkanes, aromatic hydrocarbons, alcohols, carbonyls, amines, esters, halogenated compounds and sulfides. Most of the target compounds showed recoveries of over 80%.

Samples adsorbed into solid sorbents can be collected by active or passive techniques. Active or dynamic sampling techniques involve pumping a defined volume of air through a tube with a bed of sorbent or sorbents in which the analytes are retained. While no single sample method suits all air monitoring applications, active sampling into sorbent tubes provides the most versatile option, and several official methods are based on this technique. Active sampling methods are used for determining target atmospheric contaminants at very low concentrations and, therefore, large sample volumes are needed.

One of the most important parameters that should be optimised in active sampling is the sample volume, which should ensure the preconcentration of enough analytes to

allow their subsequent detection, without any losses. The breakthrough volume is the volume of gaseous sample that can be drawn through a sample tube before an analyte is eluted from the tube. Every sorbent has a limited capacity for a given analyte which depends on the characteristics and amount of the sorbent, on the type of compound to be trapped, and on certain sampling parameters, such as the temperature and the humidity of the air [252]. To avoid breakthrough, it is necessary to choose carefully the right sorbent of combination of sorbents and the sampling flow and volume. Breakthrough can be monitored by connecting two sampling tubes in series and then analysing both sorbent tubes. A concentration <5% in the second tube of the target analytes is generally accepted [280].

Depending on the characteristics and the concentrations of the contaminants, active methods can be divided mainly into low-volume sampling and high-volume sampling. Low-volume sampling methods have been widely-used for compounds that can be found at µg or ng L^{-1} which are mostly in the gas phase, such as VOCs. Typical flow-rates can vary from 10 to 1000 mL min^{-1} and collecting sample volumes can be from 0.1 to 150 L [257]. Long or short term samples can be collected in sorbent tubes (usually ca. 6 mm o.d. and between 6-9 cm long) packed with sorbents, using a sampling pump. Figure 1.11 shows a sampling pump connected to a sorbent tube and a sequential tube sampler that allows the collection of up 32 different sampling tubes.

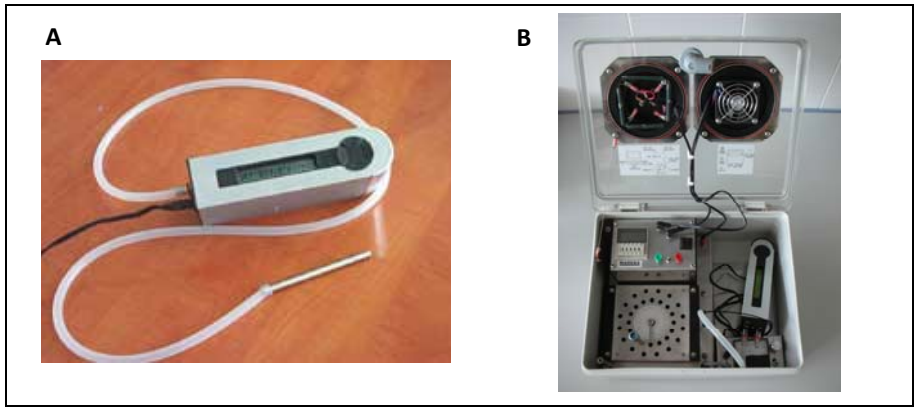


Figure 1.11. (A) Sampling pump connected to a sorbent tube; (B) Sequential tube sampler.

High-volume sampling is used for the monitoring of semi-volatile compounds that show low concentrations (< ng m^{-3}) and which can be present in both gas and particle phases. A high-volume sampler generally contains a high-volume pump, a filter and a column with solid sorbents. A modern and widely-used high-volume sampler is shown in Figure 1.12. Typical working flows are from 100 to 500 L min^{-1} for collecting volumes of 300-2000 m^3 of air samples in periods between 24 hours to 2 weeks [281]. Weak sorbents

such as XAD resins, polyurethane foams (PUFs) or combinations of both are used for trapping the gas phase contaminants. The main drawback of high-volume sampling is that the long sampling duration may enhance the risk of losing compounds due to breakthrough and degradation losses of certain organic contaminants. Blow-on (gaseous compounds adsorbed on deposited particles or on the filter material) and blow-off effects (volatile compounds desorbed from the filter) can be also common [269].

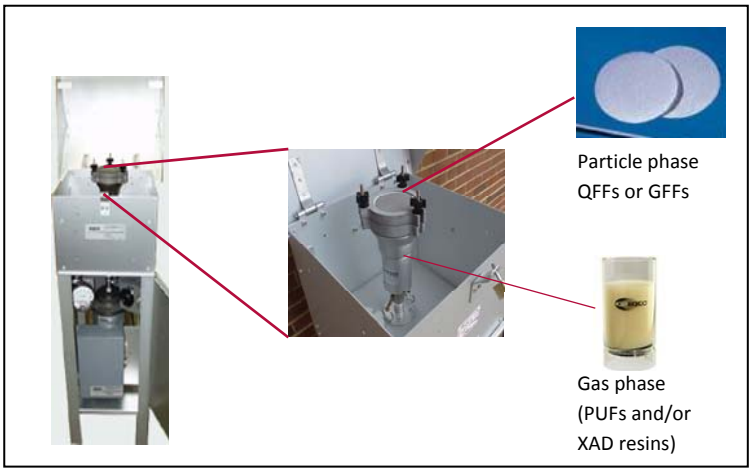


Figure 1.12. High-volume sampler for the collection of total suspended particulate matter and gas phase semi-volatile organic contaminants.

In the last few years, passive samplers have been used in several applications because of their simplicity, low price and their ease of use. Enrichment in passive samplers results from the diffusion of analytes, which are trapped in an adsorbent that has strong affinity for the contaminant, favouring the diffusion of the contaminant from the air to the adsorbent. Moreover, they can provide time-weighted-average concentrations based on exposure time [193]. However, there are several drawbacks compared with active methods. Firstly, passive samplers are difficult to calibrate because they are sensitive to several environmental factors, such as temperature fluctuations and air movement. Secondly, they are susceptible to background contamination and efficiency depends on sampler storage prior to the sampling, exposure, storage and desorption of analytes after exposure and sampler design. Furthermore, passive samplers can only collect free gaseous phase contaminants, and sampling periods are significantly higher than the usual time required using active samplers. This increases the risk of artifact formation because of the long exposure periods. The critical limitations are sorbent capacity and uptake rate in the case of high dosages and the response time and sensitivity in the case of low dosages. Moreover, the range of analytes that can be

monitored diffusively is restricted to those that are quantitatively retained by the single sorbent selected, because multi-sorbent tubes cannot be used for diffusive monitoring [235].

However, different types of passive samples are commercially available and have been successfully used for the determination of a wide range of air contaminants. Figure 1.13 shows the diffusion process of passive samplers and a radial diffusion passive sampler. Although most of the passive sampling applications are related to the determination of VOCS [282], they have been also used for determining SVOCs such as PAHs and polychlorinated naphthalenes (PCNs) [283] or polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) [284].

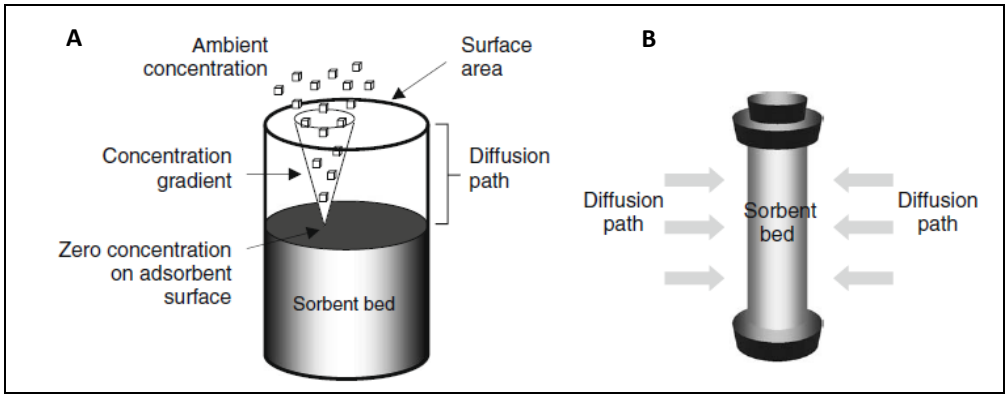


Figure 1.13. Passive samplers: (A) diffusion process and (B) radial diffusion.

Besides the techniques mentioned above, other techniques can be used for the sampling and extraction or organic contaminants in air. For instance, solid-phase microextraction (SPME) can be used as a preconcentration technique after whole-air sampling methods and can also be regarded as a special kind of passive sampler. SPME is a sorptive technique developed in the early 1990s, which combines sampling, isolation and enrichment in one single step [285]. SPME is based on the partition equilibrium of target analytes between a polymeric stationary phase (a coated fused-silica fibre), and the sample matrix. After the extraction, the analytes are usually desorbed thermally in combination with GC analysis, and, less frequently, using solvents and LC analysis. SPME provides some advantages over traditional extraction methods such as solvent-free operation, good sensitivity, cost effectiveness and operational simplicity. In addition, SPME quantification is feasible in non-equilibrium conditions once experimental parameters are held constant, which considerably reduces sampling time. However, used as a passive sampler, SPME does not provide a time-weighted average such as other passive samplers and results might indicate much lower or higher

levels than the true average due to the timing of significant concentration fluctuations during the monitoring period [9]. Quantification can also be compromised by unpredictable competitive effects, e.g. unusually high humidity or the presence of high transient concentrations of non-target organic analytes, solvents, etc. Therefore, SPME should be regarded as a qualitative tool or for short term monitoring of higher boiling compounds in air, or as a preconcentration technique after whole-air sampling [286].

To overcome some SPME drawbacks (such as fragility, low sorption capacity and bleeding from thick-film coatings), in-needle SPME has been developed as a technique in which the extraction phase is fixed inside a tube or needle. This overcomes the mechanical stability problems of fibre-SPME. The most widely-used approaches to in-needle SPME are needle trap devices (NTDs) and solid-phase dynamic extraction (SPDE). A schematic diagram of these techniques is shown in Figure 1.14.

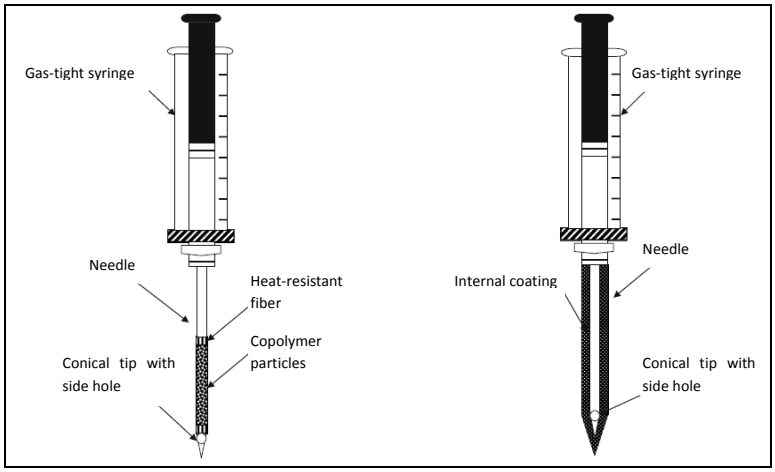


Figure 1.14. Schematic diagram of an NTD and a SPDE device [20].

In NTD methods, the needle of a gas-tight syringe is packed with polymeric sorbents [287]. As an example of an application for atmospheric samples, an NTD was recently packed with Carboxen1000 and used as a time-weighted average diffusive sampler to collect BTEX in indoor air [288]. The SPDE technique works on the same principle as SPME, but is a dynamic process in which the headspace of the sample is pumped repeatedly through a hollow needle attached to a gas-tight syringe. In SPDE approaches, the extraction phase is on the inside of the needle. The advantage of SPDE over SPME is the increased volume of sorption material which implies higher sensitivity. The in-needle-related method and the most recent applications in environmental matrices, such as air, have recently been reviewed by Lord et al. [287]. As an example of improved SPDE, Van Durme et al. [289] developed an accelerated SPDE procedure coated with

PDMS to extract toluene from ambient air that provided an extraction in 1.7 minutes with LOD of 56 ppbv. This is 6 times lower than those obtained with SPME.

1.3.1.2. Sampling of airborne particles and settled dust

Previously, a description of the most widely-used techniques for the collection and extraction of organic contaminants in air samples was provided. However, some of these organic contaminants, especially the semi-volatile ones, are partitioned between the airborne gas and particle phases. Therefore the determination of these contaminants in the airborne particle phase and in settled indoor dust is also of major interest. In order to collect the airborne suspended particles, glass fibre filters (GFFs) and quartz fibre filters (QFFs) are usually used in combination with high-volume samplers (see Figure 1.12). According to USEPA, airborne particles be classified in three main categories in regard to their size [290]: The first category is Total Suspended Particulate matter (TSP), which has particles ranging in size from 0.1 µm to about 30 µm in diameter. The second is PM_{10}, whose particles have a diameter of ≤ 10 µm, and are considered to be a respirable fraction because they can penetrate the lower respiratory tract. The third category is $PM_{2.5}$, whose particles have a diameter of ≤ 2.5 µm, and can cause health problems due to their potentially long airborne retention time and the inability of the human respiratory system to defend itself against particles of this size. Because of their different health effects, there are some specific PM_{10} and $PM_{2.5}$ samplers that, by using a cyclonic effect, can selectively collect these sizes of particles, or cascade impactors that can collect size-fractionated aerosol samples. Furthermore, it has been demonstrated that organic contaminants do not have equal accumulation in the different particulate matter fractions. For instance, Kameda et al. [96] demonstrated that the major deposit of PAHs occurred in 0.43-1.1 µm particulate fractions. Figure 1.15 shows a PM_{10} sampler and a cascade impactor sampler.

A special case of particle matter is the sampling of deposited particles such as indoor surface dust. The most frequently-used methodology is to use dust from vacuum cleaner bags, or a special vacuum cleaner mouthpiece containing a filter. However, these methods are very dependent on the sampling conditions. To avoid this, a special surface dust sampler has been developed which consists of a nozzle that can be adjusted to a defined distance from the surface, a cyclone that collects the dust particles, and an air pump and exhaust filter to capture particles that are not retained in the cyclone. SVOCs may break through the cyclone as vapours and a PUF plug can be inserted after the cyclone (ASTM, 1997, D 5038-94) [252]. House dust can either be sampled actively by vacuuming or wiping or passively by the use of dust-fall methods [12].

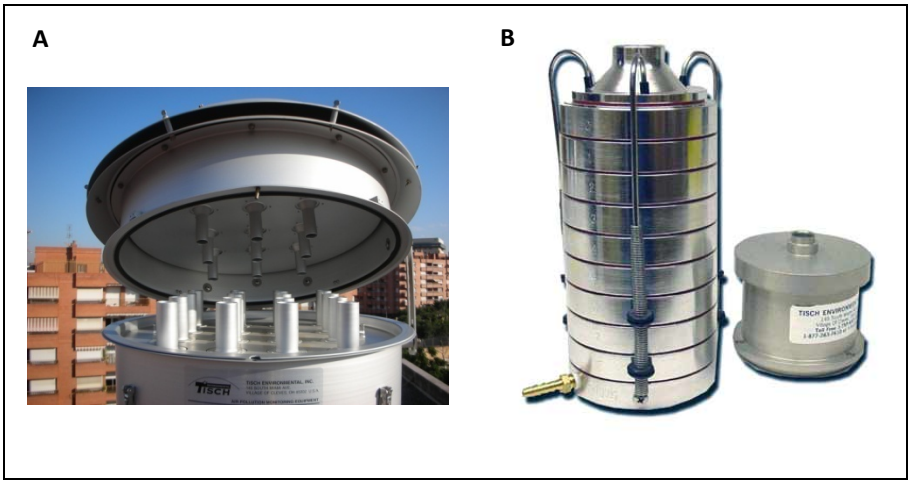


Figure 1.15. (A) PM_{10} and (B) cascade impactor sampler.

Another strategy to separate the gas phase analytes from the particulate phase is the use of denuder samplers. Denuder sampling of analytes from atmospheric air combines the features of dynamic and passive techniques. Figure 1.16 shows the most important processes that occur in a denuder sampler. It can be seen in the diagram that a forced laminar flow of air causes analytes to diffuse to the walls of the denuder, which are coated with a sorption medium. The process continues until equilibrium is reached between the gas and the sorbent surface, whereby the denuder walls act as a sorbent. The degree of enrichment of the target compounds depends on the intensity of the air flow and the specifications of the denuder [291].

The most common denuders are those with annular design, which consists of a series of coaxial tubes coated with an appropriate adsorbent through which the air flows. Vapour phase SVOCs are removed from the air stream by diffusion onto an adsorbent coating. Particles, which diffuse much more slowly, are collected onto a filter downstream. Other designs have been proposed including multicapillary and parallel plates. An interesting approach is the suspended-drop denuder, in which analytes are retained in a drop of solvent. Suspended from a syringe needle, this solvent drop is exposed for a given time to a stream of gas from which target VOCs diffuse onto it. After the exposure, the drop is sucked into the needle and transferred to a GC [291].

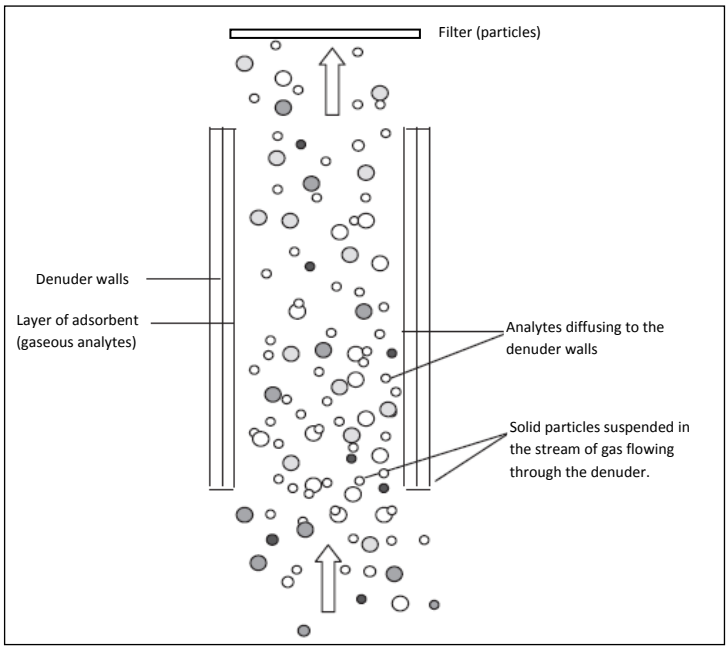


Figure 1.16. Main processes occurring in a denuder sampler.

One of the main advantages of the denuder approach is that particulate matter is retained on a filter. Therefore, diffusion denuder systems have been proposed as an alternative to high-volume samplers in order to collect air and particle samples for the determination of SVOCs [252]. Actually, denuder sampling is one of best methods for estimating the gas/particle portioning or SVOCs, but it has not been used extensively yet. This sampling technique have been applied to determine concentrations and also to investigate gas-particle partitioning of different SVOCs such as PAHs, PCBs, OCPs or carbonyl compounds [269].

1.3.1.3. Desorption techniques

After collection and preconcentration of the atmospheric organic contaminants on a sorbent, these trapped contaminants have to be transferred into an analytical system. Depending on the characteristics of the sorbent and the analyte, there are two main extraction methods: liquid desorption and thermal desorption. In this section we will review the usage and trends of both desorption techniques. As an example, Table 1.9 summarises the analytical methods proposed by the EU and the USEPA for VOCs and PAHs, indicating the sample and preconcentration, desorption and chromatographic technique.

Table 1.9. Analytical methods for VOCs and PAHs proposed by EU and USEPA.

Agency	Method	Target analytes	Sampling & Preconcentration	Desorption	Chromato-graphic technique	Ref.
EU	EN-14662-1	Benzene	Enrichment onto solid sorbents	Thermal desorption	GC	[292]
	EN-14662-2	Benzene	Enrichment onto activated carbon	Liquid desorption (carbon disulfide)	GC	[267]
	EN-14662-3	Benzene	Automated pumped sampling	-	in situ GC	[293]
	EN-14662-4	Benzene	Diffusive passive sampling	Thermal desorption	GC	[294]
	EN-14662-5	Benzene	Diffusive passive sampling	Liquid desorption (carbon disulfide)	GC	[295]
	EN-15549	Benzo[a]pyrene	High-volume sampling in quartz or glass filter fibres	Liquid desorption	GC-MS or HPLC-FLD	[296]
	EN-15483	Atmospheric gases	Long-path open-path fourier transform Infrared (FT-IR)	-	-	[297]
USEPA	TO-1	VOCs	Active enrichment into Tenax	Thermal desorption	GC-MS	[298]
	TO-2	VOCs	Active enrichment into molecular sieves	Thermal desorption	GC-MS	[299]
	TO-3	High volatile VOCs	Active sampling in a cryogenic trap	Thermal desorption	GC-MS	[300]
	TO-5	Aldehydes and ketones	Active enrichment in impringers (10 mL of 2N HC1/0.05% 2,4-dinitrophenylhydrazine (DNPH reagent) and 10 mL of isooctane)	Liquid desorption (Hexane/methylene chloride (70:30))	HPLC-UV	[301]
	TO-8	Phenols	Active enrichment in impringers (15 mL of 0.1 N NaOH)	Liquid desorption in acidic media	HPLC-UV, -ED or Fluorescence	[302]

Table 1.9 (cont.)

USEPA	TO-11A	Formaldehyde	Active sampling in a cartridge coated with acidified DNPH	Liquid desorption (acetonitrile)	HPLC-UV	[303]
	TO-12	Non-methane organic compounds	Cryogenic preconcentration	Thermal desorption	Direct FID	[304]
	TO-13A	PAHs	High-volume sampling. QFFs for particles and PUFs for gas phase PAHs	Liquid desorption (Soxhlet)	GC-MS	[305]
	TO-14A	VOCs	Subatmospheric pressure and pressurised sampling in canisters followed by a cryogenic trap preconcentrations	Thermal desorption	GC; any specific or non-specific GC detector	[253]
	TO-15	VOCs	Subatmospheric pressure and pressurised sampling in Specially-prepared stainless steel canisters followed by multisorbent trap preconcentration	Thermal desorption	GC-MS	[254]
	TO-16	Atmospheric gases	Long-path open-path fourier transform Infrared (FT-IR)	-	-	[306]
	TO-17	VOCs	Active sampling onto sorbent tubes	Thermal desorption	GC-MS or other GC conventional detectors	[280]

1.3.1.2.1. Liquid desorption

Liquid desorption (LD) has been widely-used as a desorption technique prior to the determination of airborne organic contaminants. LD is especially useful to desorb atmospheric SVOCs, such as PAHs and other POPs followed by subsequent GC or LC determination. It is also recommended for the desorption of thermally unstable contaminants. As mentioned before, several sorbents are compatible with LD, such as silica and other inorganic sorbents, activated charcoal and PUFs, among others (see Table 1.8). LD is also the most widely-used method to desorb organic contaminants

from particulate matter and settled dust. The main challenge of LD is the selection of the right solvent. Ideally this solvent should present the following characteristics: not interfere with any of the sample peaks; not react with the sample or the sorbent; present high affinity to the sorbent (strong enough to remove the sample compounds completely); and have a low response on the used detector [266]. The solvents most commonly-used are carbon disulfide, dimethylformamide and dichloromethane.

The major disadvantage of LD is that the sample is diluted with the desorbing solvent, which increases the method detection limit. As a consequence, this method requires long sampling periods and the preconcentration of large volumes of air. Moreover, polar and reactive compounds often have poor desorption efficiencies in the extraction solvent that can vary further with the presence of other polar compounds or water vapour [307]. Furthermore, the solvent can react with certain compounds. For instance, CS_2 can react with some amines, interfering with their determination and with the determination of other target compounds.

Classic solvent extraction techniques are still present in most of the official methods for the analysis of atmospheric contaminants (see Table 1.9), and are still used in some environmental analysis. For instance, to desorb the target VOCs trapped in activated charcoal, the official method EN-14662-2 [267] recommends the addition of CS_2 to the sorbent for 30 minutes with occasional shakes. However, the desorption of SVOCs requires the use of more effective techniques. In this sense, Soxhlet extraction is the most common technique for POPs retained in sorbents, such as PUFs and XAD resins, and for the extraction of these contaminants from particulate matter and house dust. For instance, the USEPA method TO-13A for the determination of PAHs in ambient air using GC-MS, recommends the Soxhlet extraction of the gas PAHs retained in PUFs and also for the PAHs bound to the particles to be collected on QFFs [305]. Soxhlet applications can be also found in the literature. For example, airborne gas and particle synthetic musk were desorbed using hexane-diethylether (90:10) for 8 hours by Kallenborn el al. [138,139] and by Xie et al. [141] with dichloromethane for 16 hours.

Ultrasound (US) assisted LD has been applied in order to increase the dissolution power of the solvents and, therefore, to reduce the volume of sorbent and the time of desorption. For instance, Elbir et al. [308] determined 60 gaseous phase VOCs trapped on active charcoal tubes with carbon disulfide using ultrasonic extraction for 15 minutes. US has also been used for the extraction of less volatile contaminants from particles. For instance, Rudel et al. [162] extracted parabens and other phenolic contaminants from house dust using acidified dichloromethane and sonication in 3 cycles of 10 minutes.

However, these LD techniques usually have low selectivity and sometimes a clean-up step is necessary prior to the chromatographic analysis. Furthermore, some of the techniques mentioned above need the use of high amounts of organic solvent. In order to reduce solvent consumption, supercritical fluid extraction (SFE) can be a valuable alternative. For instance, Calvosa et al. [309] used SFE for the extraction of polybrominated diphenyl ethers (PBDEs) from SRM 2585 (Organic Contaminants in House Dust) using 20 mL of a hydrofluorocarbon as an extraction solvent. SFE has also been used for the characterisation of organic compounds in aerosol particles from a Finnish forest [310] using CO_2 at 150 °C and 400 bar, combining static mode for 10 minutes with 400 µL of dichloromethane and dynamic extraction with CO_2 for 45 minutes.

Currently the most widely-used LD techniques to extract solid matrices are microwave-assisted extraction (MAE) and pressurised liquid extraction (PLE). These techniques also reduce the amount of organic solvent used and are more selective and quicker than classic LD techniques.

Microwave assisted extraction (MAE) allows the fast extraction of the analytes (extraction times vary between 5 to 60 minutes), with reduced organic solvent consumption and increased sample throughput in the extraction of different contaminants from environmental matrices [311-313]. The main advantages of MAE are the high extraction rates due to the very quick heating and the elevated temperature, and the ease of instrument operation, and the fact it allows multiple samples to be extracted simultaneously. The main drawback is that the heating is limited to the dielectric constant of the solvent. Therefore, the most important parameter to optimise in MAE is the extraction solvent. The solvent should be able to desorb the analytes from the matrix and absorb the microwaves without causing strong heating and so avoid analyte degradation [311]. Non-polar solvents do not absorb microwave energy and therefore are less efficient at extraction than polar solvents. In fact, the addition of small amounts of water improves the absorption of microwave energy by non-polar organic solvents and the extraction of analytes. However, for the extraction of thermolabile compounds, the microwaves may be absorbed only for the matrix, heating the sample and releasing the solutes into the cold solvent. For that purpose, an adsorbing material can also be added to the sample. Other parameters that should be optimised in MAE processes are the volume of solvent extraction, the extraction time and the microwave power.

MAE can be performed in closed-vessel and open-vessel mode. The closed-vessel mode is the most commonly-used because the temperature and pressure are controlled during extraction. After MAE, the extracts should be separated from the sample, usually

by centrifugation and decantation. MAE has low selectivity, thus extracts may be cleaned-up prior to chromatographic analysis. The most common clean-up methods are solid-phase extraction (SPE) with reverse-phase sorbents, such as C_{18}, or polar sorbents, such as silica, alumina or florisil, depending on the nature of the analytes.

MAE is becoming more important for the determination of organic contaminants in airborne particles and settled dust. Recently it has been used for the extraction of organic contaminants from indoor dust. For instance, Regueiro et al. [137] developed a method for the extraction of organochlorinated compounds, nitromusks and pyrethroid insecticides from sieved dust particles with a mixture of 8 mL hexane and 4 mL H_2SO_4 1M containing ascorbic acid 0.10% (w/w), at 80 °C for 10 minutes. The extracts were cleaned-up by adding florisil, obtaining recoveries ranging from between 88% and 97%, with %RSD between 6-8%. Garcia et al. [314] extracted organophosphate flame retardants and plasticisers from dust, using MAE with 10 mL of acetone at 130 °C for 30 minutes. After MAE, extracts were separated by centrifugation and cleaned-up in a SPE cartridge. Recoveries ranged between 85-104% and %RSD 3-13%. Recently, Castro et al. [315] used MAE to determine 18 PAHs in gas and particle phases of smoking and non-smoking homes with acetonitrile at 110 °C for 20 minutes, obtaining recoveries > 81%. MAE has also been used for the extraction of passive samplers. For instance, Esteve-Turrillas et al. [316] extracted pyrethroid insecticides from semi-permeable membrane devices (SPMD) with 20 mL of hexane-acetone (1:1) in two cycles of 20 minutes each. The extracts cleaned-up with alumina-C_{18} allowed recoveries of between 61-103% and %RSD 2.9-9.4%.

Pressurised liquid extraction (PLE) was introduced in the mid-1990s as an alternative to classic extraction methods of solid samples, such as Soxhlet or sonication [317]. This technique involves the extraction with solvents at high temperature and pressure that increases the capacity of the extraction solvent to dissolve the target analytes. The extreme conditions improve the rate of mass transport and the effectiveness of sample wetting and matrix penetration, allowing a better desorption of analytes from sample particles [318]. Other advantages of PLE regarding more classic techniques are that the extract is filtered in the cell and that the instrumentation allows the automated extraction of the samples. Instrumentation of PLE consists of a stainless-steel extraction cell, which is filled with the sample and an inert material (usually sodium sulphate or diatomaceous earth) and kept at the desired pressure and temperature with the aid of a pump for solvent delivery, a flow restrictor, electronically controlled heaters and a vial for extract collection [317]. PLE can be performed in dynamic or static mode. In the dynamic mode, the solvent is continuously pumped through the extraction cell. This form is suitable for rapidly equilibrating samples whose organic contaminants are easy to extract. In the static mode, the cell is filled with the solvent, heated and pressurised

for a specified time and then drained to the collection vial. Static PLE is used for analytes, which are more difficult to extract, and so this approach is more widely-used (about 75% of the applications) [318]. Apart from the extraction solvent, the most important parameters that should optimised in PLE are the extraction temperature, pressure, time and number of cycles (if more than one cycle of extraction is needed). Other parameters are the flush volume (volume of solvent flushed into the cell after the extraction) and the purge time (time that a stream of N_2 is passed through the cell to dry the sample).

Since its introduction, PLE has been widely-applied for the extraction of a wide variety of matrices, such as sewage sludge [319], soils and particulate matter [320], biota [321] and house dust [160]. For instance, Ras et al. [227] desorbed 16 airborne gas PAHs trapped in PUFs and in PST using diclorometh ane in 1 or 2 cycles of 5 minutes, obtaining recoveries higher than 90% for most target PAHs. Fromme et al. [135] desorbed phthalates and synthetic musk from settled dust using PLE with hexane/diethyl ether (9:1), obtaining recoveries higher than 91%.

PLE extraction is effective but sometimes shows low selectivity. Therefore, the extracts, rich in co-extracted materials, often have to be cleaned up before instrumental analysis. For instance, Albinet et al. purified the extracts of particulate matter with an SPE cartridge prior to the determination of N-PAHs and O-PAHs by GC-MS [322]. To avoid these subsequent clean-up steps, some new strategies for the PLE technique (called in-cell clean-up) have been developed which have increased the selectivity and efficiency of PLE. Figure 1.16 shows the current different PLE strategies.

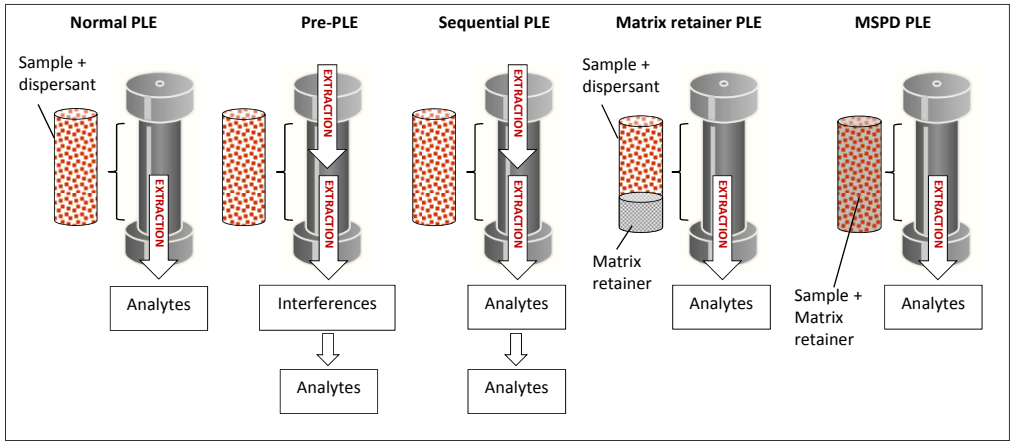


Figure 1.16. Extraction schemes for (from the left to the right): normal PLE, pre-extraction, sequential PLE, PLE with matrix retainer and matrix solid-phase dispersion (MSPD) PLE.

The first in-cell clean-up strategy is the pre-extraction of the interferences (pre-PLE) with a weak solvent to remove less strongly sorbed compounds before the extraction of the compounds of interest. The second strategy uses a sequential extraction procedure with solvents of increasing strength to separate the analytes of different polarity groups. Other strategies consist in the addition of an in-cell clean–up sorbent, which can retain the interferences and allows cleaner extracts, or the use of a matrix solid-phase dispersion (MSDP) technique in which the retainer sorbent is mixed with the sample before the PLE extraction. Some of these in-cell clean-up strategies have been used for determining organic contaminants from atmospheric samples. For instance, Canosa et al. [160] dispersed 0.5 g of house dust with 3 g of Florisil loaded in PLE cells containing 1 g of the same material as a clean-up sorbent. The non-polar interferents were first removed with n-hexane under mild conditions (40 °C and 3.4MPa) and then parabens were extracted with ethyl acetate at 100 °C and 13.8 MPa in 3 static cycles of 1 minute. Under these optimised conditions, recoveries of the target parabens ranged from 76 to 98% with %RSD < 11%.

The choice of the right extraction solvent and the clean-up sorbent are the main parameters to optimise in these applications. The most widely-used sorbents for the in-cell clean-up and the MSPD approaches are silica, florisil, alumina or C_{18}. For instance, Carpinteiro et al. [323] used 1 g of silica as an in-cell clean-up sorbent for the extraction of benzotriazole light stabilizers from indoor dust. In this work, the performance of florisil and alumina was also tested. It was shown that these sorbents retained more of the target analytes. Under optimised conditions, 0.5 g of sample was extracted in 3 cycles of 10 minutes at 90 °C and 1500 psi using a mixture of hexane:dichloromethane (7:3). Recoveries ranged between 82 and 122% and %RSD < 12%. Martínez et al. [324] used 4 g of florisil for the in-cell clean-up extraction of brominated diphenyl ethers in indoor dust. The best recoveries were obtained when mixing 2.5 g of florisil with 0.5 g dust (as MSPD clean-up) and placing 1.5 g of florisil (as an in-cell clean-up sorbent) in the bottom of the cell. The cells were extracted with n-hexane:dichloromethane (1:1), at 40 °C And 1500 psi for 1 cycle of 2 minutes. Recoveries ranged between 82 and 101% and %RSDs < 9%.

PLE can also use water as a desorbing solvent. This is called pressurised hot water extraction (PHWE) or subcritical water extraction (SWE), and it reduces or eliminates the use of the organic solvent. At high temperature and pressure, the dielectric constant of water decreases, reaching a polarity close to those of alcohols. This allows water to dissolve a wide range of medium and low polarity analytes [325]. PHWE is used in combination with other extraction techniques to concentrate and extract analytes from the aqueous solution prior to the analysis, such as SPE, SPME and SBSE. Besides

the reduction in the consumption of organic solvents, water is easily available, non-toxic and can be recycled or disposed with minimal environmental problems. Hence, PHWE is becoming an efficient and low cost method of extraction for less-polar organic analytes from solid matrices, such as sewage sludge [326] and sediments [327,328]. However, there is little information regarding the application of this technique for the extraction of organic contaminants in atmospheric samples.

1.3.1.2.1. Thermal desorption

Thermal desorption (TD) is a widely-used technique for extracting volatile compounds from atmospheric matrices, followed by GC analysis. TD is an environmentally-friendly technique which provides enhanced sensitivity (since the whole sample is analysed), is compatible with thermally stable polar and apolar compounds, enables the reuse of the adsorbent tubes, avoids the use of toxic solvents in the extraction step and, in consequence, prevents the solvent's signal from masking the analyte peaks in the sample chromatograms [329]. The main drawbacks of TD are: the incompatibility with some solid sorbents; the possible degradation of sorbents which can generate artifacts and blanks of some analytes and, therefore, interfere with the analysis; the consumption of the sample in a single analysis (although modern equipment allows the recollection of split samples in a fresh tube); and the initial cost of the required instrumentation. Moreover, thermal desorption is not recommended for thermally unstable compounds or for compounds with high boiling points because desorption efficiencies decrease. As seen in Table 1.9, TD is the recommended desorption technique for several official methods (see Table 1.9) such as the European EN-14662-1 [292] and 14662-5 methods for the determination of benzene and USEPA TO-1 for the determination of VOCs by active enrichment into Tenax [280].

Thermal desorption can be applied for the desorption of analytes preconcentrated into a solid sorbent, or bounded to the airborne particle matter or indoor settled dust. In the TD process, the sorbent tubes or the sample matrix are heated in the presence of a flow of inert gas (such as helium or nitrogen). TD can be followed by the direct injection of the analytes into the GC. However, this single-stage approach has limited practical application because it requires large elution volumes to extract the analytes completely, giving poor analytical resolution and relatively low sensitivity [252]. Therefore the two-stage process is the most widely-used nowadays. It focuses the analytes desorbed from the sample in a trap, and then, raising the temperature of the trap quickly, releases them into the analytical system using a small volume of gas.

Figure 1.17 represents the steps of two-stage thermal desorption. Previous to the desorption, air and water are purged from the sorbent tubes using dry carrier gas at ambient temperature, usually for 1 minute. In the first step, the tube or the sample containing the retained analytes is desorbed with the aid of heat and an inert gas stream. At the same time, the desorbed analytes are focused in a cooled capillary trap (see Figure 1.17 A). In the second step, analytes are rapidly desorbed from the trap by applying a fast temperature ramp and injected into the GC system (see Figure 1.17 B). In the case of multi-bed sorbent tubes, the inert gas should flow from the stronger sorbent to the weaker sorbent, to allow desorption of most of the retained analytes. Temperature of desorption of the sorbent tubes/sample and of the cryogenic trap should be optimised in order to allow the complete desorption of the analytes without the thermal degradation of the sorbents or the thermally unstable analytes. The flow-rate and time of desorption depends on the interactions between analytes-sorbent or analytes-sample. A split can also be applied in both steps so that the GC system is not overloaded and to favour the desorption of the sample and of the cryogenic trap.

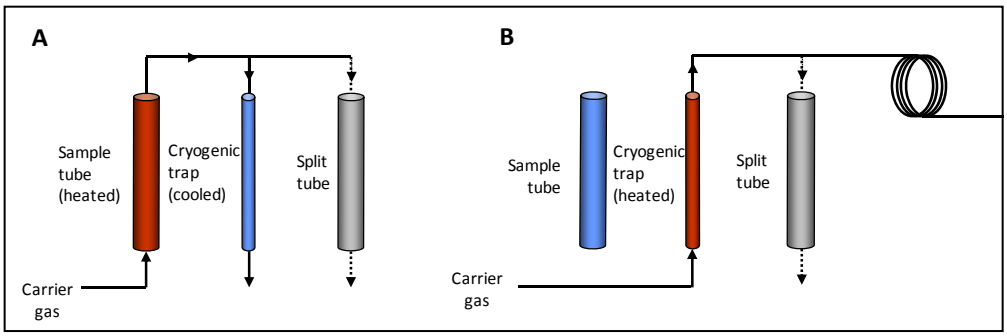


Figure 1.17. Scheme of a thermal desorption process: (A) tube desorption and cryofocusing of the analytes in the trap and (B) trap desorption step.

Basically, there are two kinds of capillary traps currently available [263]: cryofocus traps and electrically cooled sorbent traps. Capillary cryofocusing consists of a quartz tube maintained at very low temperatures during the trapping of analytes. This system is very compatible with capillary GC but it consumes large quantities of cryogenic liquid. The electrically-cooled sorbent traps consist of a tube filled with a sorbent or a mixture of them (usually the same mixture used in the sorbent tubes). In the second step, the trap is heated rapidly in a reverse flow of carrier gas (backflush) to desorb the analytes in a few seconds with volumes of 100-200 µL of carrier gas. Capillary sorbent traps are able to retain volatile analytes, such as C_2 hydrocarbons, and can also desorb the retained analytes quickly and quantitatively at the same time. Backflush desorption of the focusing trap also facilitates simultaneous analysis of very volatile and semi-volatile compounds [263].

Regarding TD equipment, two different kinds are commercially available. Figure 1.18. shows two commercial examples of these different approaches: a Markes™ TD Unity and a Gerstel™ TDU. In the first approach, the Unity TD system is connected to the GC analyser by an interface composed of a capillary column (see Figure 1.18 A). A metallic interface also connects the Ultra A autosampler and the Unity. This system uses an electrically-cooled sorbent trap to concentrate the analytes prior to the GC injection. In the second approach, the thermal desorption unity (TDU) system is coupled directly to the cooled injection system (CIS) without transfer lines (see Figure 1.18 B). The CIS system is based on a programmable temperature GC inlet cooled with liquid nitrogen.

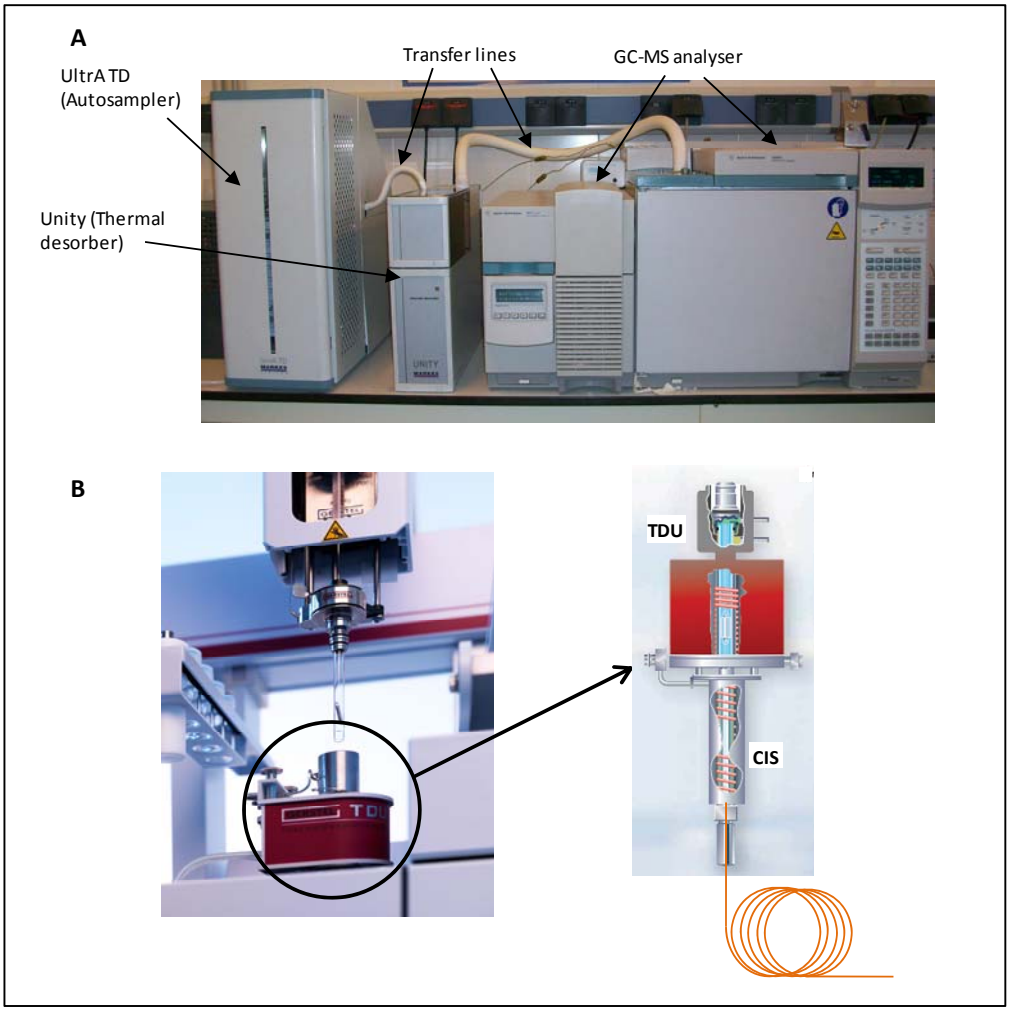


Figure 1.18. Common thermal desorption equipment: (A) Markes™ Unity and (B) Gerstel™ TDU.

The first system has been widely-used for determining atmospheric VOCs. For instance, in our research group Ras et al. [59] used a Markes Unity for determining 65 VOCs, obtaining recoveries higher than 99% for most target VOCs. Parra et al. [330] used the same equipment for determining 140 VOCs in rural areas of northern Spain. However, this approach is not usually used for the determination of semi-volatile compounds. The temperature of the interfaces can only be raised to 200-210 °C and memory effects can occur because of the accumulation of less volatile analytes in the interfaces. The second approach is usually used for the direct thermal desorption of solid samples or the desorption of stir bars used for the stir bar sorptive extraction of analytes from aqueous samples. For instance, Özel et al. [331] developed a method based on direct TD of urban aerosol samples to determine organic nitrogen compounds using a Gerstel TDU. The application of this system for water samples will be described later.

TD has significant concentration enhancement potential. When used in conjunction with sorbent tubes and two-stage desorption for monitoring trace level organic contaminants in air, concentration factors can be higher than 100. Thermal desorption is widely-used for the extraction of gas phase VOCs trapped in solid sorbents. Some reviews have summarised the most recent applications [9,214,263,268]. However, thermal desorption has not been extensively-used for the extraction of high boiling point compounds because of several limitations of the technique. For instance, solid sorbents usually used for VOCs show less efficient desorption for SVOCs, causing memory effects. Some commercial “high boiling” sorbent tubes and traps have been developed to overcome this drawback. As an example, Markes developed sorbent tubes filled with glass wool and graphitised carbon black and a cryogenic trap filled with the same sorbent and quartz [332]. This sorbent can be heated up to 370 °C, allowing desorption of the less volatile analytes. However, this cryogenic trap needed high split flows to be desorbed (30 mL min^{-1}) and this increased LODs significantly. Wauters et al. [270] developed sorbent tubes filled with polydimethylsyloxane (PDMS) and Tenax for the monitoring of 17 PAHs in ambient air. PDMS showed good desorption efficiencies for the less volatile PAHs, whereas Tenax allowed the collection of low boiling point PAHs such as naphthalene. 144 L (100 mL min^{-1} for 24 h) of sample volume was collected when these tubes were used. Quantitative desorption of the PAHs was obtained by heating the sorbent tubes to 300 °C for 12 minutes using helium carrier gas at 60 mL min^{-1}, achieving % RSD < 7.4% and LODs < 13 pg m^{-3}. This method made it possible to analyse other semi-volatile contaminants using TD. In fact, this method has been used for the determination of PCBs.

Besides inefficient desorption from the sorbent, memory effects can be also found in the interfaces of some TD equipment because, due to instrumental limitations, they

usually operate at lower temperatures (up to 210 °C) than the desorption temperatures needed for the sorbent tube or the sample and the trap (see Figure 1.19 A). These memory effects can be avoided by loading small quantities of the target analytes (low ng levels). Several applications of TD methods for semi-volatile atmospheric contaminants can be found in the literature. Most of these applications have focused on the desorption of PAHs from particulate matter [333,334].

1.3.2. Water Samples

The determination of organic contaminants in environmental waters is essential for the control of the distribution of these contaminants in the environment. Organic contaminants can reach environmental waters through direct emissions to aquatic systems or indirect emissions through waste water treatment plants (WWTPs) effluents or landfill leachates.

Environmental water samples are usually complex matrices in which the target compounds can be present at trace levels. Therefore, extraction techniques that can selectively and efficiently preconcentrate the analytes of interest are required for the reliable determination of these organic contaminants. The sample preparation method should accomplish several functions. Firstly, it should be selective for the target analytes in complex matrices, such as waste or marine water samples, and it should be able to remove interferences. Secondly, it should provide the preconcentration of the target analytes, especially when analytes in trace levels are to be determined, in order to improve determination sensitivity. Thirdly, it should be compatible with the sample matrix and the instrumental analysis.

Several sample preparation techniques have been used for the extraction of organic contaminants from environmental waters. The most classic extraction technique is liquid-liquid extraction (LLE). Although this technique has proven efficiency, it has several drawbacks such as the high consumption of organic solvents, the long time taken for the sample preparation step and the risk of background contamination of the samples. To overcome the main drawbacks of LLE, some recent miniaturisations of LLE have been applied successfully for the extraction of analytes from water samples, such as liquid-phase microextraction (LPME). Some of the more widely-used liquid-phase microextraction methods are single-drop microextraction (SDME), organic solvent film (OSF), continuous flow microextraction (CFME), dispersive liquid microextraction (DLLME) and hollow-fibre liquid-phase microextraction (HFLPME) [335].

Currently, the most widely-used sample preparation technique is solid-phase extraction (SPE) because of the wide range of commercially-available sorbents suitable for organic contaminants with a wide range of polarities. In recent years, the general trend in the determination of organic contaminants in environmental waters is for the development of methods that allow the simultaneous determination of chemically different classes of organic contaminants. These so-called multi-residue methods provide wider knowledge about the occurrence of organic contaminants which is necessary to further understand their removal, partition and fate in the environment. Nevertheless, simultaneous determination of compounds requires a compromise in the selection of experimental conditions. Currently, SPE followed by liquid desorption is the sample preparation technique most widely-used in multi-residue methods for water samples [210].

However, in the last few years, applications with other sorptive extraction techniques, such as solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE), have increased. When using these two techniques, the subsequent desorption of the analytes is usually by thermal desorption (TD) but, in some cases, liquid desorption (LD) has also been applied. The combination of these sorptive techniques with TD is especially useful because it allows the direct injection of the analytes in the GC system, achieving enhanced sensitivity.

As a result of the advances in extraction techniques, low concentrations of organic contaminants are now being detected and quantified in different kinds of environmental waters. In this section, a description of the extraction techniques used for determining organic contaminants in environmental water samples is provided, as well as examples of the most recent studies.

1.3.2.1. Solid-phase extraction

As mentioned above, solid-phase extraction (SPE) is the most commonly-used technique for extraction of organic contaminants from aqueous samples [240]. The wide variety of available sorbents allows the clean-up, retention and preconcentration of analytes with a wide range of polarities and physico-chemical properties. One of the most important parameters to optimise in SPE technique is the selection of an appropriate solid sorbent for the target analytes, because the kind of sorbent, its structure and its interactions with the analyte directly affect the extraction efficiency. Other parameters that should be optimised in SPE processes are: sample volume, pH conditions, and solvents for washing and elution.

SPE sorbents can be packed in discs or cartridges. Some recent applications related to the use of C_{18} discs can be found in the literature. For example, Hu et al. [336]

determined seven synthetic musks in urban WWTP influents and effluents using C_{18} disks, obtaining recoveries ranging from 83.6% to 105.1%. However, cartridge is the most commonly-used format because of the wider range of sorbents commercially available. Conventional SPE sorbents for the extraction of organic contaminants are C_{18} and polymeric sorbents based on styrene-divinylbenzene copolymers (St-DVB). These hydrophobic sorbents are effective at retaining apolar compounds rather than polar compounds. In order to increase the hydrophilicity of the sorbents, a polar co-monomer can be introduced during polymerization or polar functional groups can be introduced after polymerization. Examples of these sorbents are Oasis HLB or Strata-X, which present a hydrophobic and a hydrophilic portion that enable them to extract a wide range of compounds from various matrices. For example, Oasis HLB has been used by Pedrouzo et al. [238] for the extraction of UV filters, parabens and antimicrobials from waste water. Recoveries were between 38% and 92% in WWTP effluents and 36–89% in influents. Oasis HLB has also been used by Wombacher et al. [337] for determining synthetic musks in a conventional drinking water treatment plant. Recoveries higher than 90% were obtained for most target musks. Strata-X has been used as a sorbent in a multi-residue developed by Pietrogrande et al. [226] to extract 29 PCPs with polar and non-polar characteristics. In comparison with C_{18}, Strata-X provided better efficiency with an extraction recovery higher than 70% for most of the PCPs investigated.

Recent research related to polymeric sorbents has focused on the development of new sorbents that can enhance selectivity and capacity. In this sense, dual-phase or mixed-mode sorbents present high capacity and high selectivity compared to those obtained using a single material [338]. Mixed-mode sorbents are especially useful for retaining ionizable compounds from complex matrices, where analytes can be retained by ionic interactions and the rest of the matrix's components are retained by reversed phase. This favours the selective removal of interfering matrix compounds during the clean-up step. Mixed-mode sorbents can be cationic or anionic and can also have strong or weak ionic exchange abilities. The first commercially-available mixed-mode sorbent was the strong cationic Oasis MCX. This sorbent is more selective than Oasis HLB and is able to retain less matrix interferents. Oasis MCX has been applied successfully for the selective extraction of a wide range of organic contaminants in environmental waters. For instance, Kasprzyk-Hordern et al. [339] used Oasis MCX cartridges in a multi-residue method for determining 25 acidic and neutral pharmaceuticals and PCPs in river water, obtaining acceptable recoveries.

In addition to mixed-mode sorbents, other options for improving extraction selectivity include the use of immunosorbents and molecularly-imprinted polymers (MIPs). MIPs are the most commonly-used selective SPE sorbents and have been used to create so-

called molecularly-imprinted SPE (MISPE) [340]. MISPE can selectively extract one target analyte or a group of structural analogues, reducing the non-specific interactions and therefore decreasing the ionic suppression when working with LC-MS determinations. Recent applications of MISPE were the focus of two recent reviews [341-342]. In the last few years, MISPE has been applied for the determination of organic contaminants in water samples. However, few applications can be found for the determination of PCPs. As an example, Beltran et al. [343] synthesized an MISPE for determining benzyl and butyl paraben in river waters. This MISPE presented less interferences than with Oasis HLB.

Other sorbents recently used in SPE are carbon nanotubes which show higher capacity. Both single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) have attracted much interest due to their large surface area and structural characteristics. An interesting application is the MWCNT SPE of multiclass pesticides in surface waters, prior to GC-MS, by Wang et al. [344]. This application achieved LODs of between 0.01-0.03 μg m^{-3}. Recent applications have also used surfactant aggregates adsorbed on mineral oxides (hemimicelles and admicelles). Because of the amphiphilic character of surfactants, their aggregates have regions with different polarity where analytes of a wide polarity range can be solubilised. Organic contaminants that have been extracted with this approach are sulphonamides, naproxen and ibuprofen and pesticides from different environmental waters [206].

Another trend is the miniaturisation of SPE. In this sense, microextraction in packed syringe (MEPS) is a miniaturised SPE, in which approximately 1 mg of sorbent is immobilized inside a syringe barrel as a plug or tiny cartridge. For extraction, 10-250 μL of an aqueous sample is withdrawn by the syringe into an autosampler. The handling time is reduced by about 30 and 100 times compared to SPME and SBSE, respectively. The reduction in the amount of solvent, sample and sample preparation time means the MEPS process can be fully automated. Miniaturised SPE applications have been successfully applied by Möder et al. [345] for determining UV filters and polycyclic musks in water samples. In the study, two suitable SPE sorbents (C_8 and C_{18}) were compared. The analytes were extracted from 800 μL of sample and recoveries ranged from 46 to 114%. The LODs were between 34 and 96 ng L^{-1} and %RSD < 11%. Recently, Prieto et al. [346] used MEPS followed by large volume injection-GC-MS to determine 41 multi-class priority and emerging organic contaminants (including PAHs, PCBs and selected steroid hormones, among others). LODs using 800 μL of sample were between 0.2 and 266 ng L^{-1} whereas LODs of a standard SPE range from 0.2 to 736 ng L^{-1}.

SPE applications can be performed on-line or off-line. The examples discussed above have all been related to the use of SPE in off-line mode. Nevertheless, in the on-line

approach, the SPE is integrated directly into the analytical system. The main advantages of the on-line approach include minimum need of sample manipulation, potential full automation and cost efficiency. The intermediate evaporation step is avoided in on-line methods and the eluted extract is injected directly into the chromatographic system. Although SPE on-line can be followed by GC or LC determination, most of the recent applications of on-line SPE have been followed by LC. Regarding the kind of organic contaminants, most SPE on-line methods focus on the determination of pharmaceuticals in environmental waters, whereas determination of PCPs is mostly in off-line [239]. As an example of on-line SPE, López-Serna [347] developed a fully automated SPE-LC-tandem MS method for determining 74 pharmaceuticals in superficial and ground waters using a HySphere Resin GP cartridge. With this method, 2.5 mL of water sample was enough to achieve limits of detection in the low ng L^{-1} range.

Another application of SPE on-line was recently performed by Fontanals et al. [348]. For the first time, they developed an on-line SPE-LC-UV method using an in-house, mixed-mode, hypercrosslinked resin, modified with 1,2-ethylenediamine moieties (HXLPP-WAX) for determining 11 pharmaceuticals in waste and river water. The resin was used as a weak anion-exchange sorbent and enabled application of a washing step to remove the compounds with acidic, neural and basic properties. The most acid target pharmaceuticals were recovered at levels close to 100% and the most basic compounds were only recovered when the washing step was omitted, with recoveries from 67 to 92%.

1.3.2.2. Solid-phase microextraction

As mentioned before, although most applications for determining organic contaminants in environmental waters are based on SPE sample preparation methods, other sorptive techniques are acquiring increasing interest because they minimise solvent consumption. The first developed of these techniques was solid-phase microextraction (SPME). Although this technique has previously been commented on as a sampling and preconcentration technique of atmospheric organic contaminants, most SPME applications are focused on water samples. Since its development in the early 1990s, SPME has been successfully applied to the extraction of a wide variety of organic contaminants from environmental waters, especially for the extraction of volatile and semi-volatile analytes. SPME can be used for the direct extraction of analytes by immersing the fibre in the water sample or indirectly by extracting the analytes from the headspace above the sample (HS-SPME). HS-SPME is especially useful for volatile analytes and provides cleaner chromatograms than those obtained by fibre immersion.

Furthermore, SPME was recently applied as an extraction technique in multi-residue methods. For instance, Basaglia et al. [349] recently determined 23 PCPs, including fragrances, antioxidants and UV filters among others, in water samples by SPME-GC-MS, using polydimethylsiloxane (PDMS) fibres. The method developed provided LODs lower than 2 ppb for most compounds.

SPME is fast, simple, solvent-free, sensitive, provides linear results for a wide concentration of analytes, and is portable, which allows its use in field analysis. Several fibres are currently commercially-available which are suitable for apolar and low polar analytes. For instance, Polo et al. [350] tested five SPME commercial fibres to extract four nitromusks from waters. The most efficient was the carboxen-polydimethylsyloxane (CAR/PDMS) fibre, with recoveries higher than 90 %.

In order to enhance the extraction efficiency of most polar contaminants, several strategies can be developed. The most simple and cost-effective is derivatization (in situ or on-fibre). For example, Regueiro et al. [351] developed an in-situ derivatization SPME method for the determination of parabens, triclosan and related clorophenols in water. The phenolic contaminants were acetylated prior the SPME extraction using divinyl benzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fibres, obtaining LODs at low pg mL^{-1} level.

Recent trends in SPME have focused on the development of new more selective coatings that can retain polar analytes, are thermally stable and have high active surfaces. Basically, four kinds of SPME sorbents can be found in the literature [20]. The first kind are Sol-gel coatings which exhibit high thermal and chemical stability [352]. For instance, Farhadi et al. [353] investigated the performance of different sol-gel fibres for determining BTEX in water samples. They used a GC-FID for the determination and obtained LODs at low ng mL^{-1}. Other kinds of SPME coatings are the polypyrrole polymers (PPy), which exhibit high porosity [354], and immunoaffinity sorbents, which have high sensitivity, selectivity and reproducibility with application, such as the extraction of large biomolecules from complex matrices [20]. Another interesting highly selective approach is the use of MIPs on SPME coatings. For instance, He et al. [355] developed a MIP for the selective extraction of phthalates in water samples, achieving LODs of between 2.2-2.8 ng L^{-1} and recoveries higher than 95%.

In-needle SPME techniques have been developed to overcome the main fibre-related drawbacks of SPME, such as fragility, low sorption capacity and bleeding from thick-film coatings. Besides the atmospheric applications mentioned above, these techniques have also been applied successfully for the determination of organic contaminants in water samples. For instance, Bagheri et al. [356] used an in-tube solid phase dynamic

extraction (HS-SPDE) technique with a PPy sorbent inside the surface of a needle for determining PAHs in water samples. The LODs ranged from 0.002 to 0.01 ng mL^{-1} and %RSD lower than 11.4%. Jochmann et al. [357] also used a dynamic SPDE-GC-MS for determining benzene and 11 chlorinated and brominated hydrocarbons in a needle coated with PDMS. The achieved LODs ranged between 12 and 870 ng L^{-1}. Other applications of in-needle SPME have recently been reviewed by Lord et al. [287].

1.3.2.3. Stir bar sorptive extraction

Analogously to SPME, SBSE is a solventless preparation technique based on the equilibrium between the aqueous matrix and the organic layer coating a magnetic rod. Since the development of SBSE in 1999 by Baltussen et al. [358], this extraction technique has been successfully applied to the determination of trace environmental contaminants in different matrices [359-361]. For the extraction of water samples, the stir bar is added to the sample and then stirred. It can also be used in the head-space mode, known as headspace solvent extraction (HHSE). This is more suitable for volatile compounds. However, few applications can be found in the literature of HHSE for water samples [361]. Currently, the available commercial stir bars are 10 or 20 mm long coated with 0.5 mm or 1 mm film thickness of PDMS, a sorbent suitable for apolar organic contaminants. For instance, Lacorte et al. [362] used 20mm length × 1.0mm film thickness PDMS coated stir bars for the ultra-trace analysis of 48 POPs, including PAHs and PCBs, in Arctic ice. The process was followed by TD-GC-MS determination and LODs taken ranged between 0.1 and 891 pg L^{-1}. Very recently, a new phase polyacrylate (Twister PA^{TM}), more suitable for polar analytes, has been developed by Gerstel. Although few applications regarding the use of this PA phase have been published, it has shown good performance in the determination of benzothiazole in waste waters [363].

Regarding the extraction step, the most studied variables are extraction time, pH adjustment, addition of an inert salt, addition of an organic modifier and stirring speed. After extraction, the analytes are usually desorbed by TD, followed by GC, or with small amounts of organic solvents. Although TD is the most recommended desorption mode, LD is a good alternative for thermally labile analytes and analysis in LC and CE systems. For instance, Pedrouzo et al. [364] used a commercial PDMS stir bar for the extraction of 4 UV filters and 2 antimicrobials in waste and surface waters. After the extraction, stir bars were desorbed with 1 mL of acetonitrile and analysed by UHPLC-tandem MS. LODs were 2.5 ng L^{-1} for river water and 5-10 ng L^{-1} for effluent and influent waste water.

One of the main advantages of SBSE is its high sensitivity due to the fact that the extraction phase is 50-250 times larger than in SPME. Furthermore, in combination with TD, the minimal manipulation of the sample required minimises the risk of background contamination. Moreover, it has been demonstrated that loaded stir bars can be stored for 1 week without loss of solutes. This means they are suitable for field sampling [365].

SBSE is also suitable for multi-residue methods and it offers some advantages over SPE and SPME in this field. One of the main challenges of multi-residue methods is that the optimal extraction conditions for each group of target compounds can be different, and the analyst should adopt some consensus conditions that lead to a decrease in sensitivity. However, in the case of SBSE, it can be solved by using it in multi-shot method mode or in sequential mode [361]. In the multi-shot method, different sample aliquots are extracted in different conditions using SBSE while the stir bar is thermally-desorbed. This leads to an increase in sensitivity and selectivity. The multi-shot method can be also used in the same extraction conditions in order to obtain better recoveries. Figure 1.19 shows the scheme of these two multi-shot modes.

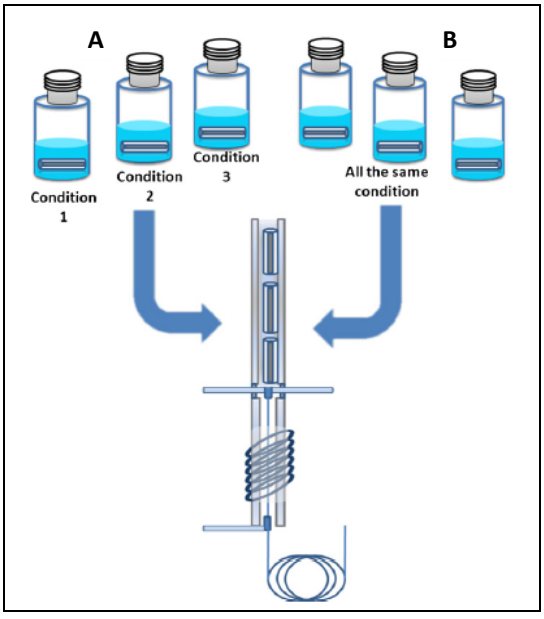


Figure 1.19. SBSE in the multi-shot mode: (A) different extraction conditions and (B) the same extraction conditions [361].

Several examples of multi-shot methods can be found in the literature. For instance, Ochiai et al. [366] developed a dual SBSE multi-residue screening method for the

determination of 85 pesticides in river water. While recovery of more hydrophilic pesticides increases with an increasing concentration of NaCl, recovery of more hydrophobic solutes decreases in the presence of the salt. Therefore, two different extraction conditions were used for SBSE and the different stir bars were then analysed together. Similarly, Van Hoeck et al. [367] used four different aliquots extracted in different conditions to determine a wide range of endocrine-disrupting compounds. In sequential SBSE, the same sample aliquot is sequentially extracted in different conditions with the same or different stir bars. Ochiai et al. [368] extracted pesticides from water, first without the addition of NaCl and then with a second stir bar and the addition of 30% NaCl.

Nowadays, the main limitation of SBSE is the reduced commercially-available coatings. As previously commented, currently PDMS is the most common coating, which is thermostable, can be used in a broad temperature range (it acts as a liquid between -20 °C and 320 °C) and has interesting diffusion properties [360]. However, polar analytes show low affinity for this phase. Derivatization is one of the main alternatives, either in situ, on stir-bar or post-extraction. These derivatization modes are showed in Figure 1.20.

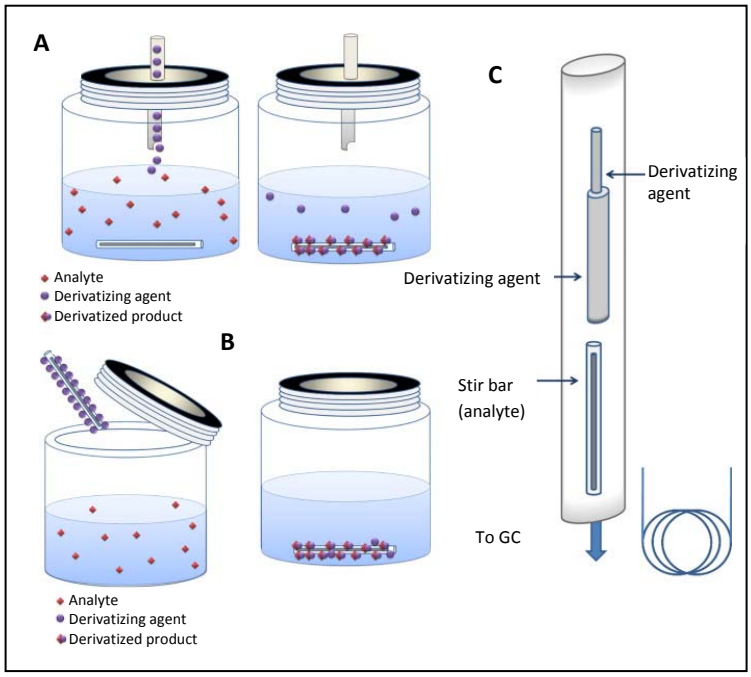


Figure 1.20. Different derivatization modes in SBSE: (A) in situ, (B) on-stir bar and (C) on-tube derivatization [361].

The simplest approach is the in-situ derivatization. In this process, the derivatization reaction occurs first, in the aqueous sample before or simultaneously to the extraction step, and the derivatives are then extracted by the stir bar (see Figure 1.20 A). The most common in-situ derivatization is the acetylation of phenolic compounds with acetic anhydride in a basic sample pH. On-stir bar derivatization can be performed either by pre-loading the stir bar with derivatization agent (see Figure 1.20 B) or by first concentrating the analytes in the PMDS phase and then exposing the stir bar to the vapour of the derivatization agent. The last strategy, post-extraction, can be performed with TD (in-tube) and LD (in-extract). For the in-tube derivatization, a small glass capillary tube containing the derivatizing agent is placed with the stir bar in the desorption cartridge (see Figure 1.20 C). For the in-extract approach, the derivatization agent is added to the organic solvent after stir bar desorption.

Currently the most widely-used derivatization modes are in-situ acetylation and in-tube silylation. Both approaches enhance sensitivity in the GC analysis of polar compounds. For instance, Casas et al. [369] used in situ acetylation for the SBSE extraction of 5 parabens, triclosan and methyltriclosan. Recoveries of the target compounds were higher than 79%, except for methyl paraben (22%). Kawaguchi et al. [370] used in-tube silylation with N,O-bis(trimethylsylil)trifluoroacetamide (BSTFA)) for the simultaneous determining of benzophenone sunscreen compounds and some derivatives in water samples. The LODs were between 0.5 and 2.0 ng L^{-1}, with %RSD <15.5%.

Besides derivatization, several research groups have, in recent years, developed in-house coatings based on sol-gel technologies [371], monolithic materials [372], porous polymers, such as PDMS/polypyrrole [373], and MIPs [374]. For example, Bratkowska et al. [372] recently developed a monolithic coating (poly(vinil-pyrrolidone-divinyl-benzene)) to extract polar pharmaceuticals and parabens from river and sewage water. This showed improved recovery levels compared with PDMS-coated stir bars. Besides, polyurethane (PU) has also been proposed for the SBSE phase to monitor the most polar of analytes. For instance, Silva et al. [375] compared the performance of PU stir bars and PDMS stir bars for the extraction of acidic pharmaceuticals. Recoveries of these analytes ranged between 45% and 91% with PU, whereas for PDMS they ranged between 10% and 73%. For HHSE applications, dual-phase stir bars have also been used. These stir bars consist of a PDMS outer coating and a second complementary inner sorbent (usually carbonaceous). This shows enhanced recoveries of analytes because of the effect of combining two extraction mechanisms: sorption and adsorption [376].

1.3.2.4. Other techniques

Although the extraction techniques mentioned above are the most widely-used in aqueous samples, some other sample preparation methods have caused increasing interest over the last few years. As previously mentioned, one major trend in analytical chemistry is the miniaturisation of the extraction techniques in order to reduce the use of organic solvents and their subsequent environmental impact. This is the case with liquid-phase microextraction (LPME) related techniques, which were introduced in order to overcome the main drawbacks of SPME fibres. These methods show high enrichment, efficient sample clean-up and low consumption of organic solvent. These microextraction techniques have been used for the extraction of a wide variety of organic contaminants, including VOCs, PAHs, pesticides, pharmaceuticals and PCPs with generally low LODs (and ng L^{-1} levels) and good repeatability [335].

Among the microextraction methods, single-drop microextraction (SDME) is the most popular, because it is inexpensive and easy to operate [20]. In this approach, a drop of an extractive solvent (an organic solvent or a liquid ionic) is suspended at the tip of a syringe and exposed by headspace to the sample for a given time and temperature. After the extraction, the drop is retracted and transferred to the GC analyser. Aguilera-Herrador et al. [377] used ionic liquid-based single-drop microextraction GC-MS for the determination of BTEX in waters, obtaining LODs between 20 and 91 ng L^{-1} and %RSD < 5.2%. In another SDME approach, Saraji et al. [378] developed a SDME method followed by in-syringe derivatization and GC-MS to determine parabens in water samples. The %RSD of the method for aqueous samples varied from 8.1 to 13%. The LODs ranged from 0.001 (n-butyl paraben) to 0.015 (methyl paraben) µg L^{-1}, and the enrichment factors were between 23 and 150.

The main disadvantages of SDME are the instability of the drop and the limited drop surface which can lead to limited sensitivity or slow kinetics. To overcome this, a number of variations have been introduced, such as organic solvent film (OSF). In OSF, a renewable extractive film is formed inside the microsyringe barrel due to the fact that the syringe plunger is moved uniformly and repeatedly by a stirring motor. This way, the extractive surface is increased and, because a supported film is generated instead of a single drop, it avoids the loss of the extraction solvent. The OSF approach has been used to determine BTEX in water samples [379] with LODs between 0.18 and 0.35 ng mL^{-1}. Another approach to overcome the instability of the drop is dynamic single drop extraction, which was used by Ahmadi et al [380] for determining organophosphorus pesticides, achieving LODs at low ng L^{-1} levels and % RSD between 1.2 and 5.6%.

Other common miniaturisation approaches include continuous flow microextraction (CFME), dispersive liquid-liquid microextraction (DLLME) and hollow-fibre liquid phase microextraction (HFLPME), among others. In CFME, an organic extractive drop is continuously in contact with a fresh liquid sample. CFME was used for extracting PAHs in 15 mL of water samples using 3 µL of benzene as an extraction solvent. LODs for the target PAHs ranged from 0.001 to 0.01 µg L^{-1} and %RSD was below 25% [381]. DLLME uses a dispersive solvent which is miscible in both the extracting solvent and the aqueous sample to increase the contact surface. DLLME has been used extensively. For instance, Panagiotou et al. [382] used 250 µL of carbon tetrachloride as an extraction solvent and 0.62 mL of methanol as a dispersant to extract phthalates and polycyclic musks from 5 mL of water sample. The repeatability method varied between 2.6% to 9.7%, recoveries were higher than 79% and the LOD values were in the range of 8–63 ng L^{-1}. The main drawback of DLLME is that the dispersant solvent usually decreases the partition coefficient of analytes into the extraction solvent. For the HFLPME approach, polymeric membranes are used as support for the small volumes of solvent. Recently, Villaverde-de-Sáa et al. [383] extracted parabens and triclosan from water samples using an in-sample acetylation followed by HFLPME, obtaining extraction efficiencies between 46 and 110%.

1.4. References

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

[1] WHO, Enviornmental Health, http://www.wpro. who.int/sites/hse/ (accessed 17.05.2011).
[2] R. Koppmann, Volatile organic compounds in the atmosphere, Blackwell Publishing, Oxford, 2007.
[3] K. Ravindra, R. Sokhi, R. Van Grieken, Atmos. Environ. 42 (2008) 2895.
[4] P.S. Monks, C. Granier, S. Fuzzi, et al., Atmos. Environ. 43 (2009) 5268.
[5] WHO, Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide, Geneva, 2005.
[6] WHO, World Health Report: Reducing Risks, Promoting Healthy Life, Geneva, 2002.
[7] P.D. Noyes, M.K. McElwee, H.D. Miller, B.W. Clark, L.A. Van Tiem, K.C. Walcott, K.N. Erwin, E.D. Levin, Environ. Int. 35 (2009) 971.
[8] R. Lohmann, K. Breivik, J. Dachs, D. Muir, Environ. Poll. 150 (2007) 150.
[9] R. Barro, J. Regueiro, M. Llompart, C. García-Jares, J. Chromatogr. A 1216 (2009) 540.
[10] C.J. Weschler, W.W. Nazaroff, Atmos. Environ. 44 (2010) 3609.
[11] C. García-Jares, J. Regueiro, R. Barro, T. Dagnac, M. Llompart, J. Chromatogr. A 1216 (2009) 567.
[12] L. Morawska, T. Salthammer, Indoor Environment. Airborne Particles and Settled Dust, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003.
[13] W. Butte, B. Heinzow, Rev. Environ. Contam. T. 175 (2002) 1.
[14] W.R. Ott, A.C. Steinemann, L.A. Wallace, Exposure Analysis, Taylor & Francis, Boca Raton, 2007.
[15] N. Bolong, A.F. Ismail, M.R. Salim, T. Matsuura, Desalination 239 (2009) 229.
[16] M. la Farré, S. Pérez, L. Kantiani, D. Barceló, Trends Anal. Chem. 27 (2008) 991.
[17] V. Matamoros, E. Jover, J.M. Bayona, Anal. Bioanal. Chem. 393 (2009) 847.
[18] I. Muñoz, M.J. Gómez-Ramos, A. Aguera, J.F. García-Reyes, A. Molina-Díaz, A.R. Fernández-Alba, Trends Anal. Chem. 28 (2009) 676.
[19] S.D. Richardson, Anal. Chem. 82 (2010) 4742.
[20] M. Urbanowicz, B. Zabiegala, J. Namiesnik, Anal. Bioanal. Chem. 399 (2011) 277.
[21] Regulation (EC) No. 1907/2006. Off. J. Eur. Commun. L 396 (2006) 1.
[22] R. Atkinson, J. Arey, Chem. Rev. 103 (2003) 4605.
[23] M. Kanakidou, J.H. Seinfeld, S.N. Pandis, I., et al., Atmos. Chem. Phys. 5 (2005) 1053.
[24] S. Corsolini, J. Chromatogr. A 1216 (2009) 598.
[25] UNEP, Final Act of the Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants. United Nations Environment Program Chemicals, Geneva, 2001.
[26] UNEP-POPS-COP-NOTIF-DN-CN524, http://chm.pops.int/2009 (accessed 06.05. 2011).
[27] UNECE, 1998. The 1998 Aarhus Protocol on Persistent Organic Pollutants (POPs). http://www.unece.org/env/lrtap/pops_h1.htm (accessed 06.05.2011).
[28] C.G. Daughton, Environ. Impact Asses. 24 (2004) 711.
[29] D. Barceló, Trends Anal. Chem. 22 (2003) XIV.

[30] USEPA, The New Contaminant Candidate List-3, www.epa.gov/safewater/ccl (accessed 25.04.2011).
[31] USEPA, An introduction to indoor air quality. Volatile organic compounds: Technical overview. http://www.epa.gov/iaq/voc2.html (accessed 25.04.2011).
[32] Council Directive 1999/13/EC. Off. J. Eur. Commun. L 85 (1999) 1.
[33] Emission Database for Global Atmospheric Research (EDGAR): http://themasites.pbl.nl/en/themasites/edgar/index.html (accessed 05.04.2011).
[34] A. Guenther, C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, P. Zimmerman, J. Geophys. Res.-Atmos. 100 (1995) 8873.
[35] USEPA, Amendments to 1990 Clean Air Act-List of 189 Hazardous Air Pollutants, 1994.
[36] European Parliament And Council Directive 94/63/EC. Off. J. Eur. Commun., L 365 (1994) 24.
[37] Directive 2008/50/EC, Off. J. Eur. Commun., L 152 (2008) 1.
[38] R. Atkinson, Atmos. Environ. 34 (2000) 2063.
[39] R.G. Derwent, M.E. Jenkin, S.M. Saunders, Atmos. Environ. 30 (1996) 181.
[40] R.G. Derwent, M.E. Jenkin, N.R. Passant, M.J. Pilling, Atmos. Environ. 41 (2007) 2570.
[41] W.P.L. Carter, J. Air Waste Manage. 44 (1994) 881.
[42] J.H. Kroll, J.H. Seinfeld, Atmos. Environ. 42 (2008) 3593.
[43] USEPA, An introduction to indoor air quality. Volatile organic compounds. http://www.epa.gov/iaq/voc.html (accessed 25.04.2011).
[44] J. Kwon, C.P. Weisel, B.J. Turpin, J.F. Zhang, L.R. Korn, M.T. Morandi, T.H. Stock, S. Colome, Environ. Sci. Technol. 40 (2006) 4074.
[45] J.A. Zhou, Y. You, Z.P. Bai, Y.D. Hu, J.F. Zhang, N. Zhang, Sci. Total Environ. 409 (2011) 452.
[46] A. Esplugues, F. Ballester, M. Estarlich, S. Llop, V. Fuentes-Leonarte, E. Mantilla, C. Iniguez, Sci. Total Environ. 409 (2010) 63.
[47] M.M. Loh, J.I. Levy, J.D. Spengler, E.A. Houseman, D.H. Bennett, Environ. Health Perspect. 115 (2007) 1160.
[48] USEPA Cancer Risk from outdoor exposure to air toxics, Office of Air Quality Planning and Standards, EPA-450/1-90-004a, 1990.
[49] M.L. Boeglin, D. Wessels, D. Henshel, Environ. Res. 100 (2006) 242.
[50] IARC, List of classifications by alphabetical order, http://monographs.iarc.fr/ENG/Classification/index.php (accessed 14.05.2011).
[51] WHO, Air Quality Guidelines for Europe, WHO Regional Office for Europe, 2n ed., Copenhagen, 2000.
[52] IRIS, http://cfpub.epa.gov/ncea/iris /index.cfm?fuseaction=iris.showSubstance List (accessed 15.03.2011).
[53] ATSDR, http://www.atsdr.cdc.gov/substances/indexAZ.asp#B (accessed 15.03. 2011).
[54] A.P. Jones, Atmos. Environ. 33 (1999) 4535.
[55] L. Massolo, M. Rehwagen, A. Porta, A. Ronco, O. Herbarth, A. Mueller, Environ. Toxicol. 25 (2010) 339.

[56] M.G. Robson, W.A. Toscano, Risk assessment for environmental health. Wiley and Sons inc., New York, 2007.
[57] S.N. Sax, D.H. Bennett, S.N. Chillrud, J. Ross, P.L. Kinney, J.D. Spengler, Environ. Health Perspect. 114 (2006) 1558.
[58] H.L. Chiang, W.H. Lin, J.S. Lai, W.C. Wang, J. Environ. Sci. Health A 45 (2010) 1397.
[59] M.R. Ras-Mallorquí, R.M. Marcé-Recasens, F. Borrull-Ballarín, Talanta 72 (2007) 941.
[60] J.B. Gilman, W.C. Kuster, P.D. Goldan, S.C. Herndon, M.S. Zahniser, S.C. Tucker, W.A. Brewer, B.M. Lerner, E.J. Williams, R.A. Harley, F.C. Fehsenfeld, C. Warneke, J.A. de Gouw, J. Geophys. Res.-Atmos. 114 (2009).
[61] R.G. Derwent, T.J. Davies, M. Delaney, G.J. Dollard, R.A. Field, P. Dumitrean, P.D. Nason, B.M.R. Jones, S.A. Pepler, Atmos. Environ. 34 (2000) 297.
[62] E.B. Bakeas, D.I. Argyris, P.A. Siskos, Chemosphere 52 (2003) 805.
[63] E.B. Bakeas, P.A. Siskos, Environ. Sci. Pollut. Res. Int. 9 (2002) 234.
[64] B. Barletta, S. Meinardi, F. Sherwood Rowland, C.-Y. Chan, X. Wang, S. Zou, L. Yin Chan, D.R. Blake, Atmos. Environ. 39 (2005) 5979.
[65] E.M. Martins, G. Arbilla, G.F. Bauerfeldt, M. de Paula, Chemosphere 67 (2007) 2096.
[66] B. Barletta, S. Meinardi, I.J. Simpson, H.A. Khwaja, D.R. Blake, F.S. Rowland, Atmos. Environ. 36 (2002) 3429.
[67] V.A. Lanz, C. Hueglin, B. Buchmann, M. Hill, R. Locher, J. Staehelin, S. Reimann, Atmos. Chem. Phys. 8 (2008) 2313.
[68] B. Wang, M. Shao, S.H. Lu, B. Yuan, Y. Zhao, M. Wang, S.Q. Zhang, D. Wu, Atmos. Chem. Phys. 10 (2010) 5911.
[69] E. Cetin, M. Odabasi, R. Seyfioglu, Sci. Total Environ. 312 (2003) 103.
[70] B.T. Jobson, C.M. Berkowitz, W.C. Kuster, P.D. Goldan, E.J. Williams, F.C. Fesenfeld, E.C. Apel, T. Karl, W.A. Lonneman, D. Riemer, J. Geophys. Res.-Atmos. 109 (2004).
[71] T.Y. Lin, U. Sree, S.H. Tseng, K.H. Chiu, C.H. Wu, J.G. Lo, Atmos. Environ. 38 (2004) 4111.
[72] B.Z. Wu, T.Z. Feng, U. Sree, K.H. Chiu, H.G. Lo, Anal. Chim. Acta 576 (2006) 100.
[73] W.H. Cheng, M.S. Chou, J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng. 38 (2003) 2521.
[74] J. Leach, A. Blanch, A.C. Bianchi, Atmos. Environ. 33 (1999) 4309.
[75] F. Dincer, A. Muezzinoglu, J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng. 43 (2008) 1569.
[76] J.L. Adgate, T.R. Church, A.D. Ryan, G. Ramachandran, A.L. Fredrickson, T.H. Stock, M.T. Morandi, K. Sexton, Environ. Health Perspect. 112 (2004) 1386.
[77] L.S.R. Brickus, J.N. Cardoso, F.R.D. Neto, Environ. Sci. Technol. 32 (1998) 3485.
[78] WHO, Polycyclic aromatic hydrocarbons, selected non heterocyclic. Environmental Health Criteria 202, 1998.
[79] EIONET, Criteria for EUROAIRNET - The EEA Air Quality Monitoring and Information Network EEA Technical report No 12, 1999.
[80] Directive 2004/107/EC, Off. J. Eur. Commun., L23 (2005) 3.
[81] Council Directive 98/83/EC, Off. J. Eur. Commun., L330 (1998) 32.

[82] Directive 2005/69/EC, Off. J. Eur. Commun., L323 (2005) 51.
[83] S.O. Baek, M.E. Goldstone, P.W.W. Kirk, J.N. Lester, R. Perry, Chemosphere 22 (1991) 503.
[84] Y.X. Zhang, S. Tao, Atmos. Environ. 43 (2009) 812.
[85] A.K. Haritash, C.P. Kaushik, J. Hazard. Mater. 169 (2009) 1.
[86] ATSDR, Toxicological Profile for Polycyclic Aromatic Hydrocarbons, 1995, http://www.atsdr.cdc.gov/ (accessed 27.03.2011).
[87] K. Ravindra, L. Bencs, E. Wauters, J. de Hoog, F. Deutsch, E. Roekens, N. Bleux, P. Berghmans, R. Van Grieken, Atmos. Environ. 40 (2006) 771.
[88] K. Srogi, Environ. Chem. Lett. 5 (2007) 169.
[89] J. Dachs, J.M. Bayona, C. Raoux, J. Albaiges, Environ. Sci. Technol. 31 (1997) 682.
[90] J.F. Collins, J.P. Brown, G.V. Alexeeff, A.G. Salmon, Regul. Toxicol. Pharmacol. 28 (1998) 45.
[91] J.M. Delgado-Saborit, C. Stark, R.M. Harrison, Environ. Int. 37 (2011) 383.
[92] B. Armstrong, E. Hutchinson, J. Unwin, T. Fletcher, Environ. Health Perspect. 112 (2004) 970.
[93] P. Plaza-Bolaños, A.G. Frenich, J.L.M. Vidal, J. Chromatogr. A 1217 (2010) 6303.
[94] I.C.T. Nisbet, P.K. Lagoy, Regul. Toxicol. Pharmacol. 16 (1992) 290.
[95] J.C. Larsen, P.B. Larsen, Chemical Carcinogens, in: R.E.Herster, R.M. Harrison (Eds.) Air Pollution and health, The Royal Society of Chemistry, Cambridge, 1998, p. 33.
[96] Y. Kameda, J. Shirai, T. Komai, J. Nakanishi, S. Masunaga, Sci. Total Environ. 340 (2005) 71.
[97] T. Bartos, P. Cupr, J. Klanova, I. Holoubek, Environ. Int. 35 (2009) 1066.
[98] H.H. Liu, H.H. Yang, C.D. Chou, M.H. Lin, H.L. Chen, J. Hazard. Mater. 181 (2010) 105.
[99] J. Dejmek, I. Solansky, I. Benes, J. Lenicek, R.J. Sram, Environ. Health Perspect. 108 (2000) 1159.
[100] R.J. Sram, B.B. Binkova, J. Dejmek, M. Bobak, Environ. Health Perspect. 113 (2005) 375.
[101] F.P. Perera, Z.G. Li, R. Whyatt, L. Hoepner, S.A. Wang, D. Camann, V. Rauh, Pediatrics 124 (2009) E195.
[102] M.A.B. Mazquiaran, L.C.O. de Pinedo, Atmos. Research 85 (2007) 288.
[103] A. Gutiérrez-Daban, A.J. Fernández-Espinosa, M. Ternero-Rodríguez, F. Fernández -Álvarez, Anal. Bioanal. Chem. 381 (2005) 721.
[104] M.R. Ras, R.M. Marcé, A. Cuadras, M. Mari, M. Nadal, F. Borrull, Int. J. Environ. Anal. Chem. 89 (2009) 543.
[105] M.S. Callén, M.T. de la Cruz, J.M. López, R. Murillo, M.V. Navarro, A.M. Mastral, Water Air Soil Pollut. 190 (2008) 271.
[106] S. Dejean, C. Raynaud, M. Meybeck, J.P. Massa, V. Simon, Environ. Monitor. 148 (2009) 27.
[107] K. Saarnio, M. Sillanpaa, R. Hillamo, E. Sandell, A.S. Pennanen, R.O. Salonen, Atmos. Environ. 42 (2008) 9087.
[108] K. Ravindra, E. Wauters, R. Van Grieken, Sci. Total Environ. 396 (2008) 100.

[109] K.F. Ho, S.S.H. Ho, S.C. Lee, Y. Cheng, J.C. Chow, J.G. Watson, P.K.K. Louie, L.W. Tian, Atmos. Environ. 43 (2009) 6343.
[110] S.S. Andra, K.C. Makris, Environ. Int. 37 (2011) 412.
[111] A.M. Peck, Anal. Bioanal. Chem. 386 (2006) 907.
[112] OECD, The 2004 OECD List of High Production Volume Chemicals, 2004.
[113] C.G. Daughton, T.A. Ternes, Environ. Health Perspect. 107 (1999) 907.
[114] C. Sommer, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part X, vol. 3, Springer-Verlag, Heidelberg, 2004, p. 1.
[115] Council Directive 98/62/EEC, Off. J. Eur. Commun. L253 (1998) 20.
[116] G.G. Rimkus, Toxicol. Lett. 111 (1999) 37.
[117] A. Behechti, K.W. Schramm, A. Attar, J. Niederfellner, A. Kettrup, Water Res. 32 (1998) 1704.
[118] Y.J. Chou, D.R. Dietrich, Toxicol. Lett. 111 (1999) 27.
[119] R. Gatermann, S. Biselli, H. Huhnerfuss, G.G. Rimkus, M. Hecker, L. Karbe, Arch. Environ. Contam. Toxicol. 42 (2002) 437.
[120] Commission Directive 2008/42/EC, Off. J. Eur. Commun., L93 (2008) 13.
[121] K. Bester, Personal care compounds in the Environment. Pathways, fate and Methods for Determination, Wiley-VCH, Weinheim, 2007.
[122] K. Bester, J. Chromatogr. A 1216 (2009) 470.
[123] F. Balk, D. Salvito, H. Blok, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part X, vol. 3, Springer-Verlag, Heidelberg, 2004, p. 311.
[124] H. Nakata, H. Sasaki, A. Takemura, M. Yoshioka, S. Tanabe, K. Kannan, Environ. Sci. Technol. 41 (2007) 2216.
[125] S.L. Simonich, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part O, vol. 5, Springer-Verlag, Heidelberg, 2004, p. 79.
[126] K. Bester, J. Environ. Monit. 7 (2005) 43.
[127] K. Bester, Chemosphere 57 (2004) 863.
[128] T.A. Ternes, A. Joss, H. Siegrist, Environ. Sci. Technol. 38 (2004) 392A.
[129] A.M. Peck, K.C. Hornbuckle, J. Environ. Monit. 8 (2006) 874.
[130] Y. Horii, J.L. Reiner, B.G. Loganathan, K.S. Kumar, K. Sajwan, K. Kannan, Chemosphere 68 (2007) 2011.
[131] N.R. Sumner, C. Guitart, G. Fuentes, J.W. Readman, Environ. Pollut. 158 (2010) 215.
[132] A.M. Peck, K.C. Hornbuckle, Atmos. Environ. 40 (2006) 6101.
[133] J. Regueiro, C. García-Jares, M. Llompart, J.P. Lamas, R. Cela, J. Chromatogr. A 1216 (2009) 2805.
[134] A. Sofuoglu, N. Kiymet, P. Kavcar, S.C. Sofuoglu, Indoor Air 20 (2010) 515.
[135] H. Fromme, T. Lahrz, M. Piloty, H. Gebhart, A. Oddoy, H. Ruden, Indoor Air 14 (2004) 188.
[136] D.H. Chen, X.Y. Zeng, Y.Q. Sheng, X.H. Bi, H.Y. Gui, G.Y. Sheng, J.M. Fu, Chemosphere 66 (2007) 252.
[137] J. Regueiro, M. Llompart, C. García-Jares, R. Cela, J. Chromatogr. A 1174 (2007) 112.
[138] R. Kallenborn, R. Gatermann, S. Planting, G.G. Rimkus, M. Lund, M. Schlabach, I.C. Burkow, J. Chromatogr. A 846 (1999) 295.

[139] R. Kallenborn, R. Gatermann, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry,Part X, vol. 3, Springer-Verlag, Heidelberg, 2004, p. 85.
[140] A.M. Peck, K.C. Hornbuckle, Environ. Sci. Technol. 38 (2004) 367.
[141] Z.Y. Xie, R. Ebinghaus, C. Temme, O. Heemken, W.G. Ruck, Environ. Sci. Technol. 41 (2007) 5654.
[142] H. Rudel, W. Bohmer, C. Schroter-Kermani, J. Environ. Monit. 8 (2006) 812.
[143] K. Kannan, J.L. Reiner, S.H. Yun, E.E. Perrotta, L. Tao, B. Johnson-Restrepo, B.D. Rodan, Chemosphere 61 (2005) 693.
[144] R. Kallenborn, R. Gatermann, G.G. Rimkus, J. Environ. Monit. 1 (1999) 70N.
[145] S.T. Glassmeyer, E.T. Furlong, D.W. Kolpin, J.D. Cahill, S.D. Zaugg, S.L. Werner, M.T. Meyer, D.D. Kryak, Environ. Sci. Technol. 39 (2005) 5157.
[146] H.P. Hutter, P. Wallner, W. Hartl, M. Uhl, G. Lorbeer, R. Gminski, V. Mersch-Sundermann, M. Kundi, Int. J. Hyg. Environ. Health. 213 (2010) 124.
[147] H.P. Hutter, P. Wallner, H. Moshammer, W. Hartl, R. Sattelberger, G. Lorbeer, M. Kundi, Sci. Total Environ. 407 (2009) 4821.
[148] H. Brunn, N. Bitsch, J. Amberg-Muller, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry,Part X, vol. 3, Springer-Verlag, Heidelberg, 2004, p. 259.
[149] G.G. Rimkus, M. Wolf, Chemosphere 33 (1996) 2033.
[150] J.L. Reiner, C.M. Wong, K.F. Arcaro, K. Kannan, Environ. Sci. Technol. 41 (2007) 3815.
[151] L. Duedahl-Olesen, T. Cederberg, K.H. Pedersen, A. Hojgard, Chemosphere 61 (2005) 422.
[152] T. Luckenbach, D. Epel, Environ. Health Perspect. 113 (2005) A803.
[153] M.G. Soni, I.G. Carabin, G.A. Burdock, Food Chem. Toxicol. 43 (2005) 985.
[154] FDA, Methyl Paraben And Propyl Paraben. Affirmation of GRAS Status of Direct Human Food Ingredients. Federal Register 38 143,1973, p. 20048.
[155] Z. Ali, V.U. Ahmad, M. Zahid, R.B. Tareen, Phytochemistry 48 (1998) 1271.
[156] H.B. Lee, T.E. Peart, M.L. Svoboda, J. Chromatogr. A 1094 (2005) 122.
[157] J. Regueiro, M. Llompart, E. Psillakis, J.C. García-Monteagudo, C. García-Jares, Talanta 79 (2009) 1387.
[158] I. González-Mariño, J.B. Quintana, I. Rodríguez, R. Cela, Rapid Commun. Mass Spectrom. 23 (2009) 1756.
[159] A. Nieto, F. Borrull, R.M. Marcé, E. Pocurull, J. Chromatogr. A 1216 (2009) 5619.
[160] P. Canosa, D. Pérez-Palacios, A. Garrido-López, M.T. Tena, I. Rodríguez, E. Rubí, R. Cela, J. Chromatogr. A 1161 (2007) 105.
[161] M.J. Gómez, M.M. Gómez-Ramos, A. Agüera, M. Mezcua, S. Herrera, A.R. Fernández-Alba, J. Chromatogr. A 1216 (2009) 4071.
[162] R.A. Rudel, D.E. Camann, J.D. Spengler, L.R. Korn, J.G. Brody, Environ. Sci. Technol. 37 (2003) 4543.
[163] R.A. Rudel, R.E. Dodson, L.J. Perovich, R. Morello-Frosch, D.E. Camann, M.M. Zuniga, A.Y. Yau, A.C. Just, J.G. Brody, Environ. Sci. Technol. 44 (2010) 6583.
[164] P. Canosa, I. Rodríguez, E. Rubí, R. Cela, Anal. Chem. 79 (2007) 1675.
[165] X.H. Fan, C. Kubwabo, P. Rasmussen, H. Jones-Otazo, J. Environ. Monit. 12 (2010) 1891.

[166] E.J. Routledge, J. Parker, J. Odum, J. Ashby, J.P. Sumpter, Toxicol. Appl. Pharmacol. 153 (1998) 12.
[167] D. Miller, B.B. Wheals, N. Beresford, J.P. Sumpter, Environ. Health Perspect. 109 (2001) 133.
[168] J.G. Chen, K.C. Ahn, N.A. Gee, S.J. Gee, B.D. Hammock, B.L. Lasley, Toxicol. Appl. Pharmacol. 221 (2007) 278.
[169] C. Bairati, G. Goi, A. Lombardo, G. Tettamanti, Clin. Chim. Acta 224 (1994) 147.
[170] S. Tayama, Y. Nakagawa, K. Tayama, Mutat. Res. Genet. Toxicol. Environ. Mutagen. 649 (2008) 114.
[171] O. Handa, S. Kokura, S. Adachi, T. Takagi, Y. Naito, T. Tanigawa, N. Yoshida, T. Yoshikawa, Toxicology 227 (2006) 62.
[172] P.D. Darbre, A. Aljarrah, W.R. Miller, N.G. Coldham, M.J. Sauer, G.S. Pope, J. Appl. Toxicol. 24 (2004) 5.
[173] P.D. Darbre, P.W. Harvey, J. Appl. Toxicol. 28 (2008) 561.
[174] R.A. Rudel, L.J. Perovich, Atmos. Environ. 43 (2009) 170.
[175] J.A. van Meeuwen, O. van Son, A.H. Piersma, P.C. de Jong, M. van den Berg, Toxicol. Appl. Pharmacol. 230 (2008) 372.
[176] USEPA, R.E.D. Facts, DEET, EPA-738-F-95-010, 1998.
[177] K. Quednow, W. Puttmann, Environ. Sci. Pollut. Res. 16 (2009) 630.
[178] R. Rodil, M. Moeder, J. Chromatogr. A 1178 (2008) 9.
[179] S.D. Costanzo, A.J. Watkinson, E.J. Murby, D.W. Kolpin, M.W. Sandstrom, Sci. Total Environ. 384 (2007) 214.
[180] K.E. Murray, S.M. Thomas, A.A. Bodour, Environ. Pollut. 158 (2010) 3462.
[181] M. Tisch, P. Schmezer, M. Faulde, A. Groh, H. Maier, Eur. Arch. Oto-Rhino-Laryn. 259 (2002) 150.
[182] A.R. Fernández-Alba, A. Agüera, in: W. Paul, T. Alan, P. Colin (Eds.), Encyclopedia of Analytical Science, Elsevier, Oxford, 2005, p. 197.
[183] S.D. Richardson, M.J. Plewa, E.D. Wagner, R. Schoeny, D.M. DeMarini, Mut. Res. - Rev. Mut. Res. 636 (2007) 178.
[184] S.D. Richardson, Anal. Chem. 79 (2007) 4295.
[185] R. Shen, S.A. Andrews, Water Res. 45 (2011) 944.
[186] Commission Directive 93/11/EEC, Off. J. Eur. Commun., L 093 (1993) 37.
[187] Technische Regeln für Gefahrstoffe, N-nitrosamine, TGRS 552, 2007.
[188] California Department of Public Health, NDMA and other nitrosamines-Drinking water, http://www.cdph.ca.gov/certlic/drinkingwater/Pages/NDMA.aspx (accessed 16.05.2011).
[189] USEPA, Ambient Water Criteria for Nitrosamines, EPA 440/5-80-064, 1980.
[190] Y.Y. Zhao, J. Boyd, S.E. Hrudey, X.F. Li, Environ. Sci. Technol. 40 (2006) 7636.
[191] A. Llop, F. Borrull, E. Pocurull, J. Sep. Sci. 33 (2010) 3692.
[192] F. de Vocht, I. Burstyn, K. Straif, R. Vermeulen, K. Jakobsson, L. Nichols, B. Peplonska, D. Taeger, H. Kromhout, J. Environ. Monit. 9 (2007) 253.
[193] C.C. Abnet, Cancer Invest. 25 (2007) 189.
[194] S.S. Hecht, D. Hoffmann, Carcinogenesis 9 (1988) 875.
[195] M. Sleiman, L.A. Gundel, J.F. Pankow, P. Jacob, B.C. Singer, H. Destaillats, Proc. Natl. Acad. Sci. U. S. A. 107 (2010) 6576.

[196] S.F. Schick, S. Glantz, Cancer Epidemiol. Biomarkers Prev. 16 (2007) 1547.
[197] G.E. Matt, P.J.E. Quintana, M.F. Hovell, J.T. Bernert, S. Song, N. Novianti, T. Juarez, J. Floro, C. Gehrman, M. García, S. Larson, Tob. Control 13 (2004) 29.
[198] J.P. Winickoff, J. Friebely, S.E. Tanski, C. Sherrod, G.E. Matt, M.F. Hovell, R.C. McMillen, Pediatrics 123 (2009) E74.
[199] S. Kim, T. Aung, E. Berkeley, G.B. Diette, P.N. Breysse, Environ. Res. 108 (2008) 289.
[200] K. Rumchev, K. Jamrozik, S. Stick, J. Spickett, Indoor Air 18 (2008) 202.
[201] M. Sleiman, R.L. Maddalena, L.A. Gundel, H. Destaillats, J. Chromatogr. A 1216 (2009) 7899.
[202] J. Zhou, R. Bai, Y.F. Zhu, Rapid Commun. Mass Spectrom. 21 (2007) 4086.
[203] IARC monographs volume 89. Available on: http://monographs.iarc.fr/ENG/ Monographs/vol89/mono89-7E.pdf (accessed 27.04.2011).
[204] X. Thomas, Y. Chelghoum, Leuk. Lymphoma 45 (2004) 1103.
[205] S.S. Hecht, J. Natl. Cancer Inst. 91 (1999) 1194.
[206] S. Rubio, D. Pérez-Bendito, Anal. Chem. 81 (2009) 4601.
[207] D. van Pinxteren, H. Herrmann, J. Chromatogr. A 1171 (2007) 112.
[208] E. Blanco, M.D. Casais, M.D. Mejuto, R. Cela, Electrophoresis 29 (2008) 3229.
[209] Y. He, H.K. Lee, Electrophoresis 18 (1997) 2036.
[210] W.W. Buchberger, J. Chromatogr. A 1218 (2010) 603.
[211] J. Tschmelak, G. Proll, G. Gauglitz, Talanta 65 (2005) 313.
[212] K. Badjagbo, S. Moore, S. Sauve, Trends Anal. Chem. 26 (2007) 931.
[213] S. Krol, B. Zabiegala, J. Namiesnik, Trends Anal. Chem. 29 (2010) 1092.
[214] M.R. Ras, F. Borrull, R.M. Marcé, Trends Anal. Chem 28 (2009) 347.
[215] P. Cuderman, E. Heath, Anal. Bioanal. Chem. 387 (2007) 1343.
[216] P. Canosa, I. Rodríguez, E. Rubí, M.H. Bollaín, R. Cela, J. Chromatogr. A 1124 (2006) 3.
[217] D.L. Poster, M.M. Schantz, L.C. Sander, S.A. Wise, Anal. Bioanal. Chem. 386 (2006) 859.
[218] J. Dalluge, J. Beens, U.A.T. Brinkman, J. Chromatogr. A 1000 (2003) 69.
[219] M. Adahchour, J. Beens, U.A.T. Brinkman, J. Chromatogr. A 1186 (2008) 67.
[220] A.C. Lewis, N. Carslaw, P.J. Marriott, R.M. Kinghorn, P. Morrison, A.L. Lee, K.D. Bartle, M.J. Pilling, Nature 405 (2000) 778.
[221] O. Amador-Muñoz, R. Villalobos-Pietrini, A. Aragón-Pina, T.C. Tran, P. Morrison, P.J. Marriott, J. Chromatogr. A 1201 (2008) 161.
[222] M.J. Gómez, S. Herrera, D. Solé, E. García-Calvo, A.R. Fernández-Alba, Anal. Chem. 83 (2011) 2638.
[223] M.C.R. Libardoni, Utilizing GCxGC for advanced analytical analysis of volatile and semi-volatile compounds, Coocon Resources, http://cocoonresources.com/ resources/GCxGC%20Overview%20II_ro.pdf (accessed 15.05.2011).
[224] M.Z. Özel, J.F. Hamilton, A.C. Lewis, Environ. Sci. Technol. 45 (2011) 1497.
[225] A. Llop, E. Pocurull, F. Borrull, J. Chromatogr. A 1217 (2010) 575.
[226] M.C. Pietrogrande, G. Basaglia, F. Dondi, J. Sep. Sci. 32 (2009) 1249.
[227] M.R. Ras, F. Borrull, R.M. Marcé, J. Sep. Sci. 32 (2009) 1051.
[228] C. Planas, O. Palacios, F. Ventura, J. Rivera, J. Caixach, Talanta 76 (2008) 906.

[229] V. Matamoros, E. Jover, J.M. Bayona, Anal. Chem. 82 (2010) 699.
[230] T. Ieda, N. Ochiai, T. Miyawaki, T. Ohura, Y. Horii, J. Chromatogr. A 1218 (2011) 3224.
[231] J. Halliday, A.C. Lewis, J.F. Hamilton, C. Rhodes, K.D. Bartle, P. Homewood, R.J.P. Grenfell, B. Goody, A. Harling, P. Brewer, G. Vargha, M.J.T. Milton, LC GC Eur. 23 (2010) 514.
[232] K. Ravindra, A.C. Dirtu, A. Covaci, Trends Anal. Chem. 27 (2008) 291.
[233] K. Ravindra, A.F.L. Godoi, L. Bencs, R. Van Grieken, J. Chromatogr. A 1114 (2006) 278.
[234] P.E. Joos, A.F.L. Godoi, R. De Jong, J. de Zeeuw, R. Van Grieken, J. Chromatogr. A 985 (2003) 191.
[235] D.K.W. Wang, C.C. Austin, Anal. Bioanal. Chem. 386 (2006) 1089.
[236] B. Jurado-Sánchez, E. Ballesteros, M. Gallego, J. Sep. Sci. 33 (2010) 610.
[237] C. García Pinto, S. Herrero Martín, J.L. Pérez Pavón, B. Moreno Cordero, Anal. Chim. Acta 689 (2011) 129.
[238] M. Pedrouzo, F. Borrull, R.M. Marcé, E. Pocurull, J. Chromatogr. A 1216 (2009) 6994.
[239] M. Pedrouzo, F. Borrull, R.M. Marcé, E. Pocurull, Trends Anal. Chem. 30 (2011) 749.
[240] M. Petrovic, M. Farré, M.L. de Alda, S. Pérez, C. Postigo, M. Kock, J. Radjenovic, M. Gros, D. Barceló, J. Chromatogr. A 1217 (2010) 4004.
[241] M. Pedrouzo, F. Borrull, E. Pocurull, R.M. Marcé, J. Sep. Sci. 34 (2011) 1091.
[242] X. Esparza, E. Moyano, F. Ventura, M.T. Galcerán, Rapid Commun. Mass Spectrom. 25 (2011) 379.
[243] A.L.N. van Nuijs, I. Tarcomnicu, W. Simons, L. Bervoets, R. Blust, P.G. Jorens, H. Neels, A. Covaci, Anal. Bioanal. Chem. 398 (2010) 2211.
[244] A.R.M. Silva, J.M.F. Nogueira, Talanta 74 (2008) 1498.
[245] R. Rodil, J.B. Quintana, P. López-Mahia, S. Muniategui-Lorenzo, D. Prada-Rodríguez, J. Chromatogr. A 1216 (2009) 2958.
[246] M. Petrovic, D. Barceló, Trends Anal. Chem. 26 (2007) 486.
[247] M. Petrovic, D. Barceló, J. Mass Spectrom. 41 (2006) 1259.
[248] M. Petrovic, M. Gros, D. Barceló, J. Mass Spectrom. 1124 (2006) 68.
[249] N. Negreira, I. Rodríguez, M. Ramil, E. Rubí, R. Cela, Anal. Chim. Acta 654 (2009) 162.
[250] L. Viglino, K. Aboulfadl, M. Prevost, S. Sauve, Talanta 76 (2008) 1088.
[251] C.J. Weschler, W.W. Nazaroff, Atmos. Environ. 42 (2008) 9018.
[252] T. Salthammer, E. Uhde, Organic Indoor Air Pollutants. Occurrence, Measurement, Evaluation, Willey-VCH Verlag, Weinheim, 2009.
[253] USEPA, Compendium Method TO-14a, EPA/625/R-96/010b, 1999
[254] USEPA, Compendium Method TO-15, 2nd ed. EPA/625/R-96/010b, 1999
[255] D.K.W. Wang, C.C. Austin, Anal. Bioanal. Chem. 386 (2006) 1099.
[256] EN-13725, Air quality. Determination of odour concentration by dynamic olfactometry, 2003
[257] A. Kumar, I. Viden, Environ. Monitor. Asses. 131 (2007) 301.

[258] USEPA, Technical Assistance Document For Sampling And Analysis Of Ozone Precursors, EPA/600-R-98/161, 1998.
[259] L. Zoccolillo, L. Amendola, S. Insogna, E. Pastorini, J. Chromatogr. A 1217 (2010) 3890.
[260] L.A. Doezema, C. Bigley, G. Canzi, K. Chang, A.J. Hirning, J. Lee, N. Von der Ahe, Atmos. Environ. 44 (2010) 900.
[261] R.S. Russo, Y. Zhou, K.B. Haase, O.W. Wingenter, E.K. Frinak, H. Mao, R.W. Talbot, B.C. Sive, Atmos. Chem. Phys. 10 (2010) 1865.
[262] M. Ajhar, B. Wens, K.H. Stollenwerk, G. Spalding, S. Yuce, T. Melin, Talanta 82 (2010) 92.
[263] E. Woolfenden, J. Chromatogr. A 1217 (2010) 2674.
[264] NIOSH, Method 2000, Issue 3, NIOSH Manual of Analytical Methods (NMAM), 4th ed., 2003.
[265] NIOSH, Method 2010, Issue 2, NIOSH Manual of Analytical Methods (NMAM), 4th ed., 2003.
[266] M. Harper, J. Chromatogr. A 885 (2000) 129.
[267] EN-14662-2. Air Quality. Standard method for measurement of benzene concentrations. Pumped sampling followed by solvent desorption and gas chromatography, 2005.
[268] E. Woolfenden, J. Chromatogr. A 1217 (2010) 2685.
[269] N. Sauret, H. Wortham, J.P. Putaud, P. Mirabel, Atmos. Environ. 42 (2008) 544.
[270] E. Wauters, P. Van Caeter, G. Desmet, F. David, C. Devos, P. Sandra, J. Chromatogr. A 1190 (2008) 286.
[271] M.R. Ras, R.M. Marcé, F. Borrull, Sci. Total Environ. 407 (2009) 4312.
[272] M.R. Ras, R.M. Marcé, F. Borrull, Environ. Monit. Assess. 161 (2010) 389.
[273] A. Ribes, G. Carrera, E. Gallego, X. Roca, M.J. Berenguer, X. Guardino, J. Chromatogr. A 1140 (2007) 44.
[274] C. Marchand, S. Le Calve, P. Mirabel, N. Glasser, A. Casset, N. Schneider, F. de Blay, Atmos. Environ. 42 (2008) 505.
[275] S. Yamashita, K. Kume, T. Horiike, N. Honma, M. Fusaya, T. Ohura, T. Amagai, J. Hazard. Mater. 178 (2010) 370.
[276] N. Watson, M. Bates, Evaluation of nanoparticles as a potential sorbent for thermal desorption. Markes International Internal Report, 2009 .
[277] G. Bunte, J. Hurttlen, H. Pontius, K. Hartlieb, H. Krause, Anal. Chim. Acta 591 (2007) 49.
[278] Q.L. Li, D.X. Yuan, Q.M. Lin, J. Chromatogr. A 1026 (2004) 283.
[279] L. Wang, J.M. Liu, P. Zhao, Z.W. Ning, H.L. Fan, J. Chromatogr. A 1217 (2010) 5741.
[280] USEPA, Compendium Method TO-17, EPA/625/R-96/010b, 1999.
[281] Z.Y. Xie, R. Ebinghaus, Anal. Chim. Acta 610 (2008) 156.
[282] S. Seethapathy, T. Gorecki, X.J. Li, J. Chromatogr. A 1184 (2008) 234.
[283] F.M. Jaward, N.J. Farrar, T. Harner, A.J. Sweetman, K.C. Jones, Environ. Toxicol. Chem. 23 (2004) 1355.
[284] F.M. Jaward, N.J. Farrar, T. Harner, A.J. Sweetman, K.C. Jones, Environ. Sci. Technol. 38 (2004) 34.

[285] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[286] M.R. Ras, R.M. Marce, F. Borrull, Talanta 77 (2008) 774.
[287] H.L. Lord, W.Q. Zhan, J. Pawliszyn, Anal. Chim. Acta 677 (2010) 3.
[288] Y. Gong, I.-Y. Eom, D.-W. Lou, D. Hein, J. Pawliszyn, Anal. Chem. 80 (2008) 7275.
[289] J. Van Durme, K. Demeestere, J. Dewulf, F. Ronsse, L. Braeckman, J. Pieters, H. Van Langenhove, J. Chromatogr. A 1175 (2007) 145.
[290] USEPA, Particulate Matter, http://www.epa.gov/pm/index.html (accessed 06.04.2011).
[291] S. Krol, B. Zabiegala, J. Namiesnik, Trends Anal. Chem. 29 (2010) 1101.
[292] EN-14662-1. Air Quality. Standard method for measurement of benzene concentrations. Pumped sampling followed by thermal desorption and gas chromatography, 2005.
[293] EN-14662-3. Ambient air quality. Standard method for measurement of benzene concentrations. Part 3: Automated pumped sampling with in situ gas chromatography, 2005.
[294] EN-14662-4. Ambient air quality. Standard method for measurement of benzene concentrations. Diffusive sampling followed by thermal desorption and gas chromatography, 2005.
[295] EN-14662-5. Ambient air quality. Standard method for measurement of benzene concentrations. Diffusive sampling followed by solvent desorption and gas chromatography, 2005.
[296] EN-15549. Air quality. Standard method for the measurement of the concentration of benzo[a]pyrene in ambient air, 2008.
[297] EN-15483. Ambient air quality. Atmospheric measurements near groundwith FTIR spectroscopy, 2008.
[298] USEPA. Method TO-1. Method for the determination of volatile organic compoundsin ambient air using tenax adsorption and Gas chromatography/mass spectrometry (GC/MS), 1984.
[299] USEPA. Method TO-2. Method for the determination of volatile organic compounds in ambient air by carbon molecular sieve adsorption and gas chromatography/mass spectrometry (GC/MS), 1984.
[300] USEPA Method TO-3. Method for the determination of volatile organic compounds in ambient air using cryogenic preconcentration techniques and gas chromatography with flame ionization and electron capture detection, 1984.
[301] USEPA Method TO-5. Method for the determination of aldehydes and ketones in ambient air using high performance liquid chromatography (HPLC), 1984.
[302] USEPA Method TO-8. Method for the determination of phenol and methylphenols (cresols) in ambient air using high performance liquid chromatography, 1986.
[303] USEPA Compendium method TO-11A. EPA/625/R-96/010b, 1999.
[304] USEPA Method TO-12. Method for the determination of non-methane organic compounds (NMOC) in ambient air using cryogenic preconcentration and direct flameionization detection (PDFID), 1984.
[305] USEPA Compendium method TO-13A. EPA/625/R-96/010b, 1999.

[306] USEPA Compendium method TO-6. EPA/625/R-96/010b, 1999.
[307] E. Matisova, S. Skrabakova, J. Chromatogr. A 707 (1995) 145.
[308] T. Elbir, B. Cetin, E. Cetin, A. Bayram, M. Odabasi, Environ. Monit. Assess. 133 (2007) 149.
[309] F.C. Calvosa, A.F. Lagalante, Talanta 80 (2010) 1116.
[310] M. Shimmo, J. Jantti, P. Aalto, K. Hartonen, T. Hyotylainen, M. Kulmala, M.L. Riekkola, Anal. Bioanal. Chem. 378 (2004) 1982.
[311] S. de Koning, H.G. Janssen, U.A.T. Brinkman, Chromatographia 69 (2009) S33.
[312] V. Yusa, C. Coscolla, W. Mellouki, A. Pastor, M. de la Guardia, J. Chromatogr. A 1216 (2009) 2972.
[313] S.S. Albaseer, R.N. Rao, Y.V. Swamy, K. Mukkanti, J. Chromatogr. A 1217 (2010) 5537.
[314] M. García, I. Rodríguez, R. Cela, J. Chromatogr. A 1152 (2007) 280.
[315] D. Castro, K. Slezakova, C. Delerue-Matos, M.C. Alvim-Ferraz, S. Morais, M.C. Pereira, Atmos. Environ. 45 (2011) 1799.
[316] F.A. Esteve-Turrillas, A. Pastor, M. de la Guardia, Anal. Chim. Acta 560 (2006) 118.
[317] B.E. Richter, B.A. Jones, J.L. Ezzell, N.L. Porter, N. Avdalovic, C. Pohl, Anal. Chem. 68 (1996) 1033.
[318] P. Haglund, E. Spinnel, LC GC Eur. 23 (2010) 292.
[319] A. Nieto, F. Borrull, E. Pocurull, R.M. Marcé, Trends Anal. Chem. 29 (2010) 752.
[320] M.M. Schantz, Anal. Bioanal. Chem. 386 (2006) 1043.
[321] C.W. Huie, Anal. Bioanal. Chem. 373 (2002) 23.
[322] A. Albinet, E. Leoz-Garziandia, H. Budzinski, E. Villenave, J. Chromatogr. A 1121 (2006) 106.
[323] I. Carpinteiro, B. Abuín, I. Rodríguez, M. Ramil, R. Cela, J. Chromatogr. A 1217 (2010) 3729.
[324] M.P. Martínez, J.D. Carrillo, M.T. Tena, Anal. Bioanal. Chem. 397 (2010) 257.
[325] C.C. Teo, S.N. Tan, J.W.H. Yong, C.S. Hew, E.S. Ong, J. Chromatogr. A 1217 (2010) 2484.
[326] A. Llop, F. Borrull, E. Pocurull, Anal. Chim. Acta 665 (2010) 231.
[327] V. Fernández-González, E. Concha-Grana, S. Muniategui-Lorenzo, P. López-Mahia, D. Prada-Rodríguez, J. Chromatogr. A 1196 (2008) 65.
[328] M. García-López, I. Rodríguez, R. Cela, J. Chromatogr. A 1216 (2009) 6986.
[329] K. Demeestere, J. Dewulf, B. De Witte, H. Van Langenhove, J. Chromatogr. A 1153 (2007) 130.
[330] M.A. Parra, L. González, D. Elustondo, J. Garrigo, R. Bermejo, J.M. Santamaría, Sci. Total Environ. 370 (2006) 157.
[331] M.Z. Özel, M.W. Ward, J.F. Hamilton, A.C. Lewis, T. Raventos-Duran, R.M. Harrison, Aerosol Sci. Technol. 44 (2010) 109.
[332] Markes, Themal Desoption Technical Support Note 53, 2008.
[333] J. Gil-Moltó, M. Varea, N. Galindo, J. Crespo, J. Chromatogr. A 1216 (2009) 1285.
[334] B.L. van Drooge, I. Nikolova, P.P. Ballesta, J. Chromatogr. A 1216 (2009) 4030.
[335] C. Nerín, J. Salafranca, M. Aznar, R. Batlle, Anal. Bioanal. Chem. 393 (2009) 809.
[336] Z.J. Hu, Y.L. Shi, S.X. Zhang, H.Y. Niu, Y.Q. Cai, Bull. Environ. Contam. Toxicol. 86 (2011) 302.

[337] W.D. Wombacher, K.C. Hornbuckle, J. Environ. Eng.-Asce 135 (2009) 1192.
[338] N. Fontanals, P.A.G. Cormack, R.M. Marcé, F. Borrull, Trends Anal. Chem. 29 (2010) 765.
[339] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, Talanta 74 (2008) 1299.
[340] E. Caro, R.M. Marcé, F. Borrull, P.A.G. Cormack, D.C. Sherrington, Trends Anal. Chem. 25 (2006) 143.
[341] A. Beltran, F. Borrull, P.A.G. Cormack, R.M. Marcé, Trends Anal. Chem. 29 (2010) 1363.
[342] E. Turiel, A. Martín-Esteban, Anal. Chim. Acta 668 (2010) 87.
[343] A. Beltran, R.M. Marcé, P.A.G. Cormack, F. Borrull, Anal. Chim. Acta 677 (2010) 72.
[344] S. Wang, P. Zhao, G. Min, G. Fang, J. Chromatogr. A 1165 (2007) 166.
[345] M. Moeder, S. Schrader, U. Winkler, R. Rodil, J. Chromatogr. A 1217 (2010) 2925.
[346] A. Prieto, S. Schrader, M. Moeder, J. Chromatogr. A 1217 (2010) 6002.
[347] R. López-Serna, S. Pérez, A. Ginebreda, M. Petrovic, D. Barceló, Talanta 83 (2010) 410.
[348] N. Fontanals, P.A.G. Cormack, D.C. Sherrington, R.M. Marcé, F. Borrull, J. Chromatogr. A 1217 (2010) 2855.
[349] G. Basaglia, L. Pasti, M.C. Pietrogrande, Anal. Bioanal. Chem. 399 (2011) 2257.
[350] M. Polo, C. García-Jares, M. Llompart, R. Cela, Anal. Bioanal. Chem. 388 (2007) 1789.
[351] J. Regueiro, E. Becerril, C. García-Jares, M. Llompart, J. Chromatogr. A 1216 (2009) 4693.
[352] A. Kumar, Gaurav, A.K. Malik, D.K. Tewary, B. Singh, Anal. Chim. Acta 610 (2008) 1.
[353] K. Farhadi, M. Mamaghanian, R. Maleki, J. Hazard. Mater. 152 (2008) 677.
[354] J.C. Wu, H.L. Lord, J. Pawliszyn, H. Kataoka, J. Microcolumn Sep. 12 (2000) 255.
[355] J.A. He, R.H. Lv, H.J. Zhan, H.Z. Wang, J. Cheng, K. Lu, F.C. Wang, Anal. Chim. Acta 674 (2010) 53.
[356] H. Bagheri, E. Babanezhad, F. Khalilian, Anal. Chim. Acta 634 (2009) 209.
[357] W.A.W. Ibrahim, H. Farhani, M.M. Sanagi, H.Y. Aboul-Enein, J. Chromatogr. A 1217 (2010) 4890.
[358] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcolumn Sep. 11 (1999) 737.
[359] F.M. Lancas, M.E.C. Queiroz, P. Grossi, I.R.B. Olivares, J. Sep. Sci. 32 (2009) 813.
[360] F. David, P. Sandra, J. Chromatogr. A 1152 (2007) 54.
[361] A. Prieto, O. Basauri, R. Rodil, A. Usobiaga, L.A. Fernández, N. Etxebarria, O. Zuloaga, J. Chromatogr. A 1217 (2010) 2642.
[362] S. Lacorte, J. Quintana, R. Tauler, F. Ventura, A. Tovar-Sánchez, C.M. Duarte, J. Chromatogr. A 1216 (2009) 8581.
[363] E. Fries, Anal. Chim. Acta 689 (2011) 65.
[364] M. Pedrouzo, F. Borrull, R.M. Marcé, E. Pocurull, Anal. Bioanal. Chem. 397 (2010) 2833.
[365] D. Benanou, F. Acobas, M.R. de Roubin, F.D.P. Sandra, Anal. Bioanal. Chem. 376 (2003) 69.
[366] N. Ochiai, K. Sasamoto, H. Kanda, S. Nakamura, J. Chromatogr. A 1130 (2006) 83.

[367] E. Van Hoeck, F. Canale, C. Cordero, S. Compernolle, C. Bicchi, P. Sandra, Anal. Bioanal. Chem. 393 (2009) 907.
[368] N. Ochiai, K. Sasamoto, H. Kanda, E. Pfannkoch, J. Chromatogr. A 1200 (2008) 72.
[369] N. Itoh, H. Tao, T. Ibusuki, Anal. Chim. Acta 535 (2005) 243.
[370] M. Kawaguchi, R. Ito, H. Honda, N. Endo, N. Okanouchi, K. Saito, Y. Seto, H. Nakazawa, J. Chromatogr. A 1200 (2008) 260.
[371] W.M. Liu, Y. Hu, J.H. Zhao, Y. Xu, Y.F. Guan, J. Chromatogr. A 1095 (2005) 1.
[372] D. Bratkowska, F. Borrull, N. Fontanals, R.M. Marcé, Anal. Chim. Acta (2011).
[373] L.P. Melo, A.M. Nogueira, F.M. Lanças, M.E.C. Queiroz, Anal. Chim. Acta 633 (2009) 57.
[374] X. Zhu, J. Cai, J. Yang, Q. Su, Y. Gao, J. Chromatogr. A 1131 (2006) 37.
[375] A.R.M. Silva, F.C.M. Portugal, J.M.F. Nogueira, J. Chromatogr. A 1209 (2008) 10.
[376] C. Bicchi, C. Cordero, E. Liberto, B. Sgorbini, F. David, P. Sandra, P. Rubiolo, J. Chromatogr. A 1164 (2007) 33.
[377] E. Aguilera-Herrador, R. Lucena, S. Cardenas, M. Valcarcel, J. Chromatogr. A 1201 (2008) 106.
[378] M. Saraji, S. Mirmahdieh, J. Sep. Sci. 32 (2009) 988.
[379] A. Mohammadi, N. Alizadeh, J. Chromatogr. A 1107 (2006) 19.
[380] F. Ahmadi, Y. Assadi, S. Hosseini, M. Rezaee, J. Chromatogr. A 1101 (2006) 307.
[381] Y. Liu, Y. Hashi, J.M. Lin, Anal. Chim. Acta 585 (2007) 294.
[382] A.N. Panagiotou, V.A. Sakkas, T.A. Albanis, Anal. Chim. Acta 649 (2009) 135.
[383] E. Villaverde-de-Saa, I. González-Marino, J.B. Quintana, R. Rodil, I. Rodríguez, R. Cela, Anal. Bioanal. Chem. 397 (2010) 2559.

2. OBJECTIVES

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

The main objective of the research presented in this Doctoral Thesis is the development of analytical methods to determine organic contaminants in different environmental atmospheres (including the gas phase, the particle phase and settled dust) and waters. The organic contaminants determined were volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and some groups of personal care products (synthetic musks fragrances, parabens and insect repellents), and nicotine and N-nitrosamines. The analytical methods developed in this Thesis have also the aim of minimising the consumption of organic solvents in the whole analytical process. All the methods discussed are based on single and comprehensive gas chromatography coupled with two different analysers: a quadrupole detector and a nitrogen chimiluminiscence (NCD) detector.

A second objective of this Doctoral Thesis is to provide new information regarding the presence of these organic contaminants in environmental atmospheres and waters in the region of Tarragona, through the analysis of outdoor and indoor air, outdoor particulate matter, house dust and various types of waste water and surface water samples.

A third objective of the Thesis is to evaluate the air quality of the region through the risk assessment of atmospheric VOCs and PAHs, which are contaminants regulated by World Health Organization (WHO) air quality guidelines.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3. EXPERIMENTAL, RESULTS AND DISCUSSION

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

As discussed in the Thesis introduction, the main pathway of anthropogenic organic contaminants into the global environment is through emissions into environmental atmospheres and waters. Therefore, the determination of air and water quality is of increasing concern because of the recognised adverse effects of some organic contaminants on human health and the environment. To this end, the development of highly sensitive and selective methods for the determination of different organic contaminants in environmental atmospheres and waters is of major importance within the scientific community. For this reason, one of the main objectives of this Thesis was to develop analytical methods to determine organic contaminants of a wide range of volatilities and polarities – VOCs, PAHs and EOCs, such as PCPs and N-nitrosamines, and nicotine and tobacco-specific N-nitrosamines – in air, airborne particulate matter, settled dust and water samples. The analytical methods proposed minimised the use of organic solvents in the entire analytical process. Furthermore, the ubiquitous presence of some of these organic contaminants leads to the inherent exposure of humans to them. Indeed, inhalation is one of the main exposure pathways of volatile and semi-volatile contaminants such as VOCs and PAHs, and their risk has also been evaluated in this Thesis.

This chapter includes the experimental part, results and discussion from different studies that have been obtained through this Doctoral Thesis. These results have already been published, or are in the process of being published, in several international scientific journals, and are presented in each section here in journal paper format. These studies have been classified in five sections. For each section, a brief introduction is included to establish the context of the research, and the most notable results are also discussed. The list of papers published as a result of this Thesis research is included in Appendix II.

The first section focuses on the presence of VOCs in industrial atmospheres and the evaluation of two standard methods for their determination. Both methods were based on active enrichment into solid sorbents, and followed by thermal desorption (TD) or by liquid desorption (LD). GC-MS determination was used in both cases. These methods were applied for determining VOC emissions from an industrial waste water treatment plant (WWTP) and from the surroundings of a petrochemical site.

In the second section, quantitative risk assessment (QRA) has been applied for the evaluation of the risk related to the inhalation of VOCs and PAHs by people living around the most important chemical site in the Mediterranean area. For the PAH risk estimations, samples were taken from the gas phase and the particulate phase using a high-volume sampler. Both kinds of samples were analysed by pressurised liquid extraction (PLE), followed by GC-MS. For the VOC risk estimates, a monitoring campaign

was performed using active enrichment into charcoal tubes, followed by liquid desorption and GC-MS analysis.

Although thermal desorption has been widely-applied for the determination of volatile air contaminants, information on the application of this methodology for determining semi-volatile compounds is still scarce. Therefore, in the third section, the development of a method for the determination of some semi-volatile PCPs on air based on TD-GC-MS is presented. This method was then applied for determining the different groups of PCPs (synthetic musks, parabens and insect repellents) in several indoor and outdoor environments.

The successful application of TD for determining semi-volatile PCPs in atmospheric samples encouraged us to develop a stir bar sorptive extraction (SBSE) process, followed by TD, for determining synthetic musks and parabens in water samples. Synthetic musks and parabens were widely determined in environmental waters but, at the beginning of our research, SBSE followed by TD had not previously been applied for their determination. Therefore, in the fourth section, two SBSE methods, followed by TD-GC-MS determination, were developed for determining musks and parabens in water samples. The methods developed were applied to determine the presence of these compounds in urban and industrial WWTP influent and effluent samples, reverse osmosis plant effluents, and river waters. It is worth mentioning that the TD equipment used in both studies was a Markes Unity^{TM} equipment normally used for the desorption of sorbent tubes, instead of the Gerstel TDU^{TM} equipment which is designed for stir bar desorption.

The last section focuses on the development of analytical methods for determining different emerging organic contaminants (EOCs) in indoor settled dust. In these methods, different types of EOCs were considered including parabens, nicotine, volatile N-nitrosamines and tobacco-specific nitrosamines. Both methods were based on PLE and used different strategies to enhance selectivity, including pressurised hot water extraction (PHWE) followed by SBSE-TD-GC-MS and in-cell clean-up PLE followed by two dimensional gas chromatography (GC×GC) and a nitrogen chimiluminiscence detector (NCD) to further enhance selectivity and sensitivity. The last study of this section was carried out in collaboration with Professor Alastair C. Lewis of the Analytical, Environmental and Atmospheric research group of the Department of Chemistry of The University of York (UK) during my stay in this university.

It is worth highlighting that most of the determinations of organic contaminants of this Doctoral Thesis were performed in different environmental matrices in the Tarragona area (outdoor and indoor air, waste waters and surface waters and in indoor dust

samples). Furthermore, the largest chemical and petrochemical site in southern Europe and the Mediterranean area is located in this zone. Because of this, this Thesis also wants to contribute to the characterization of the atmospheric pollution of this area, through the evaluation of the occurrence of atmospheric contaminants and the estimation of their health risks in the surroundings of the chemical site.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.1. Volatile organic compounds in environmental atmospheres

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

Because of their ubiquitous presence in the atmosphere and their adverse environmental and health effects, VOCs are one of the most studied groups of atmospheric contaminants. As reported in the introduction, the concentrations of these contaminants range from μg L^{-1} to ng L^{-1} and therefore, highly sensitive analytical methods are necessary for their determination. Furthermore, since VOCs comprise of hundreds of organic compounds with a wide range of physical and chemical characteristics, versatile methods are needed for their simultaneous determination. Currently, one of the most widely-used methods for sampling and extraction of VOCs from air is their enrichment into solid sorbents, which can be followed by liquid desorption (LD) or thermal desorption (TD). Enrichment into solid sorbents provides the sampling and preconcentration of the analytes in one single step, and the use of sorbent tubes allows the portability of the samples in a reduced volume. Furthermore, when followed by TD, it provides enhanced sensitivity and avoids the use of organic solvents [1,2].

Hence, this section focuses on the study of analytical methods based on enrichment into solid sorbents for determining VOCs in different industrial atmospheres. The selection of the target VOCs of both studies was based on their occurrence and their environmental and health effects. In this respect, some of the target VOCs were: ones included in the USEPA list of Hazardous Air Contaminants [3]; ozone precursors recommended for measurement by the Directive 2008/50/EC [4]; ones included in the list of priority contaminants for water policies determined in the European Directive 2455/2001/EC [5]; and some others considered as hazardous organic contaminants by the WHO Air Quality Guidelines [6]. Among the target VOCs that should be highlighted are those classified as carcinogens, such as benzene or chloroform.

Following the atmospheric research line started by our group, the first research paper focuses on the determination of organic contaminants by active enrichment into multi-sorbent tubes, followed by TD-GC-MS. The method presented is based on a previous one developed by our research group that was applied to determine up to 66 different VOCs in urban and industrial air [7-9]. In the current study, this method was adapted and validated for the simultaneous monitoring of 99 VOCs. Some screening samples were previously taken in order to select more specific industrial contaminants which were then added to the final list of target VOCs of this study. The developed method was applied to determine VOC emissions of an industrial WWTP. Since industrial discharges are a source of VOCs in WWTPs, the contribution of these plants as a source of atmospheric VOCs should be investigated. However, up to now, few studies have focused on the composition of industrial WWTP emissions [10,11]. The industrial WWTP selected in this study collects waste waters from four chemical factories which produce

a wide variety of products including isocyanates, polyurethanes, chlorinated organics, polymerisates, functional chemicals, surfactants and adhesives, among others.

Although there are many advantages of TD, as mentioned above, this extraction method is not compatible for determining thermolabile analytes or those with high boiling points. Furthermore, some sorbents, such as activated charcoal, cannot be thermally desorbed. Therefore, some standard methods recommend the use of LD for the extraction of the analytes after their sampling [12]. Moreover, LD is simple and does not require specific instrumentation. One of the most common combinations is the use of activated charcoal followed by desorption with carbon disulfide. This is because the high adsorption ability of the charcoal can trap a wide range of compounds [13,14] and the extraction of non-polar analytes provided by this solvent is very effective. In order to assess how these different analytical methods can affect the accuracy and precision of VOC estimates, the overall performances of LD and TD methods were compared in the second paper presented in this section. The solvent desorption method was based on the European standard method EN 14662-2 [12] which uses activated charcoal as an enrichment sorbent and carbon disulfide as an extraction solvent. The TD method that was optimised in the first paper is based on the standard European method EN 14662-1 [15] and the USEPA method TO-17 [16]. Analytically, the main method parameters for both methods were compared for the determination of 90 different VOCs. Initially, the 99 VOCs studied in the WWTP emissions study were also selected for this study. However, some polar VOCs such as phenol or aniline were discarded because of the low recoveries of these compounds obtained by the LD method.

Furthermore, the performance in atmospheric samples was compared by sampling air over 8 days using both analytical methods in a location next to the petrochemical complex in the Tarragona area. To our knowledge, only one previous paper compared the analytical parameters of both methods but it did so for only 8 target VOCs [17]. Therefore, the comparative study presented here represents the first time that these two different analytical methods have been compared with regards to such a wide range of VOCs and their performance in real samples. For the LD method, samples of 24 h were taken, at a flow rate of 500 mL min^{-1}, thus sampling 720 L of air. For the TD method, 2 h samples were collected at a sampling rate of 22 mL min^{-1}, collecting 2.64 L of air. Taking into account the differences of both methods, differences in their performance are expected.

A paper with the results obtained in the first study has been accepted for publication in the *International Journal of Environmental Analytical Chemistry*. The second study has been published in *Talanta* 82 (2010) 719-727 and has been carried out in collaboration with the Observatory of Health and Environment of Tarragona.

References

[1] M.R. Ras, F. Borrull, R.M. Marcé, Trends Anal. Chem. 28 (2009) 347.
[2] E. Woolfenden, J. Chromatogr. A 1217 (2010) 2674.
[3] USEPA, Amendments to 1990 Clean Air Act-List of 189 Hazardous Air Pollutants, 1994.
[4] Directive 2008/50/EC Off. J. Eur. Commun. L152 (2008) 1.
[5] Decision 2455/2001/EC Off. J. Eur. Commun. L331 (2001) 1.
[6] WHO, Air Quality Guidelines for Europe, WHO Regional Office for Europe, 2000.
[7] M.R. Ras-Mallorquí, R.M. Marcé-Recasens, F. Borrull-Ballarín, Talanta 72 (2007) 941.
[8] M.R. Ras, R.M. Marcé, F. Borrull, Sci. Total Environ. 407 (2009) 4312.
[9] M.R. Ras, R.M. Marcé, F. Borrull, Environ. Monit. Assess. 161 (2010) 389.
[10] B.Z. Wu, T.Z. Feng, U. Sree, K.H. Chiu, H.G. Lo, Anal. Chim. Acta 576 (2006) 100.
[11] X.J. Chen, U. Pauly, S. Rehfus, K. Bester, Chemosphere 76 (2009) 1094.
[12] EN-14662-2. Air Quality. Standard method for measurement of benzene concentrations. Pumped sampling followed by solvent desorption and gas chromatography, 2005.
[13] E. Matisova, S. Skrabakova, J. Chromatogr. A 707 (1995) 145.
[14] D.K.W. Wang, C.C. Austin, Anal. Bioanal. Chem. 386 (2006) 1089.
[15] EN-14662-1. Air Quality. Standard method for measurement of benzene concentrations. Pumped sampling followed by thermal desorption and gas chromatography, 2005.
[16] USEPA, Compendium Method TO-17, EPA/625/R-96/010b, 1999.
[17] M. Czaplicka, K. Klejnowski, J. Chromatogr. A 976 (2002) 369.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.1.1. Determination of volatile organic compounds in industrial waste water plant air emissions by multi-sorbent adsorption and thermal desorption-gas chromatography-mass spectrometry

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN INDUSTRIAL WASTEWATER PLANT AIR EMISSIONS BY MULTI-SORBENT ADSORPTION AND THERMAL DESORPTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Noelia Ramírez, Rosa Maria Marcé, Francesc Borrull
Department of Analytical Chemistry and Organic Chemistry
Universitat Rovira i Virgili, Marcel·lí Domingo s/n
Sescelades Campus, Tarragona 43007, Spain

Abstract

This paper describes the process of determining the presence of volatile organic compounds in air emissions from industrial wastewater treatment plants (WWTP). The analytical method, based on thermal desorption - gas chromatography - mass spectrometry, was developed to simultaneously determine of 99 volatile organic compounds (VOCs) in air samples. This method is rapid, environmentally-friendly (since no organic solvents are used to extract the analytes) and compatible with a large range of thermally stable polar and apolar compounds. The target VOCs were selected on the basis of their occurrence in real samples and their adverse effects on the environment and human health. To cover the wide range of target compounds, multisorbent tubes filled with Tenax TA and Carbograph 1TD were used. Method validation showed good repeatabilities, low detection limits, a high linear range and good recoveries. At a fixed sample volume of 600 mL no significant losses for any of the target compounds were found in the samples. Stability during storage indicated that samples must be keep refrigerated at 4 °C and analysed within three days of collection. Real samples were taken from air emissions of an industrial wastewater treatment plant located in the Southern Industrial Area of Tarragona (Spain) with the aim of studying its contribution as a source of atmospheric VOCs. This WWTP collects wastewater from several chemical factories which produce isocyanates, polyurethanes, chlorinated organics and functional chemicals among other products. Samples from the collecting tank after the primary sedimentation showed higher VOC concentrations than samples from the secondary treatment tank. The most abundant VOCs found in these emissions are included in the USEPA List of Hazardous Air Pollutants. The highest values correspond to acrylonitrile (up to 1843 μg m^{-3}) and styrene (up to 573.70 μg m^{-3}). The levels of chloroform, 1,4-dioxane, ethylbenzene, 1,2,3-trimethylbenzene and 1,4-diethylbenzene were also high.

Keywords: Thermal desorption; Industrial wastewater treatment plant emissions; Quality air monitoring; Volatile organic compounds.

Int. J. Environ. Anal. Chem (DOI: 10.1080/03067310903584073)

1. INTRODUCTION

The identification and measurement of volatile organic compounds (VOCs) in air is of considerable interest due to their direct or indirect impact on the global environment and human health. Several environmental effects of VOCs have been recognised, including their contribution to stratospheric ozone depletion; tropospheric photochemical ozone formation (which is the main cause of photochemical smog); enhancement of the global greenhouse effect; odour nuisance; and the accumulation and persistence in the environment of recalcitrant pollutants [1-3].

Furthermore, many VOCs have adverse effects on human health even at parts per billion (ppb) levels. These adverse effects include irritation of mucous membranes, neurotoxic effects (psychological stress and sensory irritation to behavioural function), epidemiology of respiratory disorders, negative impacts on reproductive systems and birth defects [4,5]. Ambient VOCs also have genotoxic effects. According to a study of the US Environmental Protection Agency (USEPA), ambient VOCs are responsible for between 35% and 55% of the outdoor air cancer risk in the US [6,7]. Hence, VOCs are considered an essential parameter for assessing the air quality in indoor and outdoor environments. It is, therefore, important to monitor these compounds in urban, industrial and rural ambient air and to determine their sources.

VOCs are released into the atmosphere as a result of natural and human activities. These activities include vehicle exhaust fumes, industrial activity, solvent usage, landfill waste and agriculture. Industrial applications of VOCs are very diverse, as they are used in the metal finishing industry, the synthetic organic chemical manufacturing industry, the petrochemical industry and the plastics industry. Industrial discharges are a source of VOCs in wastewater plants. It should be pointed out that whereas many VOCs are controlled by air quality legislation, only a few VOCs are listed in water quality legislation. For example, VOCs only account for a small number of the contaminants listed in the 'European Union list of priority pollutants for water policies' [8], whereas they account for most of the Hazardous Air Pollutants (HAPs) included in the US EPA Clean Air Act [9]. Therefore, a major concern regarding toxic VOCs in wastewater is the potential air emissions from wastewater treatment plants (WWTPs). Although several papers have focused on the monitoring of VOC emissions in industrial facilities [10-15], the emissions of VOCs from wastewaters in industrial-sewage treatment plants are often overlooked as sources of hazardous substances. Previous papers have shown the influence of urban WWTP emissions on air quality [16-21]. However, there are

only a few studies on the composition of industrial WWTP emissions [22,23] and their relative importance as a potential source of specific hazardous air pollutants must be further investigated.

Due to the complexity of VOC composition and the low levels to be detected (from ppb down to ppt), several sampling and analytical strategies have been developed and applied to identifying and quantifying of VOC emissions [1,24-29]. Most of the methods that have been developed for determining VOC emissions from urban and industrial WWTPs are either canister-based [11,22] or sorbent-based [16,18,19,21,23]. New trends in VOC determination focus on the development of versatile, portable, low-cost and environmentally-friendly techniques without compromising the limit of detection. In this respect, preconcentration on solid sorbents followed by thermal desorption (TD) has been shown to be a highly advantageous technique [30-32]. Thermal desorption provides enhanced sensitivity, is compatible with thermally stable polar and apolar compounds, allows reuse of adsorbent tubes and minimizes solvent usage with the consequent benefits for laboratory safety and waste disposal. In addition, the use of multiple-bed sorbent cartridges provides high breakthrough volumes and the quantitative retention and desorption of VOCs over a wide volatility range [14,28,33-35]. It should be noted, however, that if multisorbent adsorption tubes are used, the sample volume and the storage stability of each target compound must be evaluated [24].

This paper describes the development of a multisorbent adsorption and thermal desorption - gas chromatography - mass spectrometry (TD-GC-MS) method for simultaneously monitoring 99 VOCs in air samples. This method was used to analyse the emissions of an industrial WWTP with the aim of studying its contribution as a source of atmospheric VOCs. The compounds studied include some hazardous VOCs like ozone precursors (alkanes, alkenes, aromatics and their halogenated derivatives) and some specifically industrial compounds such as acrylates, among others.

2. EXPERIMENTAL

2.1. Chemical standards

The list of the VOCs determined is shown in Table 1. A total of 99 target compounds were selected on the basis of their occurrence in industrial wastewater emissions and their adverse effects on the environment and human health. Thirty-four of the ninety-nine compounds determined are included in the list of Hazardous Air Pollutants (HAPs) of the US EPA Clean Air Act [9], eighteen of them are ozone precursors recommended for measurement by the Directive 2002/3/EC

Table 1. Target compounds, in chromatographic elution order, their retention times (t_R), quantifier and qualifier ions, repetitivity (expressed as relative standard deviation (%RSD) for the analysis of 100 ng of VOCs standard (n=5) and calculated without and with an internal standard), method detection (MDL) and quantification limit (MQL) (expressed in μg m^{-3} and calculated for a sampling volume of 600 mL) and the instrumental recoveries (%Rec.).

No.	Target VOCs	t_R (min)	Quantifier ion	Qualifier ions[1]			Repetitivity (%RSD, n=5)		MDL (μg m^{-3})	MQL (μg m^{-3})	%Rec. (n=3)
							No I.S.	I.S.			
1	i-Pentane[b]	3.87	43	57 (71)	72 (7)		2.49	1.48	0.17	0.83	85.0
2	1-Pentene[b]	4.08	42	55 (78)	70 (49)	39 (46)	2.45	1.26	0.83	1.67	100.0
3	n-Pentane[b]	4.20	43	57 (16)	72 (10)		2.42	1.06	0.08	0.17	100.0
4	Diethyl ether	4.30	59	74 (84)	45 (62)	41(12)	2.67	0.55	0.17	0.83	100.0
5	2-Trans-pentene[b]	4.35	55	70 (43)	42 (40)	41 (30)	1.75	0.55	0.17	0.83	100.0
6	Isoprene[b]	4.38	67	68 (66)	53 (72)	40 (26)	3.38	0.35	1.23	1.67	94.9
7	2-Cis-pentene[b]	4.49	55	70 (44)	42 (33)	41 (24)	2.87	1.57	0.17	0.83	96.1
8	1,1-Dichloroethylene	4.59	61	96 (63)	98 (41)		1.14	0.69	0.13	0.17	95.7
9	Acrylonitrile[a,d]	4.63	53	52 (82)	50 (81)	38 (7)	0.99	0.99	0.01	0.08	100.0
10	3-Chloropropene[a]	4.89	39	76 (50)	78 (19)		2.24	2.24	0.17	0.83	97.0
11	Dichloromethane[a,c,d]	4.88	49	84 (83)	86 (53)	51 (31)	4.9	1.87	1.00	1.67	100.0
12	Carbon disulfide[a,d]	5.05	76	44 (12)	78 (9)		3.2	4.75	0.07	0.83	86.7
13	1-Hexene	5.37	43	56 (65)	69 (23)	84 (16)	2.13	0.08	0.17	0.83	95.2
14	Trans-1,2-dichloroethene	5.63	61	96 (71)	98 (46)		3.27	0.29	0.08	0.17	97.9
15	Methyl-tercbutylethera	5.69	73	57 (21)	43 (21)	41 (20)	0.86	0.12	0.17	0.83	85.9
16	Propionitrile	5.88	54	55 (15)	38 (4)		1.21	0.80	0.17	0.83	100.0
17	1,1-Dichloroethane	6.00	63	65 (32)	83 (13)		2.38	0.19	0.08	0.17	100.0
18	n-Hexane[a,b]	6.54	57	86 (16)	71 (6)	43 (70)	2.10	0.02	0.12	0.17	96.6
19	Methacrylonitrile	6.55	41	67 (70)	52 (26)	66 (24)	1.45	0.80	0.02	0.17	100.0
20	Cis-1,2-dichloroethylene	6.92	61	96 (80)	63 (31)		2.32	1.46	0.08	0.17	99.9
21	Methylacrilate	7.10	55	85 (19)	42 (10)		0.98	0.17	0.02	0.17	99.8
22	2,2-Dichloropropane	7.14	77	79 (31)	97 (20)		3.48	2.22	0.08	0.17	84.1
23	Bromochloromethane	7.26	130	128 (76)	93 (32)		1.46	0.89	0.13	0.17	99.6

Int. J. Environ. Anal. Chem. (DOI: 10.1080/03067310903584073)

Table 1 (cont.)

24	Chloroform[a,c]	7.33	83	85 (64)			1.85	1.06	0.08	0.17	99.8
25	Tetrahydrofuran	7.60	42	71 (46)	72 (47)	41 (58)	0.67	0.07	0.50	0.83	99.9
26	1,1,1-Trichloroethane[a]	8.29	97	99 (62)	61 (40)	119 (13)	2.75	1.37	0.08	0.83	97.5
27	1-Chlorobutane	8.40	56	41 (59)	63 (5)	49 (4)	2.24	0.96	0.05	0.83	99.5
28	1,2-Dichloroethane[c,d]	8.42	62	64 (31)	49 (21)	63 (14)	2.36	1.54	0.02	0.17	99.4
29	1,1-Dichloropropene	8.66	75	110 (37)	39 (53)	77 (30)	2.67	0.77	0.08	0.17	99.5
30	Benzene[a,b,c,d]	8.92	78	77 (23)	51 (15)	52 (15)	1.47	0.03	0.72	1.67	100.0
31	Carbon tetrachloride[a]	8.97	117	119 (93)	121 (31)	82 (21)	3.75	2.89	0.08	0.83	95.0
32	Chloroacetonitrile	9.41	75	40 (23)	48 (47)	77 (32)	3.68	2.47	0.17	0.83	99.7
33	i-Octane[b]	9.83	57	56 (34)	41 (26)	99 (5)	3.01	2.57	0.08	0.17	97.7
34	n-Heptane[b]	10.28	71	57 (54)	100 (18)		2.96	2.10	0.15	0.83	100.0
35	2-Nitropropane[a]	10.29	43	41 (87)	39 (31)		1.15	0.74	0.02	0.08	100.0
36	1,2-Dichloropropane[a]	10.38	63	76 (38)			0.41	0.28	0.05	0.08	99.6
37	Trichloroethene[a,d]	10.41	130	132 (86)	95 (92)		2.01	1.43	0.02	0.08	99.5
38	Dibromomethane	10.51	174	93 (80)	95 (73)	172 (53)	0.83	0.26	0.08	0.17	99.8
39	1,4-Dioxane[a]	10.68	88	58 (49)	43 (16)	57 (15)	6.34	3.35	1.33	1.67	99.4
40	Methylmethacrylate[a]	10.78	41	100 (35)	69 (80)	39 (55)	2.68	2.40	0.02	1.67	100.0
41	Bromodichloromethane	10.77	83	85 (52)	129 (12)		1.56	1.26	0.02	0.17	99.3
42	Cis-1,3-dichloropropene	12.02	75	39 (45)	77 (31)	110 (23)	1.46	0.73	0.08	0.17	99.5
43	Pyridine trifluoroacetate	12.17	79	52 (48)	51 (22)	39 (4)	5.65	3.21	0.02	0.17	97.4
44	Trans-1,3-dichloropropene	13.05	75	110 (24)	39 (43)	77 (30)	2.89	2.41	0.08	0.17	99.7
45	Toluene[a,b,d]	13.23	91	92 (59)			1.05	0.34	1.00	1.67	99.6
46	1,1,2-Trichloroethane[a]	13.41	97	83 (81)	99 (60)	85 (52)	3.55	0.81	0.02	0.17	100.0
47	Ethylmethacrylate	13.77	69	41 (68)	99 (22)	86 (17)	3.40	0.52	0.02	0.17	100.0
48	1, 3-Dichloropropane	13.87	76	41 (62)	78 (31)	39 (21)	2.21	1.37	0.02	0.17	99.3
49	n-Octane[b]	14.36	85	71 (60)	57 (86)	114 (14)	1.94	1.58	0.03	0.83	96.9
50	Dibromochloromethane	14.49	129	127 (77)	131 (24)		2.62	1.63	0.02	0.08	99.4

Table 1 (cont.)

51	1,2-Dibromoethane	14.89	107	109 (93)			2.95	0.52	0.05	0.08	99.7
52	Tetrachloroethene[a,d]	14.95	166	164 (79)	129 (67)	131 (65)	0.43	0.04	0.01	0.08	98.7
53	Chlorobenzene[a]	16.48	112	77 (55)	114 (31)	51 (17)	3.07	0.3	0.01	0.08	99.3
54	1,1,1,2-Tetrachloroethane	16.60	131	133 (95)	117 (65)	119 (63)	2.82	1.2	0.02	0.08	99.1
55	Ethylbenzene[a,b]	16.99	91	106 (31)			2.59	2.20	0.17	0.33	99.2
56,57	m,p-Xylene[a,b]	17.31	91	106 (56)	105 (25)	77 (14)	2.51	2.13	0.16	0.34	98.9
58	Bromoform[a]	18.10	173	171 (51)	93 (16)	81 (13)	4.08	2.81	0.05	0.08	99.5
59	Styrene[a,d]	18.13	104	103 (46)	78 (40)		3.63	3.24	0.67	0.83	99.6
60	o-Xylene[a,b]	18.22	91	106 (47)	105 (22)	77 (17)	3.84	1.47	0.003	0.17	100.3
61	1,1,2,2-Tetrachloroethanea	18.91	83	85 (64)	95 (15)	131 (11)	4.67	2.93	0.05	0.08	99.6
62	1,2,3-Trichloropropane	19.17	75	110 (34)	77 (31)	97 (18)	1.76	1.37	0.08	0.17	99.8
63	1,4-Dichloro-2-butene	19.24	75	53 (69)	89 (52)	124 (20)	3.95	2.7	0.12	0.17	99.7
64	Isopropylbenzene[a]	19.32	105	120 (28)	77 (15)	79 (13)	3.18	2.79	0.01	0.08	99.8
65	Bromobenzene	19.75	77	156 (71)	158 (69)	51 (28)	3.72	1.17	0.02	0.08	99.4
66	n-Propylbenzene	20.38	120	105 (16)			3.34	2.95	0.02	0.08	100.1
67	2-Chlorotoluene	20.42	126	125 (25)	128 (30)		3.61	3.22	0.05	0.08	99.9
68	4-Chlorotoluene	20.60	91	126 (33)	125 (13)	128 (10)	3.61	3.22	0.02	0.08	99.5
69	3-Ethyltoluene	20.62	105	120 (31)	77 (11)		3.58	3.19	0.01	0.02	99.5
70	4-Ethyltoluene	20.71	105	120 (29)	77 /11)	91 (10)	3.89	3.50	1.77	2.00	99.9
71	1,3,5-Trimethylbenzene[b]	20.87	105	120 (49)	119 (12)	77 (11)	3.80	3.41	0.01	0.02	99.9
72	Phenol[a]	20.99	94	66 (30)	55 (7)	50 (5)	4.48	4.10	2.33	2.50	102.3
73	Aniline[a]	21.21	93	66 (30)	65 (14)	52 (3)	6.91	0.18	0.002	0.02	96.8
74	2-Ethyltoluene	21.30	105	120 (31)	91 (11)	77 (11)	3.25	2.87	0.02	0.17	99.3
75	Pentachloroethane	21.35	167	117 (96)	165 (77)	130 (31)	4.03	3.64	0.08	0.17	99.7
76	tert-Butylbenzene	21.72	119	91 (63)	134 (21)		3.19	2.80	0.02	0.08	99.4
77	1,2,4-Trimethylbenzene[b]	21.78	105	120 (58)			3.52	3.13	0.03	0.08	98.2
78	1,3-Dichlorobenzene	22.30	146	148 (63)	111 (36)	75 (26)	4.56	4.17	0.02	0.08	98.3

Int. J. Environ. Anal. Chem. (DOI: 10.1080/03067310903584073)

Table 1 (cont.)

79	sec-Butylbenzene	22.31	105	134 (24)			3.85	3.46	0.01	0.02	99.4
80	1,4-Dichlorobenzene[a]	22.52	146	148 (62)	111 (35)	75 (25)	4.04	3.65	0.02	0.08	99.6
81	p-Isopropyltoluene	22.69	119	134 (31)	91 (25)	117 (15)	3.65	3.27	0.03	0.05	99.6
82	1,2,3-Trimetylbenzene[b]	22.73	105	120(44)	77(12)	91(9)	3.63	3.24	0.02	0.05	98.3
83	Benzyl alcohol	22.93	79	108 (60)	107 (43)	51 (16)	1.57	1.48	0.005	0.01	95.0
84	1,2-Dichlorobenzene	23.20	146	148 (63)	111 (38)	75 (25)	2.96	2.57	0.02	0.08	99.2
85	1,3-Diethylbenzene	23.34	105	119 (98)	134 (48)	91 (24)	4.23	3.84	0.02	0.08	99.5
86	1,4-Diethylbenzene	23.56	119	105 (82)	77 (23)		4.09	3.71	0.02	0.08	99.5
87	n-Butylbenzene	23.58	91	92 (61)	134 (32)	65 (12)	2.14	1.75	0.01	0.02	98.3
88	1,2-Diethylbenzene	23.72	105	119 (87)	134 (50)	77 (17)	4.02	3.63	0.02	0.08	97.2
89	Hexachloroethane[a]	24.37	201	117 (95)	199 (62)	166 (48)	3.80	3.41	0.08	0.17	95.1
90	1,2-Dibromo-3-chloropropane	24.45	157	155 (78)	75 (74)		4.09	3.71	0.08	0.17	98.6
91	Nitrobenzene[a]	24.52	77	123 (51)	51 (46)	93 (13)	4.25	3.86	0.08	0.17	95.2
92	1,2,4-Trichlorobenzene[c]	26.53	180	182 (96)	184 (30)	145 (27)	4.09	3.71	0.02	0.17	99.6
93	Naphthalene[a,c,d]	26.79	128	127 (18)	129 (15)		1.33	0.94	0.17	0.83	92.0
94	Hexachlorobutadiene[c]	27.17	225	227 (64)	223 (62)	190 (39)	4.16	3.77	0.02	0.08	99.5
95	1,2,3-Trichlorobenzene[c]	27.24	180	182 (90)	184 (28)	145 (25)	3.60	3.22	0.02	0.08	99.3
96	2-Methylnaphtalene[a,d]	28.77	142	141 (85)	115 (28)		1.70	3.41	0.08	0.17	91.5
97	1-Methylnaphtalene[a,d]	29.11	142	141 (95)	115 (38)		1.50	3.59	0.01	0.02	91.2
98,99	2,3,4,5-Tetrachlorophenol/2,3,4,6	34.40	232	131 (29)	166 (19)		6.12	0.96	0.0003	0.003	92.3

[1] The value in brackets next to qualifier ions represents percent abundances of each ion for that compound.
[a] Compounds included in the USEPA List of Hazardous Air Pollutants [9].
[b] Ozone precursors recommended for measurement by the Directive 2002/3/EC [36].
[c] Compounds included in the European Union list of priority pollutants for water policies [8].
[d] Compounds included as hazardous organic pollutants in the WHO Air Quality Guidelines [4].

Int. J. Environ. Anal. Chem (DOI: 10.1080/03067310903584073)

[36], eight of them are included in the European Union list of priority pollutants for water policies [8] and twelve of them are included as hazardous organic pollutants in the World Health Organization Air Quality Guidelines [4].

The standards of the 99 target compounds involve three mixtures of volatile organic compounds at 2000 mg L^{-1} in methanol (592/524 Volatile Organics Calibration Mix, EPA 524.2 Revision 4 Mix and 8270 Calibration Mix 5 from Supelco, Bellefonte, USA) and the individual standards of i-pentane, 1-pentene, n-pentane, 2-pentene (cis/trans mixture), isoprene, i-hexene, n-hexane, i-octane, n-heptane, n-octane, phenol, 1,2,3-trimethyl-benzene (Aldrich, Steinheim, Germany), 2-ethyltoluene, 3-ethyl-toluene, 4-ethyltoluene, 1,2-diethyl-benzene, 1,3-diethylbenzene, 1,4-diethylbenzene (Fluka, Buchs, Switzerland), and 2-methylnaphthalene (Riedel - deHaën, Seelze, Germany). The minimal purity of the standards was 98%. Toluene-d_8 from Aldrich was used as an internal standard, as recommended by the EPA [26].

The standards were diluted in methanol for gas chromatography with purity >99.9% (SDS, Peypin, France) and ranged between 0.01 and 500 mg L^{-1} with a toluene-d_8 constant concentration of 5 mg L^{-1}. All the standards were prepared on the day of use, and stored at 4 °C in 10 mL Certan® capillary vials provided by Supelco.

2.2. Two-bed sorbent tubes

A two-bed sorbent cartridge was chosen to cover the wide range of target compounds in this study. The cartridges were stainless-steel tubes (length: 3 in. × 0. 5 in.; o.d.: 0.25 in.) filled with a multisorbent bed of approximately 350 mg of Tenax TA/ Carbograph 1TD (Markes International Limited, Llantrisant, UK). The two sorbent materials were selected on the basis of previous studies [14,24].

Before each use, tubes were conditioned by thermal cleaning (100 °C for 15 minutes, 200 °C for 15 minutes and 325 °C for 30 minutes) under a nitrogen flow rate of 100 mL min^{-1} (purity 99.999%, Carburos Metálicos, Tarragona, Spain). After conditioning, the tubes were sealed with Swagelok end caps fitted with PTFE ferrules and stored in hermetically sealable glass jars with desiccant material in order to prevent any ambient contamination of the sorbents.

2.3. Calibration

The external liquid standards and the internal standard were loaded into the two-bed sorbent tubes using a Calibration Solution Loading Rig (Markes International Limited, Llantrisant, UK) which allows a 99.999% pure Helium flow (Carburos Metálicos, Tarragona, Spain) to pass through the tube at a fixed flow rate of 100 mL min^{-1}. The cartridges were attached to the end of the weak sorbent (Tenax TA)

in the same position as in the sample collection. A conventional GC syringe was used to inject 1 µl of each dilution of the standard solution into the sorbent cartridges. After the injection, a short time (approximately 20 s) was allowed to elapse before removing the needle from the sorbent to enable the target compounds to be fully evaporated and retained on the sorbent bed. To ensure the repeatability of the injection and the total evaporation of the solvent, the helium stream was maintained for 5 minutes before the tubes were sealed with Difflok caps and then immediately analysed. If this procedure was followed, there was no sign of methanol in the standard solution chromatograms.

2.4. Thermal desorption GC-MS analysis

Desorption of the analytes retained on the Tenax TA – Carbograph 1TD sorbent tubes was carried out in a Unity Thermal Desorption system connected to an Ultra A automatic sampler (both from Markes International Limited, Llantrisant, UK). In the first step, primary desorption, tubes were heated to 275 °C with a helium flow rate of 30 mL min^{-1} for 10 min. This was done to desorb the analytes which were refocused on a hydrophobic general purpose cold trap, filled with Tenax TA and a graphitised carbon, cooled at –10 °C. A split flow was not applied in this step, so all the mass desorbed from the tubes went into the cold trap. After flash-heating of the cold trap at 300 °C during 3 min, analytes were injected into the chromatographic column. A split flow of 5 mL min^{-1} was applied in this step. The parameters of this method were based on a previous work [14] and optimised for the 99 target VOCs.

Separation and detection were performed in a 6890N gas chromatograph and 5973 *inert* mass spectrometer (Agilent Technologies. Palo Alto, USA), using a TRACSIL Metax5 capillary column (60 m, 0.32 mm, 1.0 µm, provided by TEKNOKROMA, Barcelona, Spain) and helium gas as the carrier at a flow rate of 1.5 mL min^{-1}. The oven temperature of the GC was initially held at 40 °C for 5 min, then raised to 140 °C at a rate of 6 °C min^{-1} and then raised again to 220 °C at a rate of 15 °C min^{-1} and held at that temperature for 3 min.

The GC-MS interface was set at 280 °C. The mass spectrometer acquired data in scan mode with an *m/z* interval from 35 to 280, operating at an electron impact energy of 70 eV. Qualitative identification of the target VOCs was based on the match of the retention times and the ion ratios of the target quantifier and qualifier ions. The retention times and the quantifier and qualifier ions for each target compound are shown in Table 1. The internal standard calibration method was used for the GC-MS quantification.

2.5. Sample collection

The Tarragona area is an important industrial centre mainly based on the chemical industry. Most of the chemical industries are located in two areas: the North Industrial Complex, which has a surface area of 470 ha and an oil refinery, and the South Industrial Complex, which occupies an area of 717 ha with several chemical and petrochemical plants. In this study, field samples were taken from an industrial WWTP located in the South Industrial Complex, near some tourist locations (see Figure 1). This WWTP collects wastewater from four chemical factories which produce a wide variety of products such as isocyanates, polyurethanes, chlorinated organics, polymerisates, functional chemicals, surfactants and adhesives. The samples were collected in November 2008 in two locations: the collecting tank after the primary sedimentation and the secondary treatment tank.

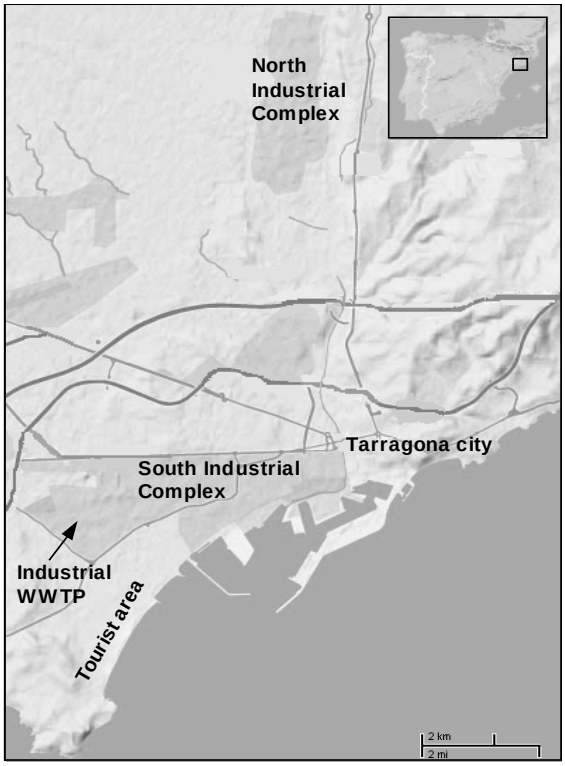


Figure 1. Map of the Tarragona area showing the location of the North and the South Industrial complexes, the sampled industrial WWTP, the main location (Tarragona city) and the tourist area

Samples were collected at the Tenax TA end of the tube in order to collect the heaviest hydrocarbons first. The tubes were placed in the headspace of the tanks at approximately 1 m from the wastewater. An air sampling pump (SKC, Eighty Four, USA) was used to pump air samples at a flow rate of 50 mL min^{-1}, for 12 min. The pump was calibrated with a flowmeter before and after sampling (Altech, Deerfield, UK) and the flow average was used to determine the volume of air sampled.

3. RESULTS AND DISCUSSION

3.1. Analytical method

3.1.1. Method optimisation

All the parameters of the instrumental method were optimised using liquid standards of the 99 target VOCs and the internal standard. Although the matrix in which the standards are dissolved can affect the calibration, accurate gas external standards for a wide range of target compounds are not easy to generate. For this reason, recent studies have shown that liquid standards loaded in the sorbents in the appropriate conditions are a reliable alternative [30, 37].

For the thermal desorption system, previous studies showed that while low desorption temperature, time and flow result in poor recovery of the target compounds, high values of these variables increase the number of artifacts and shorten the life of the sorbents [14, 34]. For the 99 target VOCs, the tube and trap desorption temperature, the time and the flow, explained in section 2.4., were optimised to ensure the highest recoveries and the lowest artifacts [14].

Chromatographic separation was satisfactory for most of analytes (see retention times in Table 1) and the co-eluted analytes were quantified using characteristic ions. Only *m*-xylene and *p*-xylene and 2,3,4,5-tetrachlorophenol and 2,3,4,6-tetrachlorophenol were quantified together as they exhibited identical mass spectra.

Sample volume for real samples was fixed to ensure that no analytes had broken through the sorbent bed during sampling. Two identical sorbent tubes were connected in series, so that the back tube would retain the analytes eluted from the front tube, and air emitted by the collecting tank after the primary treatment (the most contaminated area) was pumped through them at different sampling rates (from 100 mL min^{-1} to 20 mL min^{-1}) and periods of time (from 30 to 10 minutes). After each sampling both tubes were analysed. This test was conducted on different dates and under different atmospheric conditions (temperatures ranging from 5 °C to 25 °C, humidity between 60% to 90% and wind speeds up to 60 km h^{-1}). The flow rate of the sampling was fixed at 50 mL min^{-1} for 12 minutes collecting 600 mL of air. Under these conditions, only eleven target VOCs were present in the second tube, with concentrations

Table 2. VOCs detected in the second tube in breakthrough tests and their % concentrations compared with their respective concentrations in the first tube.

No.	Target VOCs	%
9	Acrylonitrile	0.62
24	Chloroform	0.94
39	1,4-Dioxane	4.47
55	Ethylbenzene	2.57
56,57	m,p-Xylene	1.62
59	Styrene	1.63
69	3-Ethyltoluene	0.65
71	1,3,5-Trimethylbenzene	0.52
77	1,2,4-Trimethylbenzene	0.73
82	1,2,3-Trimetylbenzene	0.45
86	1,4-Diethylbenzene	0.60

between 0.45 and 4.47% of their respective concentrations in the first tube, as is shown in Table 2. The highest value was 4.47% for the 1,4-dioxane but this does not exceed the 5% recommended by the EPA [38].

3.1.2. Artifact evaluation

Blank signals of the tubes and the formation of artifacts affect the method detection limit and the overall method performance. Although blank levels can be made extremely low by meticulous conditioning of the solid adsorbents and by properly storage [39], artifact formation may be unavoidable and needs to be taken into account [40]. Furthermore, the degradation products of Tenax TA are well known and have been widely studied [41, 42]. Blanks of the tubes were checked by analysing the 20 freshly cleaned sorbent tubes involved in this study. Their responses were compared with the responses obtained by direct injection of the standards under the same split conditions. A total of 24 target VOCs were found in these tubes in amounts ranging from 0.0012 ng, for the o-xylene, to 1.2 ng for the phenol. Table 3 shows the average concentrations and the standard deviation of the blanks of the target compounds found. The average blank concentrations were included in the calibration curves of these 24 target VOCs.

3.1.3. Method validation

To determine the instrumental repeatability, five cartridges filled with 100 ng of VOC standard were analysed

Table 3. Blank concentrations of target VOCs in the freshly cleaned tubes and their standard deviation in ng.

No.	Target VOCs	Average concentration (ng)	s.d. (ng, n=20)
6	Isoprene	0.25	0.16
11	Dichloromethane	0.29	0.10
12	Carbon disulphide	0.012	0.009
18	n-Hexane	0.03	0.01
24	Chloroform	0.14	0.01
25	tetrahydrofuran	0.09	0.07
30	Benzene	0.23	0.07
34	n-Heptane	0.05	0.01
39	1,4-Dioxane	0.18	0.18
45	Toluene	0.22	0.13
49	n-Octane	0.010	0.003
55	Ethylbenzene	0.05	0.02
56,57	m,p-Xylene	0.02	0.01
59	Styrene	0.08	0.11
60	o-Xylene	0.0012	0.0003
64	Isopropylbenzene	0.020	0.001
70	4-Ethyltoluene	0.30	0.25
72	Phenol	1.2	0.5
77	1,2,4-Trimethylbenzene,	0.010	0.004
81	p-Isopropyltoluene	0.010	0.003
82	1,2,3-Trimetylbenzene	0.010	0.001
93	Naphthalene	0.04	0.02
96	2-Methylnaphtalene	0.02	0.01
97	1-Methylnaphtalene	0.002	0.001

on the same day. Although the EPA recommends the use of internal standards in the determination of VOCs by thermal desorption [26], internal standards are not always used in these kind of studies [33, 34]. To evaluate the need for an internal standard, the relative standard deviation of the results was calculated with and without the internal standard (see Table 1). Although the repeatabilities without using the internal standard are quite good (ranging from 0.41 to 6.91% RSD), in most of the cases the use of the internal standard gave better values (ranging from 0.02 to 4.1 %RSD). Thus, toluene–d_8 was used as an internal standard in this study.

The instrumental limit of detection (LOD) and the instrumental limit of quantification (LOQ) were evaluated in two ways. For target compounds

without blank signal, LODs were determined as the concentrations corresponding to three times the noise signal of the quantifier ion and LOQs as the lowest calibration level. For target compounds which present a signal in the blank, the LODs and LOQs were established as the sum of the average concentrations of the blank responses plus three times the standard deviation of this signal, for the LOD, and plus ten times the standard deviation of the signal for the LOQ (n=20). The lowest values of LOD and LOQ correspond to the sum of 2,3,4,5 and 2,3,4,6-tetrachlorophenol (0.0001 ng and 0.001 ng, respectively) and the highest values were for phenol (1.4 ng and 1.5 ng, respectively), which has a high blank signal.

The linear range was evaluated within a VOC amount ranging from LOQ of each compound to 1500 ng. All calibration curves showed a good linearity in that range with determination coefficients (r^2) higher than 0.990 for all compounds. Once the linear range had been tested, calibration curves at amounts ranging from LOQ of each compound and 100 ng were used to quantify the samples. Due to the high concentrations of acrylonitrile and styrene found in the samples, the ranges of their calibration curves were wider (0.05 - 1200 ng and 0.5 - 500 ng, respectively).

Instrumental recoveries were measured as the percentage recovery of the response obtained by the triplicate analysis of a 100 ng standard using the TD-GC-MS method and were compared with the response obtained by direct injection of the same amount of standard under the same split conditions. As Table 1 shows, most of the target compounds have recoveries higher than 95% (n=3, %RSD between 0.02 and 4.06). The lowest recoveries correspond to i-pentane, methyl-terc-butylether and carbon disulphide (85, 86 and 87%, respectively).

The method detection limit (MDL) and the method quantification limit (MQL) ranged from 0.0003 to 2.3 μg m^{-3} and from 0.003 to 2.5 μg m^{-3}, respectively (see Table 1).The precision in real samples was determined by sampling two sorbent tubes connected in parallel at the same time and under the same conditions. The analysis of these tubes showed similar results.

3.1.4. Stability during storage

The stability during storage was investigated by analysing twelve replicates of freshly cleaned cartridges filled with 100 ng of standard solution. Three of these were immediately analysed and the others were sealed with Swagelok end caps fitted with PTFE ferrules and stored at 4 °C in hermetically sealable glass jars with desiccant material. Three of these cartridges were analysed after being stored for one day, three of them after three days and the last three after one week. Toluene-d_8 was used as the internal standard in the analysis of all samples. Figure 2 shows the fresh

sample relative responses against the corresponding results for 3 days and 7 days of storage. Good correlations (r^2>0.990) and slopes close to the ideal 1 were observed after up to three days of storage (Figure 2a). After one week of storage (Figure 2b), however, the amount of carbon disulphide and n-hexane increased in the stored tubes, possibly due to the degradation of some analytes. Furthermore, the losses of the most volatile target VOCs after one week storage, ranging between the 20% and the 50%, indicate that the samples should be analysed within three days of collection.

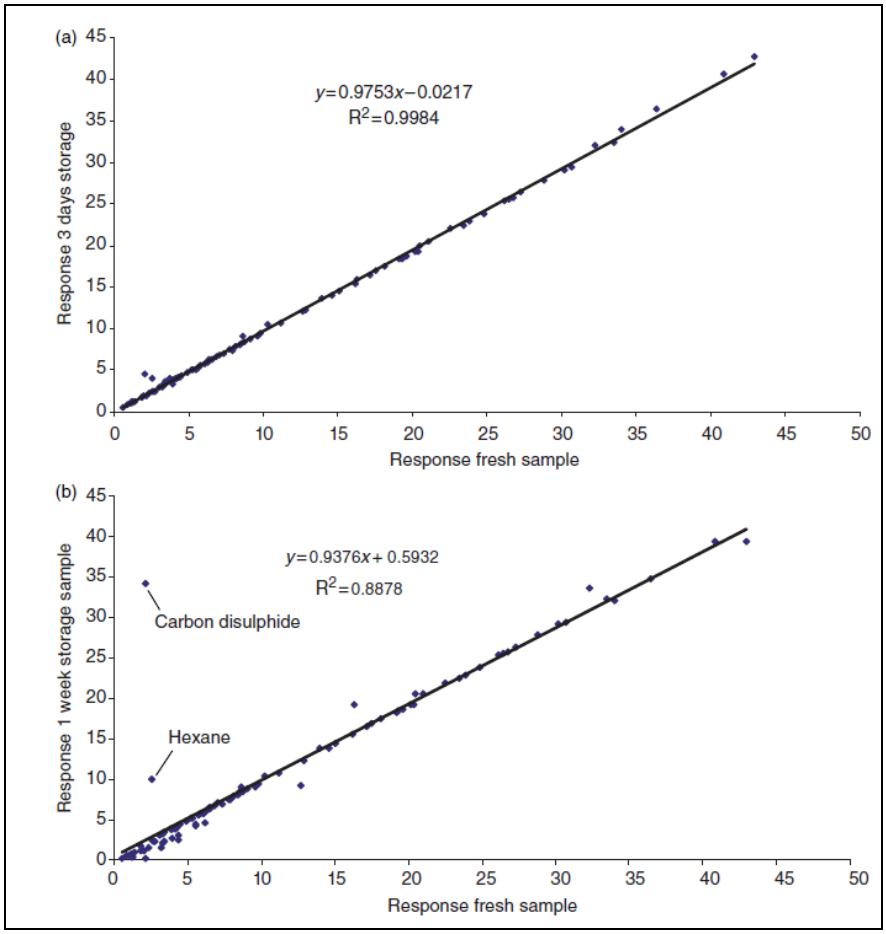


Figure 2. Correlations of the 99 target compounds after three days (a) and after one week of storage (b).

3.2. Analysis of real samples

Sixteen samples were taken in the industrial WWTP in November 2008. A total of 64 of the 99 VOCs were detected in these samples and 55 of these 64 were quantifiable by the proposed method. Table 4 shows the

Table 4. Target compounds found in real samples and their average, maximum and minimum concentrations in site 1 and 2.

No.	Target VOCs	Site 1 (μg m^{-3})			Site 2 (μg m^{-3})		
		Aver.	Max.	Min.	Aver.	Max.	Min.
1	i-Pentane	10.1	20.1	6.1	15.6	33.3	7.08
3	n-Pentane	3.64	9.08	1.27	6.52	15.8	6.13
5	2-Trans-pentene	0.004	0.03	n.q.	0.12	0.65	0.05
6	Isoprene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
7	2-Cis-pentene	0.19	1.50	n.d.	1.44	2.27	1.27
8	1,1-Dichloroethylene	0.2	1.60	n.d.	0.62	1.68	1.62
9	Acrylonitrile	843	1843	260	7.63	15.3	3.00
11	Dichloromethane	4.16	9.62	1.67	2.71	4.22	2.17
12	Carbon disulphide	1.01	6.07	n.q.	1.94	7.28	1.72
14	Trans-1,2-dichloroethene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
16	Propionitrile	0.40	3.22	n.d.	0.31	2.50	n.d.
18	n-Hexane	0.81	4.43	n.q.	1.04	4.20	n.q.
24	Chloroform	56.9	155	2.22	4.80	9.52	1.27
25	Tetrahydrofuran	0.57	2.38	n.q.	0.60	1.40	n.q.
26	1,1,1-Trichloroethane	0.51	1.42	1.35	1.03	1.42	1.33
27	1-Chlorobutane	n.d.	n.d.	n.d.	0.61	4.85	n.d.
28	1,2-Dichloroethane	0.68	2.10	0.63	1.37	3.72	0.53
30	Benzene	1.31	5.03	n.q.	1.46	2.98	n.q.
31	Carbon tetrachloride	1.31	1.48	1.13	1.34	1.45	1.15
33	i-Octane	0.61	1.35	0.95	0.47	1.28	1.22
34	n-Heptane	0.14	1.15	n.q.	0.56	2.47	n.q.
35	2-Nitropropane	0.14	0.60	n.q.	0.31	1.30	n.q.
37	Tricloroethene	0.28	2.22	n.q.	0.12	0.75	n.q.
39	1,4-Dioxane	42.0	105	14.2	43.8	63.1	21.6
40	Methylmethacrylate	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
41	Bromodichloromethane	0.06	0.48	n.d.	0.17	0.58	0.38
43	Pyridine trifluoroacetate	n.d.	n.d.	n.d.	1.01	8.12	n.d.
45	Toluene	5.71	19.1	n.q.	3.05	5.55	n.q.
49	n-Octane	0.23	1.82	n.q.	0.24	1.03	n.q.
50	Dibromochloromethane	0.16	0.38	0.15	0.17	0.47	0.10
52	Tetrachloroethene	0.88	1.63	0.38	0.91	3.00	0.17
53	Chlorobenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
55	Ethylbenzene	55.6	96.9	20.5	5.7	19.7	1.02
56,57	m,p-Xylene	76.9	137	35.3	2.54	8.13	0.52
58	Bromoform	0.04	0.23	n.q.	0.06	0.25	n.q.
59	Styrene	574	775	409	4.23	6.12	3.02
60	o-Xylene	8.73	25.9	n.q.	0.77	3.02	n.q.

Table 4 (cont.)

64	Isopropylbenzene	0.04	0.28	n.q.	0.13	1.02	n.q.
65	Bromobenzene	n.d.	n.d.	n.d.	0.08	0.67	n.d.
66	n-Propylbenzene	0.81	5.55	n.q.	0.61	3.95	n.q.
69	3-Ethyltoluene	25.7	59.1	n.q.	2.18	7.95	n.q.
70	4-Ethyltoluene	14.7	56.5	23.5	3.04	15.5	2.93
71	1,3,5-Trimethylbenzene	7.83	21.2	n.q.	0.85	4.10	n.q.
72	Phenol	n.d.	n.d.	n.d.	1.22	9.78	n.d.
74	2-Ethyltoluene	8.29	27.0	n.q.	0.80	2.85	n.q.
76	Tert-Butylbenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
77	1,2,4-Trimethylbenzene	28.9	70.8	n.q.	1.85	7.92	n.q.
78	1,3-Dichlorobenzene	n.q.	n.q.	n.q.	n.d.	n.d.	n.d.
79	sec-Butylbenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
80	1,4-dichlorobenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
81	p-Isopropyltoluene	1.22	4.25	n.q.	0.21	0.93	n.q.
82	1,2,3-Trimetylbenzene	81.7	104	56.9	2.65	10.6	0.05
83	Benzyl alcohol	n.q.	n.q.	n.q.	0.1	0.78	n.q.
84	1,2-Dichlorobenzene	n.q.	n.q.	n.q.	n.d.	n.d.	n.d.
85	1,3-Diethylbenzene	4.59	16.8	n.q.	0.44	1.95	n.q.
86	1,4-Diethylbenzene	57.5	120	n.q.	3.84	15.7	n.q.
87	n-Butylbenzene	2.03	10.6	n.q.	0.13	0.68	n.q.
88	1,2-Diethylbenzene	0.49	2.40	n.q.	0.05	0.27	n.q.
91	Nitrobenzene	n.d.	n.d.	n.d.	0.31	1.37	n.q.
92	1,2,4-Trichlorobenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
93	Naphthalene	0.60	4.82	n.q.	0.14	1.15	n.q.
94	Hexachlorobutadiene	0.23	0.5	0.42	0.19	0.40	n.d.
95	2-Methylnaphthalene	7.80	34.9	n.q.	0.19	0.97	n.q.
97	1-Methylnaphtalene	11.3	32.9	9.32	0.14	3.13	1.52

n.d.: compound not detected (value<MDL)
n.q.: compound not quantified (value<MQL)

average, maximum and minimum concentrations found in the collecting tank after the primary sedimentation (site 1) and in the secondary treatment tank (site 2). Figure 3 shows the typical chromatogram for site 1 (Figure 3a) and for site 2 (Figure 3b). The most characteristic VOCs of each site are indicated. The highest concentration in site 1 was for acrylonitrile, with a maximum concentration of 1843 μg m^{-3} and an average concentration of 843 μg m^{-3}. In this site, high concentrations of styrene were also found, between 408 and 574 μg m^{-3}. Also worthy of note were the high concentrations of chloroform (2.22-155 μg m^{-3}), 1,4-dioxane (14.2-104 μg m^{-3}), ethyl-benzene (20.5-96.9 μg m^{-3}), m,p-xylene (35.3-136 μg m^{-3}), 1,2,3-trimethyl-benzene (56.9-104 μg m^{-3}) and 1,4-diethylbenzene (<0.08-120 μg m^{-3}). In contrast, levels of most compounds were lower in site 2 than in site 1. This

is to be expected because in the secondary treatment tank is where the organic matter is biologically degraded and evaporation processes take place [43]. The exceptions were: i-Pentane, with concentrations between 6.13 and 20.08 μg m^{-3} in site 1 and between 7.08 and 33.35 μg m^{-3} in site 2; n-pentane (site 1: 1.27-9.08 μg m^{-3}, site 2: 6.13-15.8 μg m^{-3}), 2-cis-pentene (site 1: <0.17 - 1.50 μg m^{-3}, site 2: 1.27-2.27 μg m^{-3}) and n-heptane (site 1: <0.83-1.15 μg m^{-3}, site 2: <0.83.-2.47 μg m^{-3}). A plausible explanation is that these VOCs may be degradation products of some other organic water pollutants. Finally, it is important to note that the levels of 1,4-dioxane were similar in both sampling sites which may indicate that the biological degradation of this compound did not occur.

To the best of our knowledge, this is the first study of the emissions of these 99 VOCs in this kind of industrial WWTP. Therefore, the results found could only be compared to those reported for petrochemical and urban WWTPs. For example, studies of air emissions from two petrochemical WWTPs in Taiwan reported concentrations of up to 620 mg m^{-3} of benzene, 370 mg m^{-3} of styrene and 53 mg m^{-3} of acrylonitrile [11,22,23] which are much higher than the levels found in this study. In addition, the concentrations of VOCs reported for studies in urban WWTPs were generally higher than those reported in this paper except for acrylonitrile, chloroform and styrene [18,44]. Also worthy of note are the higher levels of chlorinated VOCs in urban WWTPs such as 1,1,1-trichloroethane (up to 82 μg m^{-3}) and tetrachloroethane (up to 40 μg m^{-3}).

It is significant that the most abundant VOCs found in the samples are all included in the USEPA List of Hazardous Air Pollutants [9]. Of these, acrylonitrile and styrene, which have the highest concentration levels, are also considered hazardous organic pollutants in the WHO Air Quality Guidelines [4]. Acrylonitrile is an anthropogenic product with carcinogenic effects in animals and humans. Although no safe level for acrylonitrile in air is established by the WHO, this organisation estimates a lifetime risk of $2 \cdot 10^{-5}$ at an air concentration of 1 μg m^{-3}. As indicated in this section, the levels of acrylonitrile in this study were up to 1843 μg m^{-3}.

As for styrene, it is one of the most important monomers worldwide and also occurs naturally as a degradation product of some organisms. A weekly average of 260 μg m^{-3} is established as a guideline value for this compound. In the collected samples, styrene concentrations were higher than this guideline value (up to 574 μg m^{-3}). The high concentrations of these two compounds together with the remainning 62 VOCs found in the samples show the importance of industrial WWTPs as a source of hazardous air pollutants and the need for adequate analytical methods to monitor these compounds.

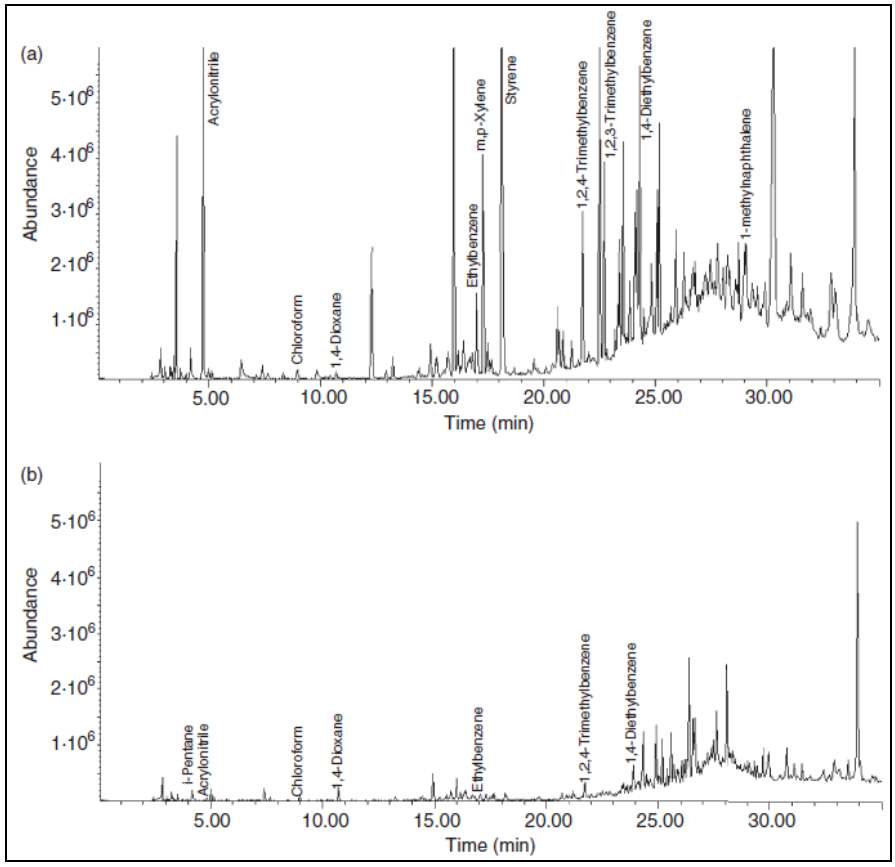


Figure 3. Chromatograms from site 1 (a) and from site 2 (b).

4. CONCLUSIONS

An analytical method for simultaneously determining 99 volatile organic compounds in air samples by TD-GC-MS was successfully optimised and evaluated. This method involves only 12 minutes of sampling and a low preconcentration volume of air (600 mL). The analysis of blanks showed the presence of some compounds of interest, mainly phenol, isoprene, dichloromethane, benzene and toluene, which affect the detection limits of these compounds. However, the high levels of the compounds in real samples indicate that the method can be useful in determining these. Although most of the compounds were stable during one week of storage at 4 °C, the losses of the most volatile compounds and the increases in the concentration of carbon disulphide and n-hexane indicate that samples should be analysed within three days of collection.

When the method was applied to air emissions from an industrial WWTP,

the concentrations of target compounds were found to be higher in the collecting tank after the primary sedimentation than in the secondary treatment tank. Acrylonitrile and styrene were the most abundant and the levels of chloroform, 1,4-dioxane, ethylbenzene, 1,2,3-trimethylbenzene and 1,4-diethylbenzene were also high.
The wide variety of hazardous VOCs found in the industrial WWTP emissions and the high concentrations of acrylonitrile and styrene indicate the importance of industrial WWTPs as a source of hazardous air pollutants and the need for fast and environmentally-friendly analytical methods that should be able to monitor a large number of these compounds. The TD-GC-MS method proposed has these characteristics and has been demonstrated to perform well in real samples.

Acknowledgments

The authors wish to acknowledge the financial support provided to this study by the Ministry of Science and Innovation of Spain through projects CTM2005-01774, CTM2008-06847-CO2-01/TECNO and PETRI 2006-0703-01.

REFERENCES

[1] J. Dewulf and H. Van Langenhove, J. of Chromatogr. A **843**, 163 (1999).

[2] R. G. Derwent, M. E. Jenkin and S. M. Saunders, Atmos. Environ. **30**, 181 (1996).

[3] R. Atkinson, Atmos. Environ. **34**, 2063 (2000).

[4] WHO - World Health Organization, Copenhagen, 2000. Air quality guidelines for Europe, 2n Edition. WHO Regional Publications, European Series, No. 29.

[5] A. P. Jones, Atmos. Environ. **33**, 4535 (1999).

[6] USEPA - US Environmental Protection Agency, Office of Air quality Planning, Washington, 1990. Cancer Risk from outdoor exposure to air toxics. EPA-450/1-90-004a.

[7] P. W. G. Liu, Y. C. Yao, J. H. Tsai, Y.C. Hsu, L.P. Chang and K.H. Chang, Sci. Total Environ. **398**, 154 (2008).

[8] Decision No. 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. Official Journal of the European Communities L331/4, 15/12/2001: 1-5.

[9] USEPA - US Environmental Protection Agency, Office of Air quality Planning, Washington, 1994. Amendments to 1990 Clean Air Act-List of 189 Hazardous Air Pollutants.

[10] E. Cetin, M. Odabasi and R. Seyfioglu , Sci. Total Environ. **312**, 103 (2003).

[11] T. Y. Lin, U. Sree, S.H. Tseng, K. H. Chiu, C. H. Wu and J.G. Lo, Atmos. Environ. **38**, 4111 (2004).

[12] Y. C. Hsu, S. K. Chen, J. H. Tsai and L. Chiang, J. Air & Waste Manag. Asso. **57**, 698 (2007).

[13] C. L. Chen, C. M. Shu and H. Y. Fang, Environ. Monit. Asses. **120**, 487 (2006).

[14] M. R. Ras-Mallorqui, R. M. Marce-Recasens and F. Borrull-Ballarin, Talanta **72**, 941 (2007).

[15] F. Dincer and A. Muezzinoglu, Atmos. Environ. **40**, 4210 (2006).

[16] A. P. Bianchi and M. S. Varney, Ann. Occ. Hyg. **41**, 437 (1997).

[17] A. K. Oskouie, D. T. Lordi, T. C. Granato and L. Kollias, Atmos. Environ. **42**, 4530 (2008).

[18] J. Leach, A. Blanch and A. C. Bianchi, Atmos. Environ. **33**, 4309 (1999).

[19] E. Atasoy, T. Dogeroglu and S. Kara, Water Res. **38**, 3265 (2004).

[20] A. Escalas, J. M. Guadayol, M. Cortina, J. Rivera and J. Caixach, Water Res. **37**, 3913 (2003).

[21] M. R. Ras, F. Borrull and R. M. Marce, Talanta **74**, 562 (2008).

[22] B. Z. Wu, T. Z. Feng, U. Sree, K. H. Chiu and H. G. Lo, Anal. Chim. Acta **576**, 100 (2006).

[23] W. H. Cheng and M. S. Chou, J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng. **38**, 2521 (2003).

[24] M. Harper, J. Chromatogr. A **885**, 129 (2000).

[25] J. Dewulf and H. Van Langenhove, Trac-Trends Anal. Chem. **21**, 637 (2002).

[26] USEPA - US Environmental Protection Agency, Washington, 1999. Compendium Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes, EPA/625/R-96/010b.

[27] D. K. W. Wang and C. C. Austin, Anal. Bioanal. Chem. **386**, 1099 (2006).

[28] K. Demeestere, J. Dewulf, B. De Witte and H. Van Langenhove, J. Chromatogr. A **1153**, 130 (2007).

[29] M. R. Ras, F. Borrull and R. M. Marcé, TrAC Trends Anal. Chem. **28**, 347 (2009).

[30] K. Demeestere, J. Dewulf, K. De Roo, P. De Wispelaere and H. Van Langenhove, J. Chromatogr. A **1186**, 348 (2008).

[31] E. Baltussen, C. A. Cramers and P. J. F. Sandra, Anal. Bioanal. Chem. **373**, 3 (2002).

[32] M. Czaplicka and K. Klejnowski, J. Chromatogr. A **976**, 369 (2002).

[33] A. Ribes, G. Carrera, E. Gallego, X. Roca, M. J. Berenguer and X. Guardino, J. Chromatogr. A **1140**, 44 (2007).

[34] O. O. Kuntasal, D. Karman, D. Wang, S. G. Tuncel and G. Tuncel, J. Chromatogr. A **1099**, 43 (2005).

[35] J. D. Donaldson, S. M. Grimes, L. Mehta and A. J. Jafari, J. AOAC Int. **86** 39 (2003).

[36] Decision No. 2455/2001/EC of the European Parliament and of the Council of 12 February 2002 relative to ozone in air. Official Journal of the European Communities L67/14, 09/03/ 2002: 1-17

[37] N. A. Martin, N. Barber, J. K. Black, R. P. Lipscombe and C. A. Tag, Atmos. Environ. **41**, 7666 (2007).

[38] USEPA - US Environmental Protection Agency, Washington, 1999. Compendium Method TO-15: Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), EPA/625/R-96/ 010b.

[39] D. Helmig, J. Chromatogr. A **732**, 414 (1996).

[40] C. H. Wu, M. N. Lin, C. T. Feng, K. L. Yang, Y. S. Lo and J. G. Lo, J. of Chromatogr. A **996**, 225 (2003).

[41] J. F. Walling, J. E. Bumgarner, D. J. Driscoll, C. M. Morris, A. E. Riley and L. H. Wright, Atmos. Environ. **20**, 51 (1986).

[42] P. A. Clausen and P. Wolkoff, Atmos. Environ. **31**, 715 (1997).

[43] WEF-ASCE. *Toxic Air Emissions from Wastewater Treatment Facilities.* (Alexandria VA, USA: Water Environment Federation-American Society of Civil Engineers, 1995).

[44] F. Dincer and A. Muezzinoglu, J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng. **43**, 1569 (2008).

3.1.2. Comparative study of solvent extraction and thermal desorption methods for determining a wide range of volatile organic compounds in ambient air

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

COMPARATIVE STUDY OF SOLVENT EXTRACTION AND THERMAL DESORPTION METHODS FOR DETERMINING A WIDE RANGE OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

Noelia Ramírez[a], Anna Cuadras[b], Enric Rovira[b], Francesc Borrull[a], Rosa Maria Marcé[a]
[a] Department of Analytical Chemistry and Organic Chemistry
Universitat Rovira i Virgili, Marcel·lí Domingo s/n,
Sescelades Campus, Tarragona 43007, Spain
[b] Observatori de Salut i Medi Ambient del Camp de Tarragona
Servei Regional de l'Agència de Protecció de la Salut de la
Generalitat de Catalunya, Tarragona, Spain

Abstract

This paper compares two analytical methods for determining levels of 90 volatile organic compounds (VOCs) commonly found in industrial and urban atmospheres. Both methods are based on two official methods for determining benzene levels and involve collecting samples by active adsorptive enrichment on solid sorbents. The first method involves solvent extraction and uses activated charcoal as a sorbent. After sampling, the sorbent is extracted with 1 mL of carbon disulfide and then 1 µL of the extract is analysed in a GC-MS. The second method involves thermal desorption (TD) and uses Tenax TA and Carbograph 1TD as sorbents, which allows the whole sample to be analysed. In general, the thermal desorption method showed the best repetitivities and recoveries and the lowest limits of detection and quantification. Because of its lower sensitivity, the solvent extraction method needs the preconcentration of large sample volumes of air (720 L vs. 2.64 L for the thermal desorption method) to yield similar limits of detection.

The performance of both methods in real samples was tested in a location near to a petrochemical complex. The results of the 24-hour samples for the solvent extraction method were compared with the average of 12 2-hour samples for the TD method. In some cases, both methods found differences in the VOC concentrations, especially in those compounds whose concentrations fluctuate significantly during the day.

Keywords**:** Thermal desorption; Solvent desorption; Comparison of methods; Air analysis; Volatile organic compounds.

1. INTRODUCTION

Volatile organic compounds (VOCs) have a significant impact on the environment and human health even at ppb levels. The environmental effects of VOCs include the accumulation and persistence of recalcitrant pollutants, the depletion of stratospheric ozone and the formation of tropospheric

photochemical ozone [1-3]. Furthermore, VOCs have neurotoxic and genotoxic effects on human health and can cause respiratory and reproductive disorders [4-6].

Because of the complexity of the environmental air matrix and the usually low concentration of VOCs, from ppb down to ppt, reliably determining VOC levels in air requires the most efficient and sensitive sampling, preconcentration and analysis techniques. In this respect, adsorptive enrichment on solid sorbents is a well-established technique which allows sampling and preconcentration in one step. After the preconcentration step, analytes are removed from the sorbent and then determined by gas chromatography. Nowadays, most official agencies use two desorption methods for determining VOC levels: solvent extraction and thermal desorption.

Solvent extraction is the commonest method of VOC desorption. The main sorbent for this method is activated charcoal (usually coconut shell charcoal) [7-10]. Activated charcoal has a very complex surface structure containing a wide range of functional groups which allow the adsorption of a wide range of compounds [11,12]. The desorbing solvent most commonly used with activated charcoal is carbon disulfide due to its high volatility, its high adsorption heat on activated charcoal (which displaces other molecules), and its effectiveness at dissolving non-polar compounds. Moreover, it elutes rapidly at the front of the analysis on most common GC columns and has a very low response on FID [13].

The solvent extraction method is simple, compatible with high molecular mass and thermally unstable compounds and allows the preconcentration of high volumes of air. However, it has several drawbacks. The major disadvantage is that the sample is diluted with the desorbing solvent, which increases the method detection limit. As a consequence, this method requires long sampling periods and the preconcentration of large volumes of air. Moreover, polar and reactive compounds often have poor desorption efficiencies that can vary further with the presence of other polar species or water vapour [11,14-16]. These low recoveries can be associated with the strength of multiple binding interactions and even irreversible adsorptions and catalytic transformations of the analytes into different products. Regarding the solvent, CS_2 can react with certain compounds such as amines, which can interfere with the analysis of volatile chlorinated carbons and may vaporise some very volatile molecules during the procedure because of the heat of the desorption [13]. Furthermore, CS_2 has highly toxic health effects [4], causes serious environmental damage and has a high response on MS.

Thermal desorption is a good alternative to solvent desorption and is also used in several official methods like the UNE-EN 14662-1 for benzene and the EPA TO-17 for VOCs [17,18]. This method provides enhanced sensitivity (since the whole sample is analysed), is compatible with thermally stable polar and apolar compounds, enables the reuse of the adsorbent tubes, avoids the use of toxic solvents in the extraction step and, in consequence, prevents the solvent's signal from masking the analyte peaks in the sample chromatograms.

There is a wide variety of commercial sorbents that can be used with the thermal desorption technique. The main types of sorbents used in air monitoring are porous organic polymers, graphitised carbon blacks and carbon molecular sieves [1,11,19]. The selection of a suitable sorbent depends not only on the physical and chemical characteristics of the VOC studied, but also on sampling conditions such as the meteorological conditions, time of sampling and sample volume. Consequently, recent studies tend to use multiple-bed sorbent cartridges which provide high breakthrough volumes and the quantitative retention and desorption of VOCs over a wide volatility range [20-24].

The main drawbacks of thermal desorption are: the initial cost of the equipment; the possible degradation of those sorbents that generate artefacts and blanks of some analytes, which can interfere in the analysis; and the consumption of the sample in a single analysis (although modern equipment allows the recollection of split samples in a fresh tube). Moreover, thermal desorption is not recommended for thermally unstable compounds and for compounds with high boiling points (above 300 °C) because the desorption efficiencies decrease.

Since the solvent and thermal desorption methods are based on quite different physical and chemical processes, it is important to study how this affects the accuracy and precision of the overall emission estimates. Hence, the aim of this paper is to compare two methods used for monitoring VOCs: one based on solvent extraction (method A) and one based on thermal desorption (method B). Both methods were used to determine the levels of 90 VOCs that are commonly found in industrial and urban atmospheres and that have a wide range of different physical and chemical characteristics.

Both methods were tested using real atmospheric samples taken from a location situated next to a petrochemical complex. As far as we know, this is the first study to compare the performance in real samples of both methods and the results when used to determine 90 compounds. Hence, this study should help in defining the most appropriate method for monitoring these compounds.

Table 1. Target VOCs in chromatographic elution order showing retention times (t_R), repetitivity, recovery and method detection and quantification limit, expressed in μg m^{-3}, for the solvent desorption (method A) and the thermal desorption method (method B).

No.	Target VOCs	t_R (min)	Repetitivity [a] (%RSD, n=5)		% Recoveries [b] (n=3)		MDL[c] (μg m^{-3})		MQL[d] (μg m^{-3})	
			Met. A	Met. B	Met. A	Met. B	Met. A	Met. B	Met. A	Met. B
1	i-Pentane [e]	3.87	0.66	2.49	99.2	85.0	0.69	0.04	1.39	0.19
2	1-Pentene [e]	4.08	3.87	2.45	96.3	99.8	0.69	0.19	1.39	0.38
3	n-Pentane [e]	4.20	2.11	2.42	99.5	99.7	0.28	0.02	0.69	0.04
4	Diethyl ether	4.30	8.79	2.67	99.0	99.8	0.69	0.04	1.39	0.19
5	2-Trans-pentene [e]	4.35	0.99	1.75	98.7	99.6	0.28	0.04	0.69	0.19
6	Isoprene [e]	4.38	1.68	3.38	97.4	94.9	0.69	0.28	1.39	0.38
7	2-Cis-pentene [e]	4.49	4.03	2.87	97.3	96.1	0.69	0.04	1.39	0.19
8	1,1-Dichloroethylene	4.59	3.77	1.14	96.1	95.7	0.28	0.03	0.69	0.04
9	Acrylonitrile [f,g]	4.63	7.06	0.99	100.1	100.0	0.14	0.002	0.69	0.02
10	1-Hexene	5.37	12.39	2.13	88.0	95.2	0.69	0.04	1.39	0.19
11	Trans-1,2-dichloroethene	5.63	4.52	3.27	95.4	97.9	0.69	0.02	1.39	0.04
12	Methyl-tercbutylether [f]	5.69	5.01	0.86	96.5	85.9	0.07	0.04	0.14	0.19
13	Propionitrile	5.88	8.30	1.21	97.4	100.1	0.07	0.04	0.14	0.19
14	1,1-Dichloroethane	6.00	7.13	2.38	96.3	100.2	1.39	0.02	2.78	0.04
15	n-Hexane [e,f]	6.54	2.67	2.10	96.7	96.6	0.28	0.03	0.69	0.04
16	Methacrylonitrile	6.55	4.45	1.45	96.8	99.8	0.01	0.004	0.07	0.04
17	Cis-1,2-dichloroethylene	6.92	5.58	2.32	100.2	99.9	0.69	0.02	1.39	0.04
18	Methylacrilate	7.10	3.95	0.98	95.9	99.8	0.69	0.004	1.39	0.04
19	2,2-Dichloropropane	7.14	4.40	3.48	97.7	84.1	0.28	0.02	0.69	0.04
20	Bromochloromethane	7.26	6.08	1.46	95.4	99.6	0.07	0.03	0.14	0.04
21	Chloroform [f]	7.33	7.15	1.85	100.8	99.8	0.01	0.02	0.07	0.04
22	Tetrahydrofuran	7.60	4.92	0.67	98.8	99.9	0.14	0.11	0.69	0.19
23	1,1,1-Trichloroethane [f]	8.29	6.86	2.75	101.3	97.5	0.07	0.02	0.14	0.19
24	1-Chlorobutane	8.40	9.02	2.24	65.1	99.5	0.07	0.01	0.14	0.19
25	1,2-Dichloroethane [g]	8.42	2.29	2.36	101.6	99.4	0.69	0.004	1.39	0.04
26	1,1-Dichloropropene	8.66	7.60	2.67	97.8	99.5	0.28	0.02	0.69	0.04
27	Benzene [e,f,g]	8.92	0.96	1.47	98.3	100.0	0.28	0.16	0.69	0.38
28	Carbon tetrachloride [f]	8.97	5.66	3.75	101.4	95.0	0.69	0.02	0.69	0.19
29	Chloroacetonitrile	9.41	10.29	3.68	87.6	99.7	0.07	0.04	0.14	0.19
30	i-Octane [e]	9.83	4.03	3.01	100.5	97.7	0.28	0.02	0.69	0.04
31	n-Heptane [e]	10.28	2.38	2.96	98.3	100.0	0.28	0.03	0.69	0.19
32	2-Nitropropane [f]	10.29	5.35	1.15	99.0	99.5	0.07	0.004	0.14	0.02

Table 1 (cont.)

33	1,2-Dichloropropane [f]	10.38	4.94	0.41	99.5	99.6	0.07	0.01	0.14	0.02
34	Trichloroethene [f,g]	10.41	8.26	2.01	100.9	99.5	0.28	0.004	0.69	0.02
35	Dibromomethane	10.51	5.96	0.83	100.3	99.8	0.14	0.02	0.69	0.04
36	1,4-Dioxane [f]	10.68	5.96	6.34	100.2	99.4	0.07	0.30	0.14	0.38
37	Methylmethacrylate [f]	10.78	5.64	2.68	91.2	99	0.07	0.004	0.14	0.38
38	Bromodichloromethane	10.77	4.90	1.56	101.4	99.3	0.07	0.004	0.14	0.04
39	Cis-1,3-dichloropropene	12.02	5.90	1.46	102.0	99.5	0.14	0.02	0.69	0.04
40	Trans-1,3-dichloropropene	13.05	5.25	2.89	101.9	99.7	0.14	0.02	0.69	0.04
41	Toluene [e,f,g]	13.23	5.95	1.05	99.9	99.6	0.07	0.23	0.14	0.38
42	1,1,2-Trichloroethane [f]	13.41	7.88	3.55	102.6	100.0	0.14	0.004	0.69	0.04
43	Ethylmethacrylate	13.77	3.86	3.40	102.8	99.8	0.07	0.004	0.14	0.04
44	1,3-Dichloropropane	13.87	12.92	2.21	104.7	99.3	0.14	0.004	0.69	0.04
45	n-Octane [e]	14.36	6.45	1.94	99.5	96.9	0.07	0.01	0.14	0.19
46	Dibromochloromethane	14.49	8.54	2.62	101.5	99.4	0.07	0.004	0.14	0.02
47	1,2-Dibromoethane	14.89	6.86	2.95	99.4	99.7	0.07	0.01	0.14	0.02
48	Tetrachloroethene [e,g]	14.95	16.93	0.43	102.3	98.7	0.07	0.002	0.14	0.02
49	Chlorobenzene [f]	16.48	5.01	3.07	100.5	99.3	0.07	0.002	0.14	0.02
50	1,1,1,2-Tetrachloroethane	16.60	4.26	2.82	99.6	99.1	0.28	0.004	0.69	0.02
51	Ethylbenzene [e,f]	16.99	4.66	2.59	101.7	99.2	0.07	0.04	0.14	0.08
52,53	m,p-Xylene [e,f]	17.31	4.55	2.51	99.8	98.9	0.01	0.02	0.07	0.04
54	Bromoform [f]	18.10	11.94	4.08	101.7	99.5	0.07	0.01	0.14	0.02
55	Styrene [f,g]	18.13	3.45	3.63	91.1	99.6	0.01	0.15	0.07	0.19
56	o-Xylene [e,f]	18.22	4.17	3.84	97.5	100.3	0.07	0.0004	0.14	0.04
57	1,1,2,2-Tetrachloroethane [f]	18.91	3.93	4.67	100.4	99.6	0.07	0.01	0.14	0.02
58	1,2,3-Trichloropropane	19.17	4.10	1.76	101.4	99.8	0.28	0.02	0.69	0.04
59	1,4-Dichloro-2-butene	19.24	1.40	3.95	103.7	99.7	0.07	0.03	0.14	0.04
60	Isopropylbenzene [f]	19.32	4.15	3.18	100.2	99.8	0.01	0.003	0.07	0.02
61	Bromobenzene	19.75	0.82	3.72	99.2	99.4	0.07	0.004	0.14	0.02
62	n-Propylbenzene	20.38	2.55	3.34	93.0	100.1	0.07	0.004	0.14	0.02
63	2-Chlorotoluene	20.42	4.47	3.61	96.5	99.9	0.01	0.01	0.07	0.02
64	4-Chlorotoluene	20.60	4.76	3.61	95.8	99.5	0.01	0.004	0.07	0.02
65	3-Ethyltoluene	20.62	5.02	3.58	93.2	99.5	0.01	0.002	0.07	0.004
66	4-Ethyltoluene	20.71	2.99	3.89	90.7	99.9	0.01	0.40	0.07	0.45
67	1,3,5-Trimethylbenzene [e]	20.87	4.51	3.80	95.5	99.9	0.01	0.002	0.07	0.004
68	2-Ethyltoluene	21.30	4.44	3.25	95.9	99.3	0.01	0.004	0.07	0.04
69	Pentachloroethane	21.35	10.85	4.03	82.4	99.7	0.07	0.02	0.14	0.04
70	tert-Butylbenzene	21.72	4.59	3.19	99.5	99.4	0.01	0.004	0.07	0.02

Table 1 (cont.)

71	1,2,4-Trimethylbenzene [e]	21.78	1.90	3.52	95.9	98.2	0.01	0.01	0.07	0.02
72	1,3-Dichlorobenzene	22.30	2.46	4.56	90.4	98.3	0.07	0.004	0.14	0.02
73	sec-Butylbenzene	22.31	4.61	3.85	99.4	99.4	0.07	0.002	0.14	0.004
74	1,4-Dichlorobenzene [f]	22.52	0.71	4.04	90.3	99.6	0.01	0.004	0.07	0.02
75	p-Isopropyltoluene	22.69	4.00	3.65	100.3	99.6	0.01	0.01	0.07	0.02
76	1,2,3-Trimetylbenzene [e]	22.73	2.67	3.63	88.8	98.3	0.01	0.004	0.07	0.01
77	Benzyl alcohol	22.93	5.35	1.57	82.6	95.0	0.01	0.0004	0.07	0.002
78	1,2-Dichlorobenzene	23.20	2.77	2.96	97.7	99.2	0.01	0.004	0.07	0.02
79	1,3-Diethylbenzene	23.34	2.51	4.23	85.3	99.5	0.01	0.004	0.07	0.02
80	1,4-Diethylbenzene	23.56	2.44	4.09	93.4	99.5	0.01	0.004	0.07	0.02
81	n-Butylbenzene	23.58	5.35	2.14	88.1	98.3	0.01	0.002	0.07	0.004
82	1,2-Diethylbenzene	23.72	3.81	4.02	91.1	97.2	0.01	0.004	0.07	0.02
83	Hexachloroethane [f]	24.37	4.83	3.80	97.6	95.1	0.07	0.02	0.14	0.04
84	1,2-Dibromo-3-chloropropane	24.45	6.28	4.09	97.0	98.6	0.28	0.02	0.69	0.04
85	1,2,4-Trichlorobenzene	26.53	1.44	4.09	82.2	99.6	0.01	0.004	0.07	0.04
86	Naphthalene [f,g]	26.79	8.28	1.33	78.3	92.0	0.07	0.04	0.14	0.10
87	Hexachlorobutadiene	27.17	3.45	4.16	100.6	99.5	0.07	0.004	0.14	0.02
88	1,2,3-Trichlorobenzene	27.24	7.98	3.60	87.8	99.3	0.01	0.004	0.07	0.02
89	2-Methylnaphtalene [f,g]	28.77	8.47	1.70	47.4	91.5	0.07	0.02	0.14	0.04
90	1-Methylnaphtalene [f,g]	29.11	8.01	1.50	47.0	91.2	0.04	0.002	0.07	0.004

[a] Repetitivity expressed as relative standard deviation (%RSD) for the analysis of 1 ng VOCs standard (n=5).
[b] Recoveries calculated as the percentage recovery of the response obtained by the triplicate analysis of a 1 ng standard using method A or method B, compared with the response obtained by direct injection of the same amount of standard under the same split conditions.
[c] Method detection limit (MDL), expressed in μg m^{-3}, calculated for a sampling volume of air of 720 L (method A) and 2.64 L (method B).
[d] Method quantification limit (MQL), expressed in μg m^{-3}, calculated for a sampling volume of air of 720 L (method A) and 2.64 L (method B).
[e] Compounds included in the USEPA List of Hazardous Air Pollutants [25].
[f] Ozone precursors recommended for measurement by the Directive 2002/3/EC [26].
[g] Compounds included as hazardous organic pollutants in the WHO Air Quality Guidelines [4].

2. EXPERIMENTAL

2.1. Chemical standards

The list of the 90 target VOCs is shown in Table 1. The VOCs were selected on the basis of their occurrence in industrial and urban air and their adverse effects on the environment and human health. Twenty-seven of the ninety compounds are included in the list of Hazardous Air Pollutants (HAPs) of the US EPA Clean Air Act [25], eighteen of them are ozone precursors

recommended for measurement by the Directive 2002/3/EC [26] and ten of them are included as hazardous organic pollutants in the World Health Organization Air Quality Guidelines [4].

The standards of the 90 target compounds involve two mixtures of volatile organic compounds at 2000 mg L^{-1} (592/524 Volatile Organics Calibration Mix and EPA 524.2 Revision 4 Mix in methanol, from Supelco, Bellefonte, USA) and the individual standards of i-pentane, 1-pentene, n-pentane, 2-pentene (cis/trans mixture), isoprene, 1-hexene, n-hexane, i-octane, n-heptane, 1,4-dioxane, n-octane, 1,2,3-trimethylbenzene, benzyl alcohol (Sigma-Aldrich, Steinheim, Germany), 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, 1,2-diethylbenzene, 1,3-diethylbenzene, 1,4-diethylbenzene (Fluka, Buchs, Switzerland), 1-methylnaphthalene and 2-methyl-naphthalene (Riedel-deHaën, Seelze, Germany). The minimal purity of the standards was 97%. Toluene-d_8 from Aldrich was used as an internal standard for method A as recommended by the UNE-EN 14662-2 [10].

The standards were diluted in methanol for gas chromatography with purity >99.9% (SDS, Peypin, France) and with a toluene-d_8 constant concentration of 5 mg L^{-1} for method A. All the standards were prepared on the day of use, and stored at 4 °C in 10 mL Certan® capillary vials provided by Supelco. Nitrogen gas of 99.999% purity was used to activate the thermal desorption sorbent tubes and 99.999% pure helium gas was used for the chromatographic analysis (Carburos Metálicos, Barcelona, Spain). Carbon disulfide from Sigma-Aldrich (purity 99.9% with less than 0.001% of benzene) was used for the solvent extraction method.

2.2. Analytical methods

2.2.1. Method A

Standard charcoal tubes Orbo™-32 (provided by Supelco) were used for the solvent extraction method. These cartridges are glass tubes with both ends flame sealed (7 cm long × 6-mm o.d.) and contain two sections of 20/40 mesh coconut activated charcoal separated by a 2-mm portion of urethane foam. The adsorbing section, which is the longest, contained 100 mg of charcoal and the back-up section 50 mg.

Samples were collected by active sampling at the large section end of the tube. A volatile organic compounds sampler CPV-COV-S (MCV, Collbató, Spain) with a module that allows the sequential sampling of up to nine samples was used to pump air samples at a flow rate of 500 mL min^{-1}, for 24 h, thus collecting 720 L of air. After sampling, the charcoal tubes were removed from the sampler and the two open sides were tightly closed with special PTFE caps to avoid undesirable desorption. Then samples were stored in hermetic glass jars at –20°C until the

analysis, in order to prevent the risk of contamination and deterioration. Samples were analysed no later than 1 week after collection. To detect possible contamination, weekly field blanks were tested by putting a charcoal tube with broken ends in a channel of the sampler but without passing any air sample though it. The blank tube was then collected and analysed.

In preparation for the analysis, each charcoal tube was scored with a quartz blade (Orbo™ tube cutter, Supelco) in the front of the first section (i.e. the adsorbing section) of charcoal and broken open. The glass wool was removed and discarded. The charcoal in the adsorbing section was transferred to a 2-mL capped vial. The separating foam was removed and discarded; the second section (back-up section) was transferred to another capped vial. These two sections were analysed separately.

To desorb the samples, 1 mL of desorbing solution was pipetted into each sample vial. The desorption solution consisted of 5 ppm of internal standard solution in carbon disulfide. The sample vials were capped with PTFE as soon as the solution was added. Desorption was done for 30 minutes with occasional shaking.

Immediately after the solvent process, 1 µl of sample extract was injected into a split/splitless inlet port. Chromatographic conditions are detailed in Section 2.3.

2.2.2. Method B

The cartridges used for the thermal desorption method were stainless-steel tubes (89 mm long × 6.4 mm o.d.) filled with a multisorbent bed of approximately 350 mg of Tenax TA/ Carbograph 1TD (Markes International Limited, Llantrisant, UK). The selection of the two sorbent materials was based on previous studies [13,20,27].

Before each use, tubes were conditioned by thermal cleaning (100 °C for 15 minutes, 200 °C for 15 minutes and 325 °C for 30 minutes) under a nitrogen flow rate of 100 mL min^{-1} (purity 99.999%, Carburos Metálicos, Tarragona, Spain). After conditioning, the tubes were sealed with Swagelok end caps fitted with PTFE ferrules and stored in hermetically sealable glass jars with desiccant material in order to prevent any ambient contamination of the sorbents. An MTS-32™ sequential tube sampler coupled with a constant flow sampling pump (FLEC Air Pump 1001, from Markes) was used to pump air samples. This equipment allows the sequential sampling of 32 tubes. The sampling volume was fixed at 22 mL min^{-1}, for 2 hours and 2.64 L of air were collected. Samples were collected at the Tenax TA end of the tube in order to collect the heaviest hydrocarbons first. The Tenax TA end of the tubes were capped with DiffLok™ caps which allow air to pass when sampling while also protecting the sample tubes for up to 8 days.

Blanks of the total process were checked by putting two blank tubes into the sequential tube sampler every sampling day without passing any of the air sample through it.

Desorption of the analytes retained on the Tenax TA – Carbograph 1TD sorbent tubes was carried out in a Unity Thermal Desorption system connected to an Ultra A automatic sampler (both from Markes International Limited, Llantrisant, UK). In the primary desorption the sorbent tubes were heated to 275 °C with a helium flow rate of 30 mL min^{-1} for 10 min and no split. The desorbed VOCs were refocused into a cold trap, filled with Tenax TA and Carbograph 1TD and cooled at -5 °C. In the secondary desorption the cold trap was flash-heated at 300 °C for 3 min, with a split flow of 5 mL min^{-1}, and analytes were injected into the chromatographic column. Additional details about the thermal desorption system were given in previous studies [20,27].

2.3. Chromatographic conditions

In both methods, separation and detection were performed in a 6890N gas chromatograph and 5973 inert mass spectrometer (Agilent Technologies. Palo Alto, USA), using a TRACSIL Meta.X5 capillary column (60 m, 0.32 mm, 1.0 µm, provided by TEKNOKROMA, Barcelona, Spain). Analyses with method A were performed by injecting 1 µL of extract in a split/splitless port at 180 °C with a split of 5 mL min^{-1} and a helium flow rate of 1.2 mL min^{-1}. The oven temperature of the GC was initially held at 40 °C for 5 min, then raised to 140 °C at a rate of 6 °C min^{-1} and then raised again to 220 °C at a rate of 15 °C min^{-1} and held at that temperature for 8 min.

For method B, the interface between the thermal desorption system and the GC was set at 200 °C. The analyses were performed with a helium flow rate of 1.5 mL min^{-1} and the same GC oven program of temperatures as method A. The flow rate for method B was higher than for method A because higher flow rates were needed to completely desorb the trap.

In both methods, the GC-MS interface was set at 280 °C. The mass spectrometer acquired data in scan mode with an *m/z* interval from 35 to 280 and an electron impact energy of 70 eV. Qualitative identification of target VOCs was based on the match between the retention times and the ion ratios of the target quantifier and qualifier ions. The retention times are shown in Table 1. The quantifier and qualifier ions for each target compound have been published elsewhere [27]. The internal standard calibration method was used for the GC-MS quantification in method A and the external standard calibration was used in method B.

2.4. Calibration

Calibration in both methods was done by enriching the sorbent tubes with the liquid standards using a Calibration Solution Loading Rig (Markes Inter-

national Limited, Llantrisant, UK). Volumes of between 1 and 5 µL were injected into the sorbent tubes while a flow of 100 mL min^{-1} of helium passed through the tube to carry the analytes into the sorbent. To ensure the full retention of the analytes and the repeatability of the injection, the syringe was placed in the sorbent for 20 s and in the helium stream for 5 minutes before the tubes were sealed and immediately desorbed and analysed as described above.

2.5. Sampling sites

Field samples were taken at Perafort (Tarragona, Spain). This location is sited less than 1 km from the North Industrial Complex and about 15 km from the main city, Tarragona. Some of the products manufactured at this complex are vinyl acetate, benzene, chloroform, methylene chloride, acrylonitrile, methylmetacrylate, ethyl-benzene, styrene, fuels, propane and kerosene [28]. Samples were collected in October and November 2008.

3. RESULTS AND DISCUSSION

3.1. Comparison of the analytical methods

Although both analytical methods have been proposed by several official organisations for monitoring benzene and other VOCs in air, they differ regarding the sorbent used for the preconcentration step in the analyte extraction method. These differences were tested for the 90 target VOCs because they affect the analytical parameters.

Due to the dilution of the sample with the extraction solvent, method A needs a high volume of air to be preconcentrated in order to achieve acceptable limits of detection, whereas a low volume is enough for method B. Prior to determining the sample volume for each method, blank signals of the sorbents were checked because they affect the method detection limits and overall performance. To quantify these blanks, the responses of the blank tubes were compared with the responses obtained by directly injecting the standards under the same split conditions. Blanks of the activated charcoal tubes (method A) were determined by extracting and analysing the sorbent, from the adsorbing section of 8 new tubes under the same conditions as the samples (see Section 2.2.1.). These blanks showed the presence of only two of the target compounds: n-hexane (0.09±0.05 ng per tube) and benzene (0.07±0.04 ng per tube). Blanks of the thermal desorption tubes (method B) were checked by analysing 8 freshly cleaned sorbent tubes also under the same conditions as the samples (see Section 2.2.2.). A total of 21 target VOCs were found in the method B tubes in amounts ranging from 0.0012±0.0003 ng for the o-xylene, to 0.30±0.25 ng for 4-ethyltoluene. The method B blanks for n-hexane and benzene were

0.03±0.01 ng and 0.23±0.07 ng, respectively. The values of the average blank concentrations for the remaining compounds in method B were similar to those reported in a previous paper [27]. The subsequent analysis of real samples showed that amounts of VOCs in the blank tubes were less than 5% of the average amounts found in samples, as recommended by EPA [18].

To fix the sample volume, breakthrough tests were performed for both methods. For method A, the back-up section of the charcoal tubes was analysed under the same conditions as the adsorptive section. In the eight samples analysed with method A the concentration of the target VOCs in the back-up section was under the method quantification limit at the fixed rate of 500 mL min^{-1} for 24 hours (720 L of air collected). To set the sampling volume of method B, two fresh cleaned sorbent tubes were connected in series so that the back tube would retain the analytes eluted from the front tube. Although the recommended sampling volume for method A for benzene is 10 L [17], the presence of more volatile target analytes caused the rate to be set at 22 mL min^{-1} for 2 hours, which meant that 2.64 L of air was collected. At this volume, ten target compounds were present in the second tube at concentrations ranging from 2.4% for chloroform to 4.8% for n-pentane, compared with their respective concentrations in the first tube. This does not exceed the 5% recommended by the EPA [18].

Table 1 shows the repetitivity and recovery as well as the method detection and quantification limit for the 90 target VOCs determined by both methods. The repetitivity of both methods was calculated as the relative standard deviation (%RSD) of the analyses of five replicates of 1 ng from VOC standard mixture. The method A tubes were filled with 1000 ng of each VOC, extracted with 1 mL of solvent (see Section 2.2.1.) and then 1 µL of the extract was analysed. The method B tubes were directly filled with 1 ng of standard mixture and then analysed (see Section 2.2.2). Repetitivities of method A (ranging from 0.66% RSD for i-pentane to 12.9 % RSD for 1,3-dichloropropene) were generally higher than those of method B (ranging from 0.41 % RSD for 1,2-dichloropropane to 6.34 % RSD for 1,4,-dioxane). None of them exceeded the 25% recommended by EPA [29].

Recoveries were measured as the percentage recovery of the response obtained by the triplicate analysis of 1 ng of VOCs using method A or method B and compared with the response obtained by direct injection of the same amount of VOCs under the same split conditions. Recoveries for most of the target compounds were higher than 95% for both methods. However, polar compounds tended to show lowest recoveries with method A. For instance, 1-chlorobutane had a recovery of 65.1% with method A and 99.5% with method B and benzyl alcohol had a recovery of 82.6% for method A and

95% for method B. The same trend was seen with voluminous compounds like naphthalene (78.3% with method A vs. 92% with method B), 2-methylnaphthalene (47.4% with method A, 91.5% with method B) and 1-methylnaphthalene (47% method A, 91.2% method B). These results agree with similar trends that have previously been reported [11, 13, 30].

The method detection limits (MDLs) of both methods were evaluated in two ways. For target compounds without blank signal, MDLs were determined as the concentrations corresponding to three times the noise signal of the quantifier ion. For target compounds which present a signal in the blank, the MDLs were established as the sum of the average concentrations of the blank responses plus three times the standard deviation of this signal (n=8). For all target VOCs the method quantification limits (MQLs) were fixed as the lowest calibration level. The MDLs of method A for 720 L of sample (ranging from 0.01 μg m^{-3} for several compounds such as methacrylonitrile or m,p-xylene, to 1.39 μg m^{-3} for 1,1-dichloroethane) were generally higher than those of method B for 2.64 L of sample, (ranging from $4x10^{-4}$ μg m^{-3} for o-xylene and benzyl alcohol, to 0.4 μg m^{-3} for 4-ethyltoluene). Exceptions were 1,4-dioxane (0.07 μg m^{-3} by method A and 0.3 μg m^{-3} by method B), toluene (0.07 μg m^{-3} by method A, 0.23 μg m^{-3} by method B), styrene (0.01 μg m^{-3} by method A and 0.15 μg m^{-3} by method B) and 4-ethyltoluene (0.01 μg m^{-3} by method A and 0.40 μg m^{-3} by method B) because of the presence of a signal of both compounds in the blanks of method B sorbent tubes.

Similarly, MQLs for method A were generally higher than those for method B. For method A MQLs ranged from 0.07 μg m^{-3} for some compounds such as m, p -xylene and n-propylbenzene, to 2.78 μg m^{-3} for 1,1-dichloroethane. For method B MQLs ranged from 0.002 μg m^{-3} for benzyl alcohol to 0.45 for 4-ethyltoluene. Exceptions were also 1,4-dioxane (0.14 μg m^{-3} by method A and 0.38 μg m^{-3} by method B)), toluene (0.14 μg m^{-3} by method A, 0.38 μg m^{-3} by method B), styrene (0.07 μg m^{-3} by method A and 0.19 μg m^{-3} by method B) and 4-ethyltoluene (0.07 μg m^{-3} by method A and 0.45 μg m^{-3} by method B). These results agree with those reported in a previous study, which compared the solvent extraction and the thermal desorption method for eight VOCs (benzene, toluene, ethylbenzene, m,p,o-xylene and 1,2,4 and 1,3,5-trimetylbenzene), and also showed lower detection limits and better instrumental repetitivities for the thermal desorption method [31].

3.2. Comparison of the performance in real samples

Results of both methods in real samples were compared by sampling atmospheric air over eight days in a location situated next to a petrochemical complex. Eight samples collected for 24 hours and analysed by

method A were compared with the mean daily values of 96 samples (12 per day) collected for 2 hours and analysed by method B in the same period of time. Figure 1 shows the typical chromatograms of the samples with method A (Figure 1A) and with method B (Figure 1B). Some of the most representative compounds of each sample are marked. Of particular note in Figure 1A is the high and wide signal of carbon disulfide, the extraction solvent. Table 2 shows the average concentrations of the compounds found in the samples by both methods. Signals of the target compounds in field blanks were taken into account when calculating sample concentrations.

It is worth mentioning that in the period sampled only 18 of the 90 VOCs were detected and quantified by method A, while method B quantified 50 of them.

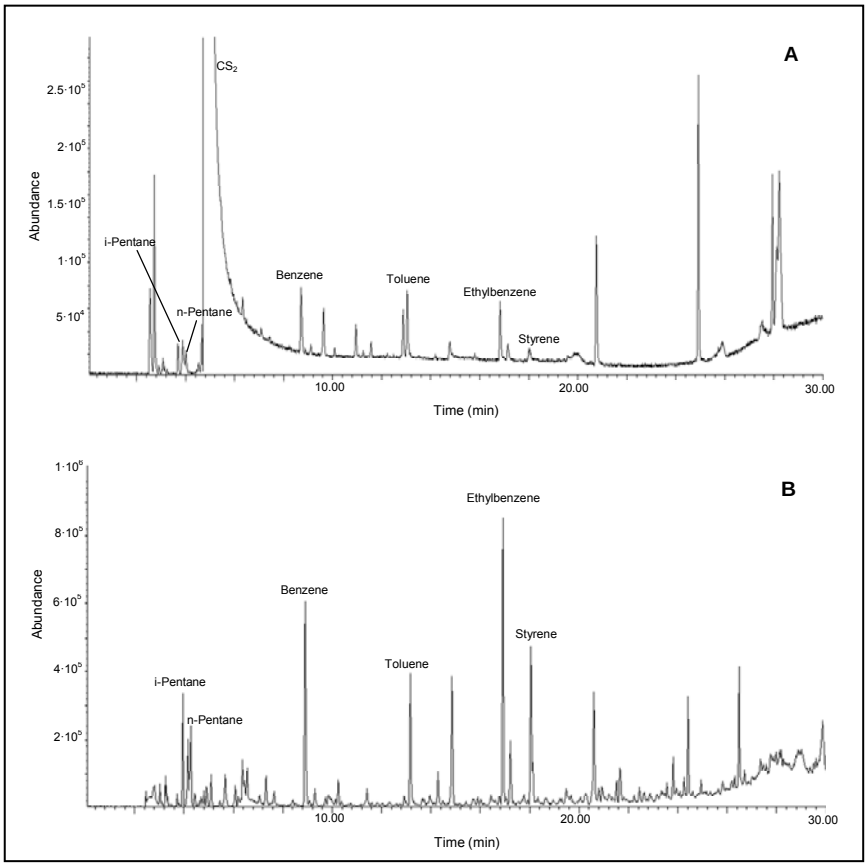


Figure 1. Total ion chromatograms of an air sample by method A (A) and by method B (B). Some of the most representative compounds are marked.

Table 2. Average concentration, expressed in μg m^{-3}, of target compounds found in real samples by the solvent extraction method (A) and the thermal desorption method (B).

Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7		Day 8	
A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
3.90	33.04	6.90	32.25	3.70	17.94	5.90	54.90	10.60	49.49	9.90	76.85	5.10	52.09	5.40	61.44
2.80	10.55	3.50	12.53	2.80	9.57	3.50	19.82	5.20	20.55	4.00	17.51	2.70	11.74	2.80	15.92
n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n.d.	1.15	n.d.	2.86	n.d.	1.23	n.d.	1.79	n.d.	2.57	n.d.	1.16	n.d.	1.17	n.d.	1.61
n.d.	4.21	n.d.	4.87	n.d.	2.05	n.d.	3.84	n.d.	3.97	n.d.	1.31	n.d.	0.87	n.d.	1.88
n.d.	1.43	n.d.	4.50	n.d.	1.41	n.d.	2.09	n.d.	2.32	n.d.	1.18	n.d.	1.46	n.d.	1.74
n.d.	0.95	n.d.	2.45	n.d.	2.82	n.d.	26.59	n.d.	6.64	n.d.	42.01	n.d.	47.77	n.d.	6.05
n.d.	0.88	n.d.	0.39	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n.d.	0.54	n.d.	0.13	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1.40	2.38	1.70	5.84	2.30	2.47	2.30	4.17	3.70	6.69	2.20	4.74	2.00	2.58	1.90	4.20
n.d.	1.08	n.d.	0.38	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
0.80	0.69	0.80	1.20	0.80	0.36	0.80	0.52	0.90	0.64	0.80	0.32	0.80	0.38	0.80	0.71
n.d.	0.98	n.d.	0.33	n.d.	0.15	n.d.	0.38	n.d.	0.27	n.d.	0.11	n.d.	0.53	n.d.	0.55
n.q.	1.68	n.d.	3.25	n.d.	0.22	n.d.	0.82	1.50	2.96	n.d.	0.13	n.d.	0.31	n.q.	3.81
1.40	2.53	1.60	7.77	2.90	8.52	3.60	17.15	6.40	14.46	4.00	14.10	1.70	10.50	1.30	9.18
1.30	1.04	1.40	1.00	1.50	1.06	1.60	1.08	2.20	1.16	1.30	0.84	1.20	0.96	1.20	1.29
1.30	0.77	1.60	2.62	1.50	0.86	1.50	1.47	2.10	2.35	1.60	1.65	n.d.	1.03	n.d.	1.58
0.80	0.66	1.00	2.34	0.90	0.67	0.90	1.04	1.40	1.53	1.10	1.17	1.30	0.79	1.40	1.15
2.10	0.69	2.10	0.54	2.00	0.08	2.00	0.15	2.00	0.25	2.00	0.10	0.70	0.10	0.80	0.28
n.d.	0.86	n.d.	0.02	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.10
n.d.	0.67	0.70	4.05	n.d.	0.25	n.d.	1.42	n.d.	0.24	0.80	1.11	0.50	0.63	n.d.	0.18
3.90	8.60	5.20	12.08	3.60	5.05	4.10	8.18	3.90	8.96	3.90	6.64	2.20	3.93	2.50	6.17
n.d.	0.44	1.20	1.59	1.10	0.40	1.20	0.87	1.10	1.32	1.30	0.71	1.10	0.72	1.20	0.98
0.20	0.87	0.20	0.81	n.q.	0.31	0.10	0.48	n.q.	0.62	n.q.	0.28	n.q.	0.25	n.q.	0.58
1.40	1.68	1.90	3.50	1.50	1.57	4.60	13.60	5.70	7.06	5.60	13.76	2.20	5.13	1.80	3.88

Table 2. (cont.)

1.50	2.23	1.90	3.29	1.20	0.94	1.30	1.55	2.00	1.87	1.40	1.28	1.10	0.82	1.20	1.42
1.30	0.54	1.60	2.67	1.70	1.82	2.80	4.45	3.50	4.09	4.30	5.74	3.20	7.52	1.70	1.59
1.10	1.00	1.68	1.53	1.00	0.46	1.00	0.79	1.50	0.88	1.10	0.61	0.70	0.44	0.90	0.65
n.d.	0.08	n.d.	0.12	n.d.	0.05	n.d.	0.05	n.d.	0.04	n.d.	0.05	n.d.	0.02	0.80	0.04
n.d.	0.26	n.d.	0.61	n.d.	0.20	n.d.	0.35	n.d.	0.28	n.d.	0.26	n.d.	0.18	n.d.	0.24
n.d.	0.34	n.d.	0.56	n.d.	0.22	n.d.	0.34	n.d.	0.37	n.d.	0.28	n.d.	0.21	n.d.	0.29
n.d.	0.84	n.d.	2.43	n.d.	0.82	n.d.	1.56	n.d.	0.76	n.d.	0.61	n.d.	0.29	n.d.	0.65
n.d.	0.29	n.d.	0.45	n.d.	0.18	n.d.	0.22	n.d.	0.24	n.d.	0.18	n.d.	0.13	n.d.	0.19
n.d.	0.10	n.d.	0.22	n.d.	0.03	n.d.	0.09	n.d.	0.10	n.d.	0.07	n.d.	0.03	n.d.	0.06
n.d.	0.09	n.d.	0.09	n.d.	0.06	n.d.	0.06	n.d.	0.05	n.d.	0.02	0.70	0.04	0.70	0.02
n.d.	0.36	n.d.	1.13	n.d.	0.22	0.90	0.49	n.d.	0.56	0.90	0.34	n.d.	0.21	n.d.	0.35
n.d.	0.10	n.d.	0.13	n.d.	0.05	n.d.	0.07	n.d.	0.06	n.d.	0.05	0.90	0.03	0.90	0.05
n.d.	0.15	n.d.	0.13	n.d.	0.07	n.d.	0.06	n.d.	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01
0.80	0.24	n.d.	1.44	n.d.	0.01	n.d.	0.06	n.d.	0.07	n.d.	0.03	n.d.	0.01	0.80	0.02
n.d.	0.07	n.d.	0.42	n.d.	0.04	n.d.	0.07	n.d.	0.08	n.d.	0.04	n.d.	0.02	0.80	0.04
n.d.	2.01	n.d.	4.33	n.d.	0.04	n.d.	0.80	n.d.	0.64	n.d.	0.00	n.d.	1.17	n.d.	0.07
n.d.	0.04	n.d.	0.08	n.d.	0.11	n.d.	0.15	n.d.	0.12	n.d.	0.14	n.d.	0.08	n.d.	0.08
n.d.	0.25	n.d.	0.29	n.d.	0.19	n.d.	0.26	n.d.	0.28	n.d.	0.20	n.d.	0.15	n.d.	0.19
n.d.	0.03	n.d.	0.35	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n.d.	0.18	n.d.	0.13	n.d.	0.17	n.d.	0.12	n.d.	0.02	n.d.	0.04	n.d.	0.01	n.d.	n.d.
n.d.	n.d.	n.d.	2.98	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n.d.	0.19	n.d.	0.13	n.d.	0.17	n.d.	0.12	n.d.	0.01	n.d.	0.05	n.d.	0.02	n.d.	0.01
n.d.	0.02	n.d.	1.45	n.d.	0.02	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n.d.	n.d.	n.d.	2.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
25.70	88.12	34.60	134.7	28.50	63.22	38.10	172.1	63.90	145	46.20	195.7	28.30	154.4	28.90	134.1

n.d.: compound not detected (value < MDL) and n.q.: compound not quantified (value< MQL).

In general concentrations from method A were lower than the daily average concentrations obtained from method B. However, some compounds showed occasionally higher concentrations with method A, for instance, chloroform, carbon tetrachloride, n-heptane, trichloroethene, n-octane, m,p-xylene, styrene, o-xylene and p-iso-propyltoluene. The analytes which had the highest differences in the values obtained by both methods were i-pentane, n-pentane, benzene, toluene and ethylbenzene. These compounds also showed the highest concentrations and the highest dispersion of the values in the 12 two-hour samples collected per day by method B. For example, Figures 2A and 2B show, for benzene and o-xylene respectively, the correlation between the values for method A and the average values of the 12 method B samples for each sampled day. These figures show some correlation between the results obtained by both methods for both compounds. However, the slope of benzene, which showed high concentration values for both methods and high dispersion for method B (method A 2.9±1.8 μg m^{-3}, method B 10.5±12.4 μg m^{-3}), is further from the ideal slope 1 than that of o-xylene, which had low concentration values for both methods and less dispersion for method B (method A 1.1±0.2 μg m^{-3}, method B 0.8±0.7 μg m^{-3}).

Furthermore, Figure 3 compares the results obtained in the real samples by both methods for four compounds: benzene, m,p-xylene, styrene and o-xylene (Figures 3A to 3D, respectively). In these figures it can be observed that the variability in the concentrations of the investigated compounds that can be detected by method B is not detected by method A. Specifically, the high increases in the concentrations detected by method B do not correspond to a proportional increase in the average concentration detected by method A. For instance, the maximal concentration of benzene that was detected on the 4th day of sampling between 12 to 14 hours (70.4 μg m^{-3}, Figure 3A) and which considerably increases the average concentration of this compound for method B does not correspond to a proportional increase in the average concentration detected by method A. However, in the case of styrene (Figure 3C), method A and B seemed to correlate on most of the days sampled except for the 7th day. Hence, in most cases method A does not detect the dynamics of changes in ambient air quality over small periods of time.

Moreover, method B identifies which compounds could have the same origin. For instance, the similar profile of concentrations in method B for m,p-xylene and o-xylene (Figures 3B and 3D) can indicate the same focus of emission and similar behaviour in atmospheric samples. Other analytes showed similar profiles in method B, such as i-pentane, n-pentane (figures not shown).

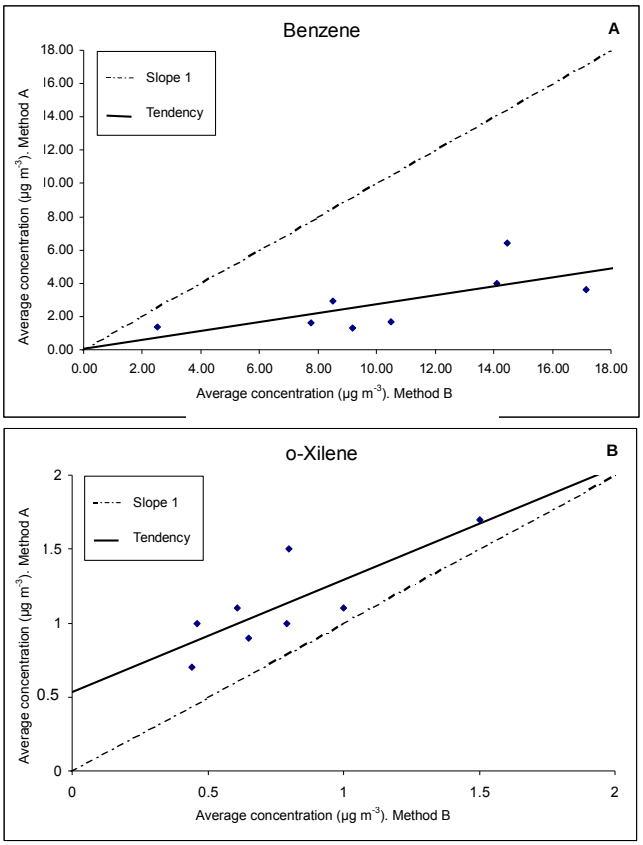


Figure 2. Correlations of the average concentrations, in µg m^{-3}, obtained by both methods for benzene (A) and o-xylene (B).

As far as we know, this is the first study to compare the performance of both methods in real samples. Nevertheless, some authors have studied the factors which can affect the performance of both methods. For example, it is known that meteorological conditions, particularly humidity, can considerably influence the methods [11, 13]. The sorbents used in method B (Tenax TA and Carbograph 1TD) are relatively hydrophobic and are poorly affected by ambience humidity [13]. However, when relative humidity is greater than 50%, water can be adsorbed in the active sorbent centres of the activated charcoal surface, which becomes hydrophilic. The water adsorbed can displace organic molecules, react with them or form an immiscible phase on desorption into which polar molecules can partition and essentially be lost to analysis [13].

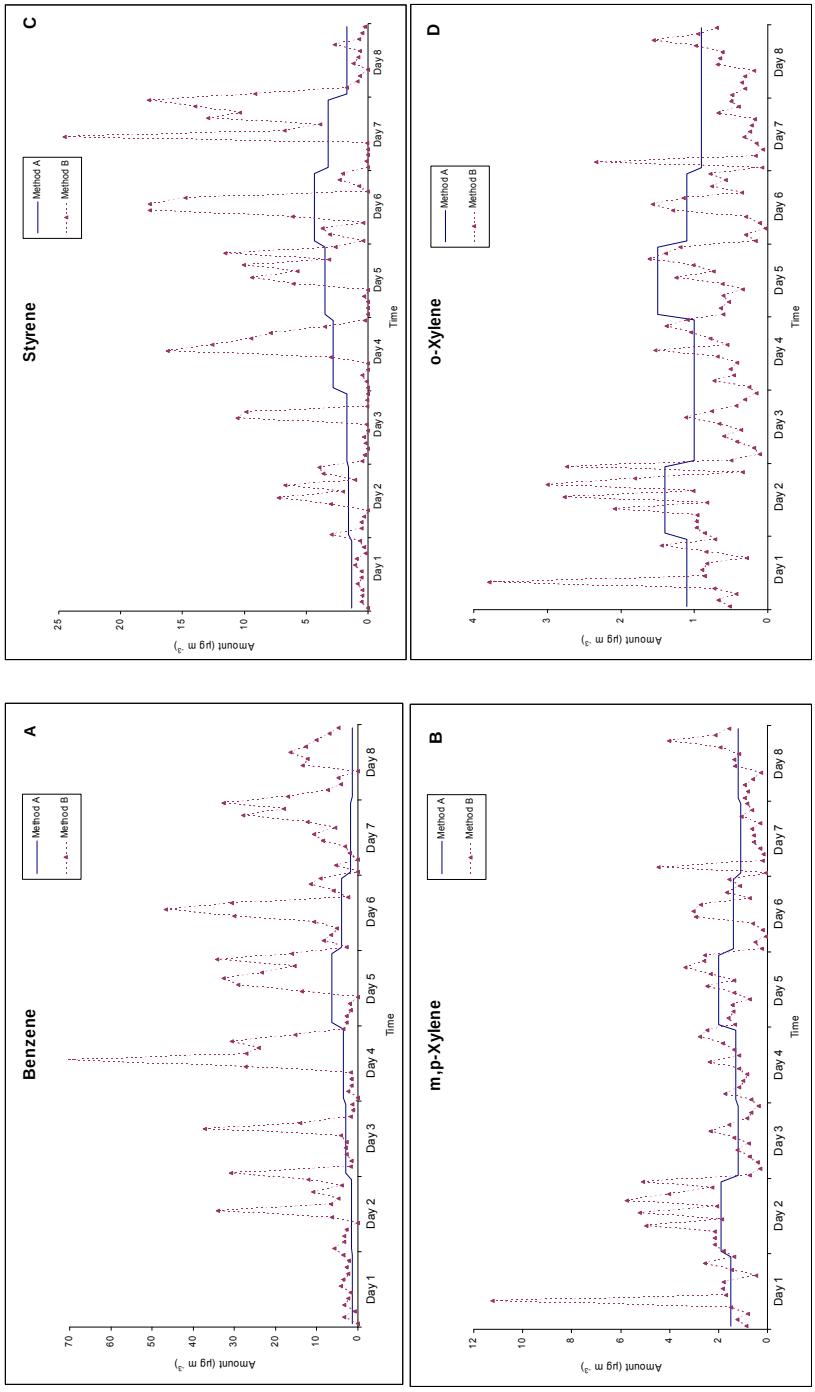


Figure 3. Concentrations, in µg m^{-3}, obtained by both methods for some of the main compounds: benzene (A), m,p-xylene (B), styrene (C) and o-xylene (D).

It should be noted that the relative humidity of the sampled days was higher than 50% (from 62% to 95%). Nevertheless, in this study there was no correlation between the different values of methods A and B and the increased humidity. Moreover, the activated charcoal can have chemical reactions with other inorganic compounds present in industrial air such as NO_2, Cl_2, H_2S, SO_2 and ozone, which can also decrease the active sorbents centres [12]. Furthermore, it is also known that the precision and the accuracy of the solvent extraction method can be affected by the presence of other polar compounds in the air samples which do not affect the thermal extraction method [11,13].

4. CONCLUSIONS

This study compared the performance of two analytical methods for determining 90 VOCs in air. The repetitivity, recovery and detection and quantification limit of the thermal desorption method were generally better than those of the solvent extraction method for the target compounds. However, blanks of the thermal desorption sorbent tubes showed the signal of 21 target VOCs whereas blanks of the solvent extraction tubes showed only signals of low concentrations of hexane and benzene.

Performance in real samples showed in some cases differences in the VOC concentrations, with those determined by thermal desorption generally being higher. Furthermore, the thermal desorption method allows short periods of sampling and can give more precise information about the daily variability of the VOC concentration whereas the solvent extraction method, which gives daily average values, can not reflect punctual emissions of the pollutants.

Acknowledgments

The authors wish to acknowledge the financial support of this study by the Spanish Ministry of Science and Innovation through project CTM2008-06847-CO2-01/TECNO and the Observatori de Salut i Medi Ambient del Camp de Tarragona, of the Servei Regional de l'Agència de Protecció de la Salut (Generalitat de Catalunya).

REFERENCES

[1] J. Dewulf and H. Van Langenhove, J. Chromatogr. A 843 (1999) 163.
[2] R.G. Derwent, M.E. Jenkin and S.M. Saunders, Atmos. Environ. 30 (1996) 181.
[3] R. Atkinson, Atmos. Environ. 34 (2000) 2063.
[4] WHO, Air Quality Guidelines for Europe, WHO Regional Office for Europe, 2000.
[5] A.P. Jones, Atmos. Environ. 33 (1999) 4535.
[6] USEPA, EPA-450/1-90-004a , Cancer Risk from outdoor exposure to air toxics, Office of Air

Quality Planning and Standards, 1990.

[7] NIOSH, Method 1500, Issue 3, NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 2003.

[8] NIOSH, Method 1501, Issue 3, NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 2003.

[9] OSHA, Samplig and analytical methods for Benzene monitoring and measurement procedures-1910.1028 App D, 1987.

[10] Norma Española UNE-EN 14662-2. Calidad del aire ambiente. Método normalizado de medida de las concentraciones de benceno. Parte 2: Muestreo por aspiración seguido de desorción por disolvente y cromatografía de gases, 2006.

[11] E. Matisova and S. Skrabakova, J. Chromatogr. A 707 (1995) 145.

[12] D.K.W. Wang and C.C. Austin, Anal. Bioanal. Chem. 386 (2006) 1089.

[13] M. Harper, J. Chromatogr. A 885 (2000) 129.

[14] C.W. Chung, M.T. Morandi, T.H. Stock and M. Afshar, Environ. Sci. Technol. 33 (1999) 3659.

[15] C.W. Chung, M.T. Morandi, T.H. Stock and M. Afshar, Environ. Sci. Technol. 33 (1999) 3664.

[16] J.C. Posner and J. R. Okenfuss, Am. Ind. Hyg. Assoc. J. 42 (1981) 643.

[17] Norma Española UNE-EN 14662-1. Calidad del aire ambiente. Método normalizado de medida de las concentraciones de benceno. Parte 1: Muestreo por aspiración seguido de desorción térmica y cromatografía de gases, 2006.

[18] USEPA, Compendium Method TO-17, EPA/625/R-96/010b, 1999.

[19] M.R. Ras, F. Borrull and R.M. Marcé, Trac-Trends Anal. Chem. 28 (2009) 347.

[20] M.R. Ras-Mallorquí, R.M. Marcé-Recasens and F. Borrull-Ballarín, Talanta 72 (2007) 941.

[21] A. Ribes, G. Carrera, E. Gallego, X. Roca, M. J. Berenguer and X. Guardino, J. Chromatogr. A 1140 (2007) 44.

[22] O.O. Kuntasal, D. Karman, D. Wang, S. G. Tuncel and G. Tuncel, J. Chromatogr. A 1099 (2005) 43.

[23] K. Demeestere, J. Dewulf, B. De Witte and H. Van Langenhove, J. Chromatogr. A 1153 (2007) 130.

[24] J.D. Donaldson, S.M. Grimes, L. Mehta and A.J. Jafari, J. AOAC Int. 86 (2003) 39.

[25] Amendments to 1990 Clean Air Act-List of 189 Hazardous Air Pollutants, US Environmental Protection Agency, 1994.

[26] Decision 2002/3/EC. Off J. Eur. Communities L 67/14; 09/03/ 2002: 1-17.

[27] N. Ramírez, R.M. Marcé, F. Borrull, Int. J. Environ. Anal. Chem., DOI: 10.1080/03067310903584073.

[28] AEQT, Associació Empresarial Química de Tarragona. http:// www.aeqt.com (accessed on: 10th january 2010)

[29] USEPA, Compendium Method TO-15, EPA/625/R-96/010b, 1999.
[30] K. Andersson, J.O. Levin, R. Lindahl and C.A. Nilsson, Chemosphere 13 (1984) 437.
[31] M. Czaplicka and K. Klejnowski, J. Chromatogr. A 976 (2002) 369.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.1.3. Discussion of results

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

The results presented in this section demonstrate the applicability of sorbent enrichment methods for the determination of a wide range of VOCs with different levels of volatility and polarity.

As seen in the papers, the main parameters that should be optimised when using active sorbent enrichment methods are the sample volume and the sampling flow-rate to avoid breakthrough of the most volatile and polar compounds. For the TD methods, two sorbent tubes were connected in series, in order that the back tube could retain the analytes eluted from the front tube, and different volumes of air at different flow-rates were sampled. The optimal sample volume was fixed in order to allow the detection of the target VOCs in the samples without the breakthrough of any of the analytes (concentrations in the second tube < 5% in respect to those in the first tube [1]). At the fixed rates and volumes, some VOCs were found in the second tube, such as chloroform, 1,4-dioxane or ethylbenzene, but their concentrations did not exceed the recommended 5%. For the LD method, the sampling flow-rate and volume were fixed by the sampler characteristics. Possible breakthroughs of the target VOCs were evaluated by analysing the back-up section of the charcoal tubes after the sampling and comparing the concentrations with those obtained from the front section of the tubes. No VOCs were found in the back-up section over their respective LODs for the LD method.

Concerning the TD methods, the use of multi-sorbent tubes provides interesting perspectives, since one single sorbent cannot cover the wide range of target VOCs. Therefore, two sorbents were used to fill the TD cartridges: Tenax TA, which is a weak polymeric porous sorbent that can trap the less volatile VOCs, and Carbograph 1TD, which can trap the more volatile target VOCs. Indeed, it should be pointed out that some of the most polar target VOCs determined in the industrial WWTP by TD were discarded because they broke through the activated charcoal tubes and could not, therefore, be considered when comparing the analytical methods. For instance, phenol and aniline were some of the VOCS which were discarded.

Another important parameter to take into account is the presence of artifacts due to sorbent degradation, especially with the TD methods. Although Tenax TA and Carbograph TD emit low levels of artifacts when thermally desorbed [2,3], blank signals corresponding to 24 target VOCs were found in the TD tubes. As seen in the first paper, the highest concentrations in the blanks corresponded to phenol and other aromatic VOCs such as benzene, toluene and 4-ethyltoluene, as well as isoprene and dichloromethane. Nevertheless, blanks of the activated charcoal tubes, which were desorbed with carbon disulphide, only showed the presence of n-hexane and benzene. Although the signals found in the blanks were taken into account for LODs and LOQs

calculations, instrumental LODs with the TD method were at low ng levels for all target VOCs. In general, TD methods also showed the best repeatability and recovery and the lowest LODs and LOQs. Since only a thousandth part of the extract is analysed (1 µL of 1 mL of extract) in the LD method, high preconcentration volumes - and therefore high sampling periods - are needed to achieve similar sensitivity to the TD method.

Our results concur with a previous study that compared the analytical parameters of a LD and a TD method. Czaplicka et al. [4] compared the use of activated charcoal tubes and carbon disulfide extraction versus the use of carbotrap tubes followed by TD for the determination of 8 VOCs: benzene, toluene, ethylbenzene, o, m and p-xylene, and 1,2,4- and 1,3,5-trimethylbenzene. The TD method showed, in general, better repeatability and higher sensitivity. The TD method was then used to determine the variability of BTEX in ambient air.

Furthermore, the study that evaluated the two methods was the first to compare the performance of both methods in real samples. As seen in the paper, the 24-hour samples collected over 8 days with the solvent desorption method were compared with the mean daily values of 96 samples (12 per day) collected over 2 hours and analysed by the TD method in the same period of time. In these samples, the TD method was able to determine more target VOCs (only 18 of the 90 VOCs were detected by the solvent method, whereas 50 VOCs were quantified by the TD method). In general, the average concentrations obtained by the TD method were higher. Furthermore, the short periods of sampling of the TD method allow the detection of the variability of the VOC concentrations that, in most of the samples, was not reflected in the daily average concentrations of the LD method.

Another important conclusion derived from both studies is the presence in industrial atmospheres of hazardous VOCs, whose emissions are not specifically regulated by current legislation. The total concentrations of VOCs in the industrial WWTP emissions were up to 3800 µg m^{-3} and some of the most abundant VOCs are considered priority pollutants in air by the WHO [5]. Among the VOCs emitted from the industrial WWTP, acrylonitrile should be highlighted because of its clear industrial origin and its high concentrations, with values up to 1843 µg m^{-3} in emissions from the waste water collecting tank after primary sedimentation. Styrene, chloroform, 1,4-dioxane and ethylbenzene were also among the most abundant compounds emitted from the industrial WWTP. For the industrial WWTP emissions, it can also be concluded that most of the VOCs are removed during the biological treatment or by evaporation of the waste water, because VOC emissions from the collecting tank were higher than those found in the secondary treatment tank. However, as seen in the paper, the emissions from this industrial WWTP are much lower than those reported previously in Taiwan [6-8] and

even in urban WWTPs in UK [9] and in Turkey [10], except for some VOCs such as acrylonitrile, chloroform and styrene. The high levels of these compounds in the WWTP emissions indicate the importance of industrial WWTPs as a source of hazardous air contaminants.

In the surroundings of the petrochemical site, the most abundant VOCs were pentane with daily average concentrations with the TD method up to 75.8 μg m^{-3} and 19.8 μg m^{-3}, for i- and n-pentane, respectively; acrylonitrile (47.8 μg m^{-3}); n-hexane (6.7 μg m^{-3}); benzene (17.1 μg m^{-3}), toluene (12.1 μg m^{-3}) and m,p-xylene (3.29 μg m^{-3}), among others. It is worth mentioning the punctual VOC emissions detected in the 2 h samples of the TD method for some compounds. For instance, punctual concentrations of benzene were up to 70 μg m^{-3}.

Both studies presented in this section have demonstrated the presence of VOCs in industrial atmospheres and the feasibility of the use of multi-sorbent bed tubes followed by TD for simultaneous determining of a wide range of VOCs.

References

[1] USEPA, Compendium Method TO-15, EPA/625/R-96/010b, 1999.
[2] E. Woolfenden, J. Chromatogr. A 1217 (2010) 2685.
[3] M.R. Ras, F. Borrull, R.M. Marcé, Trends Anal. Chem. 28 (2009) 347.
[4] M. Czaplicka, K. Klejnowski, J. Chromatogr. A 976 (2002) 369.
[5] WHO, Air Quality Guidelines for Europe,WHO Regional Office for Europe, 2000.
[6] T.Y. Lin, U. Sree, S.H. Tseng, K.H. Chiu, C.H. Wu, J.G. Lo, Atmos. Environ. 38 (2004) 4111.
[7] B.Z. Wu, T.Z. Feng, U. Sree, K.H. Chiu, H.G. Lo, Anal. Chim. Acta 576 (2006) 100.
[8] W.H. Cheng, M.S. Chou, J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng. 38 (2003) 2521.
[9] J. Leach, A. Blanch, A.C. Bianchi, Atmos. Environ. 33 (1999) 4309.
[10] F. Dincer, A. Muezzinoglu, J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng. 43 (2008) 1569.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.2. Risk assessment of atmospheric organic contaminants

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

In the two studies presented in the previous section, the relevance of the chemical site located in the Tarragona area as an important source of atmospheric VOCs was demonstrated. Furthermore, previous studies in our research group showed higher concentrations of atmospheric PAHs around the chemical site, compared to urban areas [1,2]. Besides these studies, several monitoring campaigns have also been carried out in collaboration with the Observatory of Health and Environment of Tarragona regarding PAH and VOC concentrations in the area. Because of the proven high presence of VOCs and PAHs in this area, we were encouraged to carry out two studies with the aim of estimating the risk to people living around the chemical site by inhalation of VOCs and PAHs. The results of these studies are presented in this section.

According to the WHO, the human health risk assessment of chemicals refers to methods and techniques applied for the evaluation of hazards, exposure and harm posed by chemicals [3]. The risk assessment process begins with problem formulation and includes four additional steps: hazard identification, hazard characterisation, exposure assessment and risk characterisation [4]. The environmental health risk of an organic contaminant mainly depends on the amount of this contaminant present in an environmental medium (e.g. soil, water, air); the exposure a person has to the contaminant; and the toxicity of the chemical.

As previously discussed, both VOCs and PAHs are ubiquitous atmospheric contaminants with recognised non-cancer and cancer health effects. Some VOCs are considered carcinogenic or possibly carcinogenic for humans (IARC, groups 1 and 2), and have associated unit risk (UR) levels by the international agencies. Furthermore, non-cancer risk effects for some VOCs are also quantified using reference concentrations (RfCs). In the case of PAHs, the most relevant health risks are those related to their carcinogenic and mutagenic properties. Benzo[a]pyrene (BaP), considered carcinogenic for humans (IARC group 1), is the most studied PAH and other PAHs are ranked using toxic equivalence factors (TEFs) according to their cancer potency relative to BaP.

For the risk assessment of both studies, samples were taken in three locations which were selected on the basis of their proximity to the industrial complexes and the prevailing wind directions (north-north-westerly in cold seasons and south-south-westerly in warm seasons). The chemical site in the Tarragona area has two main areas known as the North and the South Industrial Complexes, dedicated to the refining and the production of chemical products, with a total annual production of 21 MT in the year 2009 [5]. The first monitoring site was in Perafort-Puigdelfí, which is a semi-rural area located less than 0.5 km east of the North Industrial complex. The second location was Tarragona-Bonavista, which is a suburban area of the main city (Tarragona) less than 1 km north of the South industrial complex and less than 0.5 km from a road with

moderate traffic density. The third sampling point was located in Vila-seca, which is also a suburban area located less than 1 km from the South industrial complex and a road, also with moderate traffic intensity. Samples were taken using the installations of the atmospheric pollution vigilance and prevention net of the Generalitat de Catalunya Environmental Department (XVPCA, Xarxa de Vigilància i Prevenció de la Contaminació Atmosfèrica).

The first study presented in this section estimates the lifetime lung cancer risk for people living around the chemical site by inhalation of PAHs. PAHs are semi-volatile organic contaminants which are present in both the airborne gas phase and particle phase. As mentioned in the introduction, only BaP present in PM_{10} particles is regulated in European countries by the Directive 2004/107/CE [6] and, therefore, most studies have omitted the contribution of the gas phase PAHs on human risk estimates. To that end, we determined 18 PAH compounds (most of them included in the USEPA Priority List [7]), in both the gas and particle phases of the three locations near the industrial site. 153 matched air and total suspended particle samples were collected in a year, from June 2008 to June 2009. Samples were collected during two phases in each location, including two months during a high temperature period and two months during a low temperature period, to determine whether temperature influences atmospheric PAH concentrations. Samples were taken using a high-volume sampler, which preconcentrated approximately 300 m^3 of air for 24 hours. Quartz fibre filters (QFFs) were used to collect the particle phase and polyurethane foams (PUFs) to trap the gas phase contaminants. The distribution of PAHs in the gas and particle phase, their seasonal and spatial distribution, and the contribution of individual PAHs to the estimated risks were evaluated.

In the second study of this section, the chronic risk assessment for both cancer and non-cancer effects are estimated around the chemical site by inhalation of VOCs. Eighty-six different VOCs were selected according to their adverse environmental and health effects. The monitoring campaign was conducted over two periods: from October 2008 to January 2009 and from October 2009 to June 2010. The analytical method for the monitoring was the LD method described in the previous section. Furthermore, to determine how the analytical method can have an influence on the risk estimates, simultaneous samples were collected for 24 days in the first period of sampling using the TD method described in the previous section. The main cancer risk parameters were evaluated and compared for the VOC concentrations obtained by both methods.

To our knowledge, the studies presented in this section evaluate for the first time the risk by inhalation of atmospheric PAHs (in both the air and the particle phase) and VOCs for people living near a chemical site of this size. The results of the first study have been

accepted for publication in the journal *Environmental Health Perspectives*. A paper discussing the results obtained in the second study has been submitted for publication to the journal *Environmental International*. Both studies have also been performed in collaboration with the Observatory of Health and Environment of Tarragona.

References

[1] M.R. Ras, R.M. Marcé, A. Cuadras, M. Mari, M. Nadal, F. Borrull, Int. J. Environ. Anal. Chem. 89 (2009) 543.
[2] M.R. Ras, F. Borrull, R.M. Marcé, J. Sep. Sci. 32 (2009) 1051.
[3] WHO, Air Quality Guidelines for Europe, WHO Regional Office for Europe, 2000.
[4] WHO-IPCS, Harmonization Project Document No. 1; Available: http:// www.who.int/ipcs/methods/harmonization/areas/ipcsterminologyparts1and2.pdf (accessed 20.04.2011).
[5] AEQT, Public report 2009. Available: http://www.aeqt.com (accessed 20.04.2011).
[6] Directive 2004/107/EC, Off. J. Eur. Commun. L23 (2005) 3.
[7] ATSDR, CERCLA Priority List of Hazardous Substances. Available: http:// www.atsdr.cdc.gov/cercla/07list .html (accessed 22.04.2011).

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.2.1. Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

RISK ASSESSMENT RELATED TO ATMOSPHERIC POLYCYCLIC AROMATIC HYDROCARBONS IN GAS AND PARTICLE PHASES NEAR INDUSTRIAL SITES

Noelia Ramírez[1], Anna Cuadras[2], Enric Rovira[2], Rosa Maria Marcé[1], Francesc Borrull[1]
[1] Department of Analytical Chemistry and Organic Chemistry Universitat Rovira i Virgili, Marcel·lí Domingo s/n Sescelades Campus, Tarragona 43007, Spain
[2] Observatory of Health and Environment of Tarragona Agència de Protecció de la Salut Departament de Salut. Generalitat de Catalunya, Tarragona, Spain

Abstract

Background: Inhalation is one of the main means of human exposure to polycyclic aromatic compounds (PAHs) due to their ubiquitous presence in the atmosphere. However, most studies have only considered PAH found in the particle phase and omitted the contribution of the gas phase PAHs to the risk.
Objective: This study estimates the lifetime lung cancer risk from PAH exposure by inhalation in people living next to the largest chemical site in Southern Europe and the Mediterranean area.
Methods: We determined 18 PAHs in the atmospheric gas and particle phase. We monitored the PAHs over one year in three locations near the chemical site in different seasons. We used Toxic Equivalence Factors to calculate Benzo[a]pyrene (BaP) equivalents for individual PAH, and applied the World Health Organization Unit Risk for BaP (UR= 8.7×10^{-5}) to estimate lifetime cancer risks due to PAH exposures.
Results: There was some spatial and seasonal variability in PAH concentrations. The contribution of gas phase PAH to the total BaP equivalent value was between 34% and 86%. The total estimated average lifetime lung cancer risk due to PAH exposure in the study area was 1.2×10^{-4}.
Conclusions: The estimated risk was higher than WHO and USEPA recommended values, but lower than the threshold value of 10^{-3} that is considered an indication of definite risk according to similar risk studies. The results also showed that risk may be underestimated if the contribution of gas phase PAHs are not considered

***Keywords*:** Air quality; Gas phase; Particulate phase; Polycyclic aromatic hydrocarbons; Risk assessment

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic contaminants, characterized by the presence of at least two fused aromatic rings. These compounds mainly come from pyrolytic processes and the incomplete combustion of organic matter at high temperatures, and anthropogenic activities are the main source of PAHs in the environment.

Because of their adverse effects on human health, their persistence in environmental matrices and their reactivity and ability to transform into more active species, PAHs have been classified as priority pollutants by both the United States Environmental Protection Agency (USEPA) (USEPA 1994) and the European Environment Agency (EEA) (EEA 1999).

PAH health effects have been widely studied, primarily because of their potential carcinogenic and mutagenic properties. Several toxicological studies in animals (WHO 1998) and occupational studies in humans (Armstrong et al. 2004) demonstrate an excess risk of lung cancer associated with PAH inhalation. The potential influence of PAH exposure on the development of bladder and urinary system cancer also has been studied (Bosetti et al. 2007). In general, the carcinogenic properties of PAHs increase with the number of aromatic rings. Benzo[a]pyrene (BaP) has been the most extensively studied PAH and is the usual marker for carcinogenic levels of PAHs in environmental studies. However, uncertainties about the suitability of BaP as a cancer risk indicator have also been discussed (Boström et al. 2002). The International Agency for Research on Cancer (IARC) classified BaP as carcinogenic to humans (Group 1); other PAHs, such as dibenzo[a,h]anthracene, as probably carcinogenic to humans (Group 2A); and others – such as naphthalene, benzo[a]anthracene, chrysene, benzo [b]fluoranthene, benzo[j]fluoranthene and indeno[1,2,3-cd]pyrene – as possibly carcinogenic to humans (Group 2B). PAHs can also metabolize and become reactive electrophilic intermediates that can form DNA adducts which may induce mutations and ultimately tumors (IARC 2010). Some PAHs, such as fluoranthene, which are classified as weak carcinogens (Group 3, IARC), have mutagenic characteristics and may therefore play an important role in carcinogenesis (Boström et al. 2002).

Studies of other outcomes have suggested effects of PAHs on the development of arteriosclerosis (WHO 2000), reproductive outcomes such as intrauterine growth retardation (Dejmek et al. 2000; Srám et al. 2005), and children's neurological development (Perera et al. 2009). Furthermore, because PAHs are highly hydrophobic, they have an affinity for environmental matrices such as sediments, soils and biota, and can bioaccumulate in adipose tissues and become magnified through the food chain (WHO 1998). Because of their lipophylic characteristics and limited biodegradation, PAHs are classified as persistent organic pollutants.

Ingestion is quantitatively the main route for PAH human exposure. However, inhalation is also a significant route because of the ubiquitous presence of these compounds in the atmosphere (ATSDR 1995; Li et al. 2010). PAHs can be associated with the atmospheric gas phase and particulate

phase (Ravindra 2008; WHO 1998). The most lipophylic compounds are mainly associated with the particle fraction, which can accumulate in the tracheobronchial epithelium, where they increase PAH concentrations even at low environmental PAH exposures (Boström et al. 2002; Gerde et al. 1993). Meanwhile, PAHs present in the gas phase or those that rapidly elute from particles upon inhalation can reach the alveolar epithelium and rapidly enter the circulatory system (Boström et al. 2002; Gerde et al. 1993).

Risk estimation for PAH exposures is complex for several reasons. There are few reported human epidemiological studies of individual PAHs, and individual PAHs are likely to induce cancer through different mechanisms. As mentioned above, BaP is the most studied PAH and other PAH have been ranked according to cancer potency relative to BaP using Toxic Equivalence Factors (TEFs). The application of TEFs combined with the World Health Organization (WHO) Quantitative Risk Assessment methodology (WHO 2000) can be used to estimate the excess lifetime lung cancer risk due to PAH exposures. This methodology was used previously to establish guideline values for PAH exposures and inform environmental policies (Morello-Frosch et al. 2000).

The aim of this study is to estimate the lifetime lung cancer risk of PAH exposure by inhalation in people living in urban and suburban areas near an important industrial chemical site in the Tarragona region (NE Spain). To that end, we determined 18 PAH compounds (most of them included in the USEPA Priority list (ATSDR 2007)), in both the gas and particle phases. We monitored three locations near the two industrial complexes in the region from June 2008 to June 2009. We evaluated the distribution of PAHs in the gas and particle phase, their seasonal and spatial distributions, and the contribution of individual PAHs to estimated risks.

There are few studies related to industrial atmospheres that consider the contribution of both the atmospheric gas phase and the particle phase to risk (Liu et al. 2010). To our knowledge, this is the first study to estimate lifetime lung cancer risk due to inhalation of PAH in both phases in people living near a petrochemical and chemical industrial site of these characteristics.

2. MATERIALS AND METHODS

2.1. Study area

The largest chemical site in Southern Europe and the Mediterranean area is located in the Tarragona region (ECRN 2010). Most of the chemical industries are located in two areas known as the North and the South Industrial Complexes. The North Industrial Complex has an area of 470 ha and includes an oil refinery and other chemical industries. Among the

products manufactured in the North Complex are benzene, ethylene, fuel-oil, gasoline, kerosene, propylene, propylene oxide, polypropylene and styrene. The South Industrial Complex occupies an area of 717 ha and includes several chemical and petrochemical plants. Among the products manufactured in the South complex are acrylonitrile-butadiene-styrene (ABS), butane, chlorine, ethylene oxide, polyethylene, kerosene, halogenated organic compounds, polyols, polypropylene, polystyrene, polyethylene, polyvinyl chloride, propane and vinyl acetate. The total production of the two complexes is about 21 MT per year [refining: 8.3 MT; chemical products: 12.7 MT (AEQT 2009)].

Figure 1 shows the map of the studied area. We selected three sampling sites on the basis of their proximity to the industrial complexes, and the prevailing wind. Site 1 is located in Perafort-Puigdelfí, a semirural area < 0.5 km east of the North Industrial Complex.

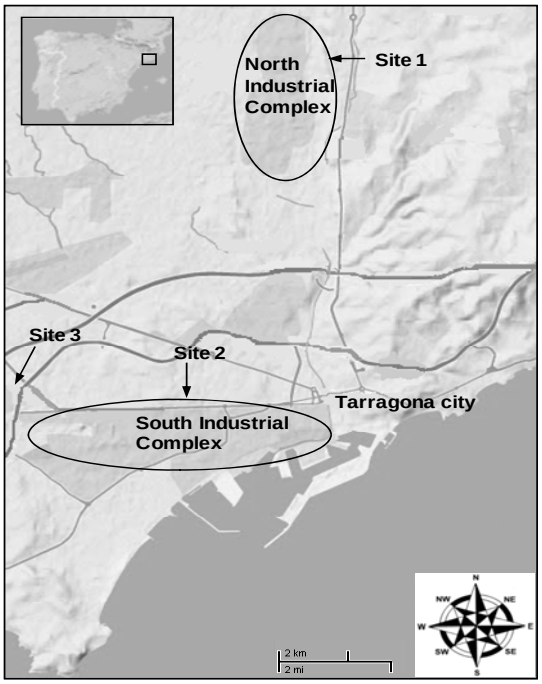


Figure 1. Map of the Tarragona region showing the location of the main city (Tarragona), the North and South Industrial Complexes and the three sampling points: Site 1 (Perafort-Puigdelfí) near the North Industrial Complex and Site 2 (Tarragona -Bonavista) and Site 3 (Vila-seca) near the South Industrial Complex.

Site 2, Tarragona-Bonavista is in a suburban area of the main city – Tarragona – < 1 km north of the South Industrial Complex and < 0.5 km from a road with a moderate traffic density (14,041 vehicles per day, Spanish Ministry of Public Works, 2007).Finally, Site 3 is also located in a suburban area – Vila-seca – < 1 km from the west end of the South Complex and < 1 km from a road (20,049 vehicles per day, Spanish Ministry of Public Works, 2007). Wind speeds are light (annual average < 3 m s^{-1}) and the prevailing wind directions are north-north-westerly in cold seasons and south-south-easterly in warm seasons.

2.2. Sample collection

We collected samples using a TE-1000 PUF Poly-Urethane Foam High Volume Air Sampler (Tisch Environmental, Inc., Village of Cleves, Ohio, USA), which simultaneously collects total suspended particles (TSP) and airborne pollutant vapors, meeting the specifications of the USEPA TO-13 method (USEPA 1999). We took samples for 24 h at a flow rate of ca. 0.2 m^3 min^{-1} on quartz microfiber filters (QFFs, 10.16 cm diameters, Grade QM-A from Whatman, Maidstone, UK) for trapping particulate matter and polyurethane foam cartridges (PUFs, diameter 63 mm, 76 mm long, also from Tisch) for vapor phase pollutants. Before the sampling step we conditioned the QFFs at 400 °C for at least 6 h and the PUFs using dichloromethane Soxhlet extraction for 24 h and then dried in a vacuum desiccator. After the conditioning step, we individually wrapped the QFFs and PUFs in aluminum foil, protected them with a saleable plastic bag and kept them at –18 °C before and after the sampling and until the analysis. We analyzed the samples within two weeks of collection. We conducted the sampling campaign from June 2008 to June 2009. During this period, we took a total of 153 samples of matched air and particulate matter in three weekly samples over approximately four months in each location (52 samples in Site 1, 48 samples in Site 2 and 53 samples in Site 3). We collected samples during two phases in each location, including two months during a high temperature period and two months during a low temperature period, to determine whether temperature may influence PAH values in the atmosphere.

2.3. Chemical standards and reagents

We measured 18 target PAHs and we used 5 deuterated PAHs as internal standards. Standards for naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (AcP), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FluT), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a] pyrene (BaP), and dibenzo[a,h] anthracene (DahA) were supplied by Sigma-Aldrich (Saint Louis, Missouri,

USA). Standards for benzo[j] fluoranthene (BjF), benzo[e]pyrene (BeP), indeno[1,2,3-cd]pyrene (Ind), benzo[g,h,i]perylene (BghiP) and the deuterated PAHs (d_8-naphthalene, d_{10}-acenaphthene, d_{10}-phenanthrene, d_{12}-crysene and d_{12}-perylene) were supplied by Supelco (Bellefonte, Pennsylvania, USA). Dimethylformamide (DMF) was provided by Merck (Darmstadt, Germany). The purity of all standards was >96%.

Dichloromethane (DCM) with purity >99.9% (SDS, Peypin, France) was use to extract the analytes and prepare the standard dilutions. Helium and nitrogen gas (99.999% purity) were used for the chromatographic analysis and extractions, respectively (Carburos Metálicos, Barcelona, Spain) and Hyflo Super Cel diatomaceous earth (Sigma-Aldrich) was used to fill the QFF extraction cells of the pressurized liquid extraction equipment. Diatomaceous earth was conditioned at 400 °C for 6 hours and then kept in a desiccator.

2.4. Sample extraction

We extracted PAHs by Pressurized Liquid Extraction (PLE) using an Accelerate Solvent Extraction ASE 200 equipment (DIONEX, Sunnyvale, USA) and DCM as solvent. For the pressurized solvent extraction of the PUFs, we cut them in two pieces using acetone-rinsed scissors and we then placed them in 33 mL extraction cells. Extraction of the PUFs consisted of one cycle that began with a preheating step of 5 min and a static time of 5 min with a temperature of 100 °C and a pressure of 1500 psi. Flush volume was 50% and purge time 120 s. We cut the QFFs into small pieces, mixed them with diatomaceous earth and placed them in an 11 mL cell. Extraction of QFFs was performed in two cycles under the same conditions as the PUF extraction. The PLE extraction conditions of PUFs and QFFs were optimized in a previous study (Ras et al. 2009a).

We placed the extract from PLE in a 100 mL round-bottom flask and added 400 µL of DMF to prevent the evaporation of the most volatile PAH (Lintelmann et al. 2005). We reduced the extract to the DMF volume (400 µL) on a rotary evaporator and then transferred it to a 1 mL volumetric flask by adding DCM. We then added 20 µL of 50 mg L^{-1} deuterated PAH solution (to obtain an internal standard concentration of 1 mg L^{-1}) and the volumetric flask was filled to the mark with DCM. Recoveries of the extraction were higher than 90% for all target PAHs (see Supplemental Material, Table 1).

2.5. Gas chromatography-mass spectrometry analysis

We analyzed extracts in a 6890N gas chromatograph coupled with a 5973 *inert* mass spectrometer (Agilent Technologies, Palo Alto, USA), using a capillary column Zebron ZB-5 (5% methyl-phenyl 95% dimethylpolysiloxane, 30 m × 0.25 mm i.d. × 0.25 µm, provided by Phenomenex, Le Pecq

Cedex, France). The gas chromatography-mass spectrometry (GC-MS) analysis was performed by injecting 1 µL of extract at 270 °C, in splitless mode at a helium constant flow of 1 mL min^{-1}. The oven temperature program started at 100 °C, held for 4 min, was raised to 290 °C at a rate of 6 °C min^{-1}, and held there for 10 minutes.

The GC-MS interface was set at 280 °C. The mass spectrometer acquired data in scan mode with an *m/z* interval from 35 to 280, operating at electron impact energy of 70 eV. Qualitative identification of target PAHs was based on the match of the retention times and the ion ratios of the target quantifier and qualifier ions. We quantified the isomers BjF and BbF together because they coelute and exhibit similar mass spectra.

We used the internal standard calibration method for GC-MS quantification. The standards, diluted in DCM, ranged between 0.01 and 50 mg L^{-1} with an internal standard constant concentration of 1 mg L^{-1}. We prepared all the standards on the day of use and we kept them refrigerated. For an average air preconcentration of 300 m^3, limits of detection (LODs) ranged from 0.002 ng m^{-3} to 0.033 ng m^{-3} and limits of quantification (LOQs) between 0.033 ng m^{-3} and 0.167 ng m^{-3}. Repeatability and reproducibility were below the 10% RSD (n=5) for all target compounds. See the Supplemental Material, Table 1 for further information about the validation parameters of the analytical method.

2.6. Quality assurance

Due to the ubiquitous presence of PAHs in the atmosphere, precautions to avoid sample contamination were taken throughout the entire process. In addition to the precautions mentioned previously, we followed USEPA TO-13 (USEPA 1999) method guidelines. Furthermore, components of the extraction cells and collecting vials were ultra-sound cleaned with isopropanol followed by DCM and dried inside a fume cupboard. All glassware, including GC syringes, was rinsed three times with isopropanol and three times with DCM prior to being used. Field blanks, process blanks, and solvent blanks were also performed according to Section 14 of the TO-13. Taking these precautions into account, no blank showed any detectable signals for the target PAHs.

2.7. Toxic equivalency factors. Benzo[a]pyrene equivalency

For risk assessment calculations, we ranked the 18 target PAHs according to their cancer potency relative to BaP. Most of the TEFs used in this study were proposed by Larsen and Larsen (1998) based on current knowledge of PAH carcinogen effects. However, for volatile PAHs such as naphthalene, acenaphthylene and acenaphthene we applied TEFs proposed by Nisbet and Lagoy (1992).

We calculated BaP equivalents (BaP-eq) by multiplying each individual PAH

concentration with its corresponding TEF and determined the concentration of total PAH expressed as BaP-eq.
Following USEPA criteria (USEPA 2000) for risk assessment calculations, we substituted half the minimum detectable level (LOD) value for measured values < LODs and substituted half the minimum quantifiable level (LOQ) value for measured values < LOQs.

2.8. Lifetime lung cancer risk of PAHs in the atmosphere defined by the WHO unit risk

The estimated lifetime lung cancer risk from PAHs in the atmosphere based on the WHO Unit Risk (UR) (WHO 2000) is 8.7 cases per 100,000 people with chronic inhalational exposure to 1 ng m^{-3} of BaP (UR = 8.7×10^{-5}) over a lifetime of 70 years. The risk of developing lung cancer can thus be calculated as follows:

Lifetime lung cancer risk = BaP-eq (ng m^{-3}) × UR [1]

We estimated the corresponding annual number of lung cancer cases in the population around the chemical site that could be attributed to PAH as: Population exposed (number of inhabitants) x Lifetime lung cancer risk / 70 (years of exposure). We defined the exposed population for this study (170,263 inhabitants, Statistical Institute of Catalonia 2008) based on proximity to the industrial complexes and the prevailing winds.

3. RESULTS AND DISCUSSION

3.1. PAH gas and particle phase values

PAHs in air can be present either in the gas phase or in the particulate phase. The phase distribution of the PAHs depends on the vapor pressure of the compound, the atmospheric temperature, the PAH concentration, the affinity of the PAH for the atmospheric suspended particles (determined by the partitioning coefficients K_{oc}), and the nature and concentrations of the particles (ATSDR 1995; Baek et al. 1991). Table 1 shows the summary of the PAH concentra-tions of the campaign. In general, PA showed the highest average concentration in the gas phase. Nap, Flu, FluT and Pyr also were common gas phase PAHs, whereas BaA, BjF, BkF and Chr formed the majority of the particle phase. Temperature appeared to have a considerable influence on PAH concentrations because the highest levels of PAHs occured in winter, with Nap, AcPy, AcP, Flu, PA, Ant, FluT, BaA and Chr increasing at lower temperatures. Furthermore, in samples collected during the low temperature periods, the heaviest PAHs (BbF, BjF, BkF, BeP, BaP, Ind, DahA, BghiP) were mainly present in the particulate phase, whilst a more equitable distribution of these compounds in both phases was observed in samples collected during the high temperature periods. As an example Supplemental Material, Table 2 and Table 3 present the daily PAH

concentrations obtained in Site 1 over high and low temperature periods. For instance, in samples collected at Site 1 during the winter, BaP was not detected in most of gas phase samples, ranging between n.d. and 0.37 ng m^{-3}, and its concentrations in the particle phase ranged between 0.14 and 1.53 ng m^{-3}, whereas in summer concentrations ranged between n.d. and 1.11 ng m^{-3} in the gas phase and between n.d. and 1.36 ng m^{-3} in the particle phase. One possible explanation is that when the temperature is high some particle-bound PAHs may evaporate and be trapped in the PUFs during sampling (USEPA 1999).

Although low temperatures facilitate the condensation of volatile and semi-volatile PAHs onto pre-existing particles, we found that PAH concentrations in the gas phase increased more than those in the particle phase when temperatures decreased (Table 1). This trend has been also reported in previous studies (Cincinelli et al. 2007; Ravindra et al. 2006). One possible explanation may be that photochemical reactions with $^{\cdot}OH$ and $NO_3^{\cdot}$ radicals increase with higher temperatures. However, other factors (plants routine maintenance and seasonal holidays, etc.) may also influence seasonal variation in PAH distributions.

In general, the highest total PAH values were associated with the gas phase in both sampling periods, especially in winter (Table 1). This trend has been detected in previous studies (Ravindra et al. 2006). It is also worth noting that these concentrations in the gas phase can be even higher because the trapping efficiency of PUFs for the 2-3-ring PAHs is about the 35% (USEPA 1999).

The European legislation only regulates some heavy PAHs (BaA, Chr, BbF, BjF, BkF, BaP, BeP, DahA) in the particulate phase (EEC 2005). According to the results obtained in this study, the current legislation therefore appears to underestimate the main contribution of PAHs to the atmosphere.

3.2. Spatial distribution of PAHs

The volatile PAHs (Nap, AcPy, AcP, Flu, PA, Ant) were most abundant at all three sampling sites, especially in the gas phase, and they made a large contribution to the total PAH values (between 49 and 84% of the gas phase and between 11 and 36 % of the particle phase) (Table 1). Site 1 presented the highest average concentrations of PAHs in the particle phase with an average total PAH concentration of 5.61 ng m^{-3} in summer and 7.00 ng m^{-3} in winter. Of particular interest are the high concentrations of some of the heavy PAHs in the gas phase, such as the maximum concentrations of DahA or BghiP (5.34 ng m^{-3} and 2.19 ng m^{-3}, respectively). Since Site 1 is a rural area, the PAH values primarily may reflect activities in the North Industrial Complex, particularly refining, which can be an

Table 1. Minimum, maximal and average PAH concentrations, in ng m^{-3}, found in the three locations over the two seasonal sampling periods. The periods of sampling, the number of samples and the average temperatures of each period are also indicated.

	Site 1						Site 2						Site 3					
PAHs	**Summer**			**Winter**			**Summer**			**Winter-Spring**			**Spring**			**Autumn**		
	Min.	**Max.**	**Av.**	**Min.**	**Max.**	**Av.**	**Min.**	**Max.**	**Av.**	**Min.**	**Max.**	**Av.**	**Min.**	**Max.**	**Av.**	**Min.**	**Max.**	**Av.**
Gas phase																		
Nap	n.d.	3.53	1.37	0.24	20.4	3.92	n.d.	0.86	0.36	0.48	1.68	0.92	0.24	0.68	0.37	0.53	13.4	2.97
AcPy	n.d.	2.21	0.51	0.31	11.6	3.18	n.d.	0.60	0.23	0.33	1.29	0.74	n.d.	0.41	0.28	0.14	15.5	2.89
AcP	n.d.	1.88	0.33	0.15	5.77	1.26	n.d.	0.47	0.22	0.38	0.93	0.63	0.16	0.98	0.43	0.25	8.26	2.31
Flu	0.39	1.62	0.69	0.42	14.4	5.52	n.d.	0.84	0.41	0.70	2.10	1.42	0.53	2.66	1.35	0.24	33.0	6.95
PA	0.80	2.46	1.43	1.26	91.1	28.2	0.54	2.23	1.13	1.69	8.57	4.15	1.29	25.3	12.1	0.31	197	35.2
Ant	n.d.	1.58	0.64	0.19	9.00	2.66	n.d.	2.27	0.35	0.29	0.70	0.46	0.11	1.07	0.46	n.d.	17.1	2.43
FluT	0.29	0.94	0.56	0.32	20.4	6.01	0.43	1.18	0.64	0.40	1.74	0.82	0.38	4.39	2.03	0.24	43.3	5.84
Pyr	n.d.	0.83	0.38	0.24	24.1	6.31	n.d.	0.21	0.05	0.38	1.13	0.76	n.d.	2.17	0.65	0.23	32.9	4.93
BaA	n.d.	1.11	0.30	n.d.	1.38	0.58	n.d.	0.35	0.08	n.d.	0.46	0.20	n.d.	0.30	0.27	n.d.	6.37	0.77
Chr	n.d.	1.26	0.25	0.07	7.43	1.30	n.d.	0.20	0.02	n.d.	0.43	0.23	n.d.	0.45	0.35	n.d.	2.94	0.46
BbF	n.d.	1.56	0.35	n.d.	0.13	n.d.	n.d.	0.78	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.29	0.63
BjF/BkF	n.d.	1.79	0.78	n.d.	0.66	0.14	n.d.	0.95	0.64	n.d.	n.d.	n.d.	n.d.	0.04	0.04	n.d.	1.11	0.21
BeP	n.d.	0.17	0.01	n.d.	0.36	0.04	n.d.	0.33	0.15	n.d.	n.d.	n.d.	n.d.	0.13	0.09	n.d.	2.11	0.27
BaP	n.d.	1.11	0.29	n.d.	0.37	0.03	n.d.	0.35	0.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.06	0.26
Ind	n.d.	1.15	0.32	n.d.	0.59	0.09	n.d.	0.45	0.25	n.d.	n.d.	n.d.	n.d.	0.44	0.32	n.d.	2.78	0.33
DahA	n.d.	5.34	0.50	n.d.	0.89	0.17	n.d.	0.77	0.51	n.d.	0.57	0.02	n.d.	0.71	0.60	n.d.	3.82	0.46
BghiP	n.d.	2.19	0.29	n.d.	0.74	0.09	n.d.	0.35	0.23	n.d.	n.d.	n.d.	n.d.	0.51	0.32	n.d.	3.00	0.32
Total PAH	2.13	28.5	8.99	3.60	167	59.5	2.72	8.48	5.52	5.26	18.2	10.4	4.63	34.6	17.8	2.14	361	67.2
Particle phase																		
Nap	n.d.	3.28	0.24	n.d.	0.11	0.04	n.d.	0.72	0.16	n.d	0.72	0.21	n.d.	0.28	0.07	n.d.	0.33	0.14
AcPy	n.d.	2.52	0.10	n.d.	0.10	0.01	n.d.	0.54	0.12	n.d	0.24	0.04	n.d.	n.d.	n.d.	n.d.	0.12	n.d.
AcP	n.d.	1.53	0.11	n.d.	0.17	0.04	n.d.	0.59	0.16	n.d	0.31	0.14	n.d.	0.43	0.09	n.d.	0.42	0.05
Flu	n.d.	0.95	0.08	n.d.	0.31	0.08	n.d.	0.40	0.08	n.d	0.36	0.05	n.d.	n.d.	n.d.	n.d.	0.13	0.01
PA	n.d.	1.11	0.26	n.d.	1.37	0.37	n.d.	0.32	0.15	n.d	0.15	0.01	n.d.	0.68	0.04	n.d.	0.17	0.06
Ant	n.d.	1.45	0.26	n.d.	0.44	0.20	n.d.	0.36	0.12	n.d	0.31	0.20	n.d.	0.27	0.04	n.d.	0.14	0.01
FluT	n.d.	0.88	0.17	n.d.	2.28	0.51	n.d.	0.50	0.31	n.d	0.28	0.12	n.d.	0.41	0.07	n.d.	0.37	0.11
Pyr	n.d.	3.44	0.38	0.32	1.57	0.63	n.d.	0.17	0.05	n.d	0.39	0.26	n.d.	0.21	0.05	n.d.	0.34	0.15
BaA	n.d.	2.67	0.37	0.12	3.44	0.99	n.d.	0.32	0.11	0.20	0.59	0.34	n.d.	0.30	0.19	n.d.	1.05	0.17
Chr	n.d.	3.44	0.39	0.11	1.88	0.75	n.d.	0.17	0.04	0.27	0.49	0.38	n.d.	0.45	0.09	n.d.	1.25	0.17
BbF	n.d.	2.67	0.44	n.d.	0.07	n.d.	n.d.	0.37	0.11	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	0.13	0.01
BjF/BkF	n.d.	2.39	1.05	n.d.	1.93	1.03	n.d.	1.57	0.75	n.d.	0.20	0.04	n.d.	n.d.	n.d.	n.d.	1.63	0.27
BeP	n.d.	0.12	0.06	0.14	0.38	0.23	n.d.	0.50	0.25	n.d.	n.d.	n.d.	n.d.	0.17	0.03	n.d.	0.17	0.06
BaP	n.d.	1.36	0.39	0.14	1.53	0.84	n.d.	0.45	0.24	n.d.	0.46	0.02	n.d.	n.d.	n.d.	n.d.	0.46	0.09
Ind	n.d.	2.25	0.48	n.d.	0.96	0.60	n.d.	0.76	0.35	n.d.	0.45	0.10	n.d.	n.d.	n.d.	n.d.	0.19	0.02
DahA	n.d.	1.86	0.42	n.d.	0.87	0.26	n.d.	0.82	0.54	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BghiP	n.d.	1.53	0.47	n.d.	1.20	0.65	n.d.	0.55	0.29	n.d.	0.37	0.10	n.d.	n.d.	n.d.	n.d.	0.28	0.07
Total PAH	0.61	33.3	5.61	1.08	14.4	7.00	0.46	7.71	3.82	1.16	3.72	2.01	n.d.	1.65	0.67	n.d.	5.94	1.39
Sampling period	02/06/08-30/07/08			01/12/08-04/02/09			04/08/08-25/09/08			11/02/09-08/04/09			20/04/09-17/06/09			29/09/08-26/11/08		
No. Samples	26			26			22			26			26			27		
Average Temp.	23.2±2.5			9.0±2.5			25.0±2.7			12.0±1.5			20.5±2.8			15.5±4.3		
% PAHs Air/PM	62.0/38.0			89.5/10.5			59.1/40.9			83.8/16.2			96.4/3.6			98.0/2.0		

n.d., values under the limit of detection of each sample.

important source of particulate phase bounded PAHs.

Site 3 presented the highest average concentrations for the gas phase with average total PAH values of 17.8 ng m^{-3} in the high temperature season and 67.2 ng m^{-3} in the low temperature season, whereas Site 2 presented the lowest average values in both phases (Table 1). These sites are suburban areas near the South Industrial Complex and roads with moderate traffic intensity. The high maximal PAH values found in gas phase in Site 3 could be reflect both traffic intensity and industrial activities in the South Complex.

The average total PAH levels of the industrial sites of this study were comparable with those measured in industrial sites and in suburban areas in Europe (Cincinelli, et al. 2007; Ravindra et al. 2006), much higher than those previously reported for some urban areas (Ras et al. 2009b) and very much higher than those reported in high mountain regions of Europe (Fernandez et al. 2002). The PAH levels of the sampling sites therefore seem to be related to the activities of the petrochemical industry in the vicinity.

3.3. Benzo[a]pyrene equivalents of particle and gas phase PAHs

Table 2 shows the average BaP-eq in the gas phase and in the particle phase, for the 18 target PAHs and the total PAH, by site and sampling period and the TEFs applied for the 18 PAHs. We also indicate the individual PAH compounds that were quantified in <15% of the samples.

The contribution of the gas phase to the total BaP-eq in this study was substantial, with values ranging between 34% and 86%. This high contribution was due to the presence of some heavy PAHs in the gas phase with high TEFs, and because of the high concentrations of the most volatile PAHs in the gas phase.

It is worth noting that BaP-eq values for the particle phase were higher than those for the gas phase in winter in Site 1, but comparable between the particle and gas phases in summer at this site, and comparable between the two phases during both seasons at Site 2 (Table 2). For Site 3 the major contribution to the total BaP-eq came from the gas phase due to the lo w concentrations of heavy PAHs- such as BaP and DahA- in particle phase samples from this site. Site 1 showed the highest total BaP-eq for the combined gas and particle phases in summer (2.073 ng m^{-3}) and in winter (1.992 ng m^{-3}).

3.4. Lifetime lung cancer risk of 18 PAHs in the atmosphere

Figure 2A shows the average lifetime lung cancer risk estimated for each PAH, by sampling site and sampling period. Site 1 showed the highest estimated risk with values of 1.8×10^{-4}

Environ. Health Perspect. (DOI: 10.1289/ehp.1002855)

Table 2. Average benzo[a]pyrene equivalents, expressed in ng m^{-3}, for the gas and particle phases in the three sampling sites, over the two seasonal sampling periods.

		Site 1		Site 2		Site 3	
PAH	TEF[(a)]	Summer Gas/PM	Winter Gas/PM	Summer Gas/PM	Winter-Spring Gas/PM	Spring Gas/PM	Autumn Gas/PM
Nap	0.001	$1.4x10^{-3}/2.5x10^{-4}$ (b)	$4.2x10^{-3}/5.0x10^{-5}$	$3.7x10^{-4}/1.6x10^{-4}$	$9.2x10^{-4}/2.1x10^{-4}$	$3.7x10^{-4}/7.0x10^{-5}$	$3.0x10^{-3}/1.3x10^{-4}$
AcPy	0.001	$5.2x10^{-4}/1.9x10^{-4}$ (b)	$3.4x10^{-3}/3.0x10^{-5}$	$2.3x10^{-4}/1.3x10^{-4}$	$7.4x10^{-4}/5.0x10^{-5}$	$1.2x10^{-4}/2.0x10^{-5}$ (b)	$3.0x10^{-3}/2.5x10^{-5}$ (b)
AcP	0.001	$3.1x10^{-4}/1.2x10^{-4}$ (b)	$1.3x10^{-3}/4.0x10^{-5}$	$2.1x10^{-4}/1.7x10^{-4}$	$6.3x10^{-4}/1.5x10^{-4}$	$4.2x10^{-4}/1.0x10^{-4}$	$2.2x10^{-3}/5.0x10^{-5}$
Flu	0.0005	$3.5x10^{-4}/5.0x10^{-5}$	$3.0x10^{-3}/3.5x10^{-5}$	$2.1x10^{-4}/4.5x10^{-5}$	$7.1x10^{-4}/3.0x10^{-5}$	$6.8x10^{-4}/8.0x10^{-6}$ (b)	$3.6x10^{-3}/2.5x10^{-5}$ (b)
PA	0.0005	$7.1x10^{-4}/1.3x10^{-4}$	$1.5x10^{-2}/1.9x10^{-4}$	$5.7x10^{-4}/7.5x10^{-5}$	$2.1x10^{-3}/2.0x10^{-5}$	$6.2x10^{-3}/3.0x10^{-5}$ (b)	$1.9x10^{-2}/3.5x10^{-5}$
Ant	0.0005	$3.4x10^{-4}/1.4x10^{-4}$	$1.4x10^{-3}/9.5x10^{-5}$	$1.8x10^{-4}/6.5x10^{-5}$	$2.3x10^{-4}/1.0x10^{-4}$	$2.3x10^{-4}/3.0x10^{-5}$	$1.3x10^{-3}/2.5x10^{-5}$ (b)
FluT	0.05	$2.8x10^{-2}/8.0x10^{-3}$	$0.32/2.5x10^{-2}$	$3.2x10^{-2}/1.5x10^{-2}$	$4.1x10^{-2}/6.0x10^{-3}$	$0.11/3.5x10^{-3}$	$0.31/5.5x10^{-3}$
Pyr	0.001	$3.8x10^{-4}/3.8x10^{-4}$	$6.8x10^{-3}/6.2x10^{-4}$	$5.0\ x10^{-5}/5.0x10^{-5}$	$7.6x10^{-4}/2.0x10^{-4}$	$6.4x10^{-4}/6.0x10^{-5}$	$5.3x10^{-3}/1.5x10^{-4}$
BaA	0.005	$1.5x10^{-3}/1.9x10^{-3}$	$3.1x10^{-3}/4.6x10^{-3}$	$4.0x10^{-4}/5.5x10^{-4}$	$1.0x10^{-3}/1.7x10^{-3}$	$2.7x10^{-4}/1.0x10^{-4}$	$4.3x10^{-3}/8.5x10^{-4}$
Chr	0.03	$7.5x10^{-3}/1.2x10^{-2}$	$4.2x10^{-2}/2.3x10^{-2}$	$6.0x10^{-4}/1.2x10^{-3}$	$6.9x10^{-3}/1.1x10^{-2}$	$2.1x10^{-3}/3.0x10^{-3}$	$1.5x10^{-2}/5.4x10^{-3}$
BbF	0.1	$3.5x10^{-2}/4.6x10^{-2}$	$2.0x10^{-3}$ (b)$/2.0x10^{-3}$	$9.0x10^{-3}/1.2x10^{-2}$	$1.0x10^{-3}$ (b)$/1.0x10^{-3}$ (b)	$1.0x10^{-3}$ (b)$/1.0x10^{-3}$ (b)	$7.1x10^{-2}/2.0x10^{-3}$
BjF/BkF	0.05	$3.9x10^{-2}/4.9x10^{-2}$	$7.5x10^{-3}/5.2x10^{-2}$	$3.2x10^{-2}/3.7x10^{-2}$	$5.0x10^{-5}$ (b)$/2.0x10^{-3}$	$1.5x10^{-4}$ (b)$/1.5x10^{-4}$ (b)	$1.1x10^{-2}/1.5x10^{-2}$
BeP	0.002	$2.0x10^{-5}/1.8x10^{-4}$ (b)	$8.0x10^{-5}$ (b)$/4.8x10^{-4}$	$3.6x10^{-4}/5.8x10^{-4}$	$2.0x10^{-6}$ (b)$/2.0x10^{-5}$ (b)	$1.8x10^{-5}$ (b)$/6.6x10^{-5}$	$5.8x10^{-4}/1.4x10^{-4}$
BaP	1	0.30/0.40	$5.0x10^{-2}/0.85$	0.15/0.21	$2.0x10^{-2}$ (b)$/6.0x10^{-2}$ (b)	$2.7x10^{-2}$ (b)$/3.8x10^{-3}$ (b)	0.28/0.14
Ind	0.1	$3.2x10^{-2}/4.7x10^{-3}$	$1.0x10^{-2}/6.1x10^{-2}$	$2.5x10^{-2}/3.5x10^{-2}$	$2.0x10^{-3}$ (b)$/1.3x10^{-2}$	$6.4x10^{-3}/1.6x10^{-3}$ (b)	$3.9x10^{-2}/8.0x10^{-3}$
DahA	1.1	0.56/0.48	0.21/0.27	0.56/0.59	$4.4x10^{-2}$ (b)$/4.4x10^{-2}$ (b)	$0.12/1.8x10^{-2}$ (b)	$0.58/4.4x10^{-2}$ (b)
BghiP	0.02	$6.0x10^{-3}/9.4x10^{-3}$	$2.0x10^{-3}/1.3x10^{-2}$	$4.6x10^{-3}/6.0x10^{-3}$	$4.0x10^{-4}$ (b)$/2.6x10^{-3}$	$1.3x10^{-3}/3.2x10^{-4}$ (b)	$7.6x10^{-3}/2.4x10^{-3}$
Total PAH (Gas/PM)		1.014/1.059	0.685/1.307	0.817/0. 913	0.122/0.143	0.272/0.067	1.363/0.223
Total PAH (Gas+PM)		2.073	1.992	1.730	0.265	0.339	1.586

(a) TEFs for Nap, AcPy and AcP are from Nisbet and Lagoy (1992), all others are from Larsen and Larsen (1998)

(b) < 15% of the samples quantified

(1.8 additional cases per 10,000 people exposed) for the summer period and 1.7×10^{-4} for the winter period. In the 2008 sampling periods, Site 2 and Site 3 had estimated lifetime lung cancer risks of 1.5×10^{-4} and 1.4×10^{-4} corresponding to a summer and autumn season, respectively, that are consistent with estimates for Site 1.

However, in the 2009 sampling periods the estimated risks for Site 2 and Site 3 were 2.2×10^{-5} (winter-spring) and 2.9×10^{-5} (spring), respectively, which were much lower than those estimated for 2008. These differences could reflect external factors, such as the international economic crisis which affected many industries located at the chemical site and probably caused reductions in the production or shutdowns of some chemical plants (AEQT 2009), changing the origin of emissions.

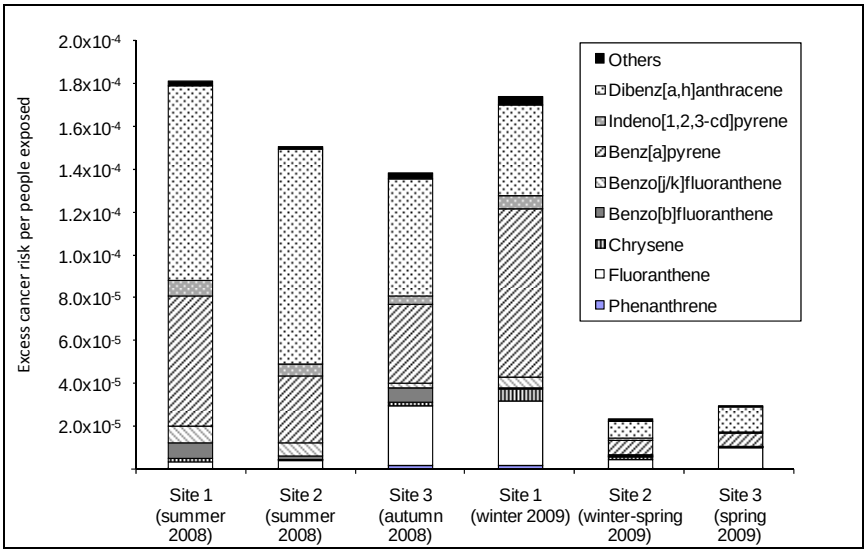


Figure 2A. Average estimated lifetime lung cancer risk expressed as excess cancer risk per people exposed, by sampling location, by period and PAH.

Concerning the individual toxicity of the target PAHs, the compounds that contributed most to the total estimated risk were BaP (19-45%), DahA (24-67%) and FluT (2-32%) (combined contribution between 81% and 92%). The contribution of FluT, which was mainly found in the gas phase and had high values in Site 1 in winter and in Site 3 in autumn, was also noteworthy. Although FluT is classified as a weak carcinogen, it is mutagenic and, therefore, has a high TEF (0.05). BbF, BjF, BkF, Chr and Ind also contributed to the overall risk with maximum individual contributions between 4% and 7%. Although PA had the highest average concentration of the individual

PAHs at the three sampling sites, it made a small contribution to the overall risk because of its low TEF.

The average, the maximum and the minimum excess lifetime lung cancer risks per people exposed by period and sampling site are shown in Figure 2B. An average lifetime lung cancer risk of 1.2×10^{-4} (1.2 additional cases per 10,000 people exposed) was estimated for the study area as a whole.

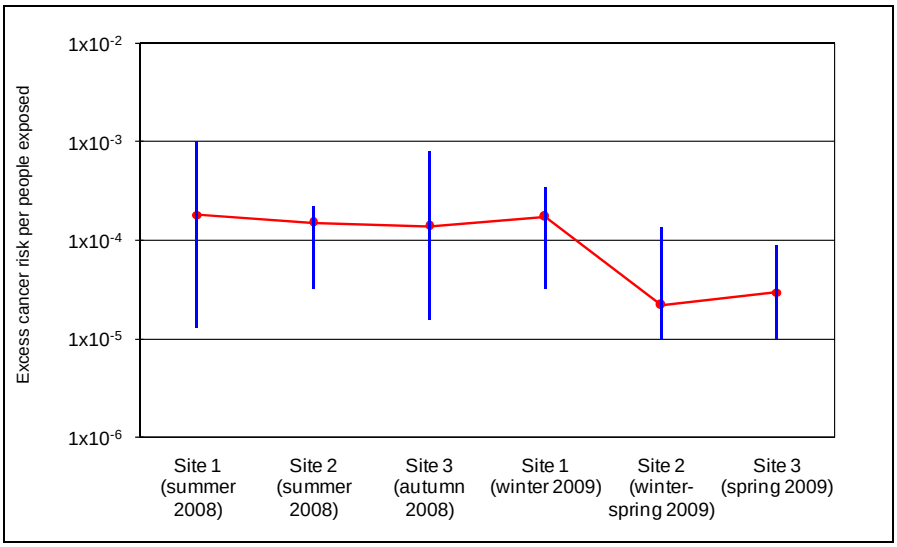


Figure 2B. Minimum, maximum and average estimated excess lifetime lung cancer risk per people exposed, in the three sampling sites by period. The vertical lines indicate the range of risk obtained with the daily concentrations.

This represents the estimated risk above the baseline lifetime lung cancer risk in the absence of atmospheric PAH exposure. Taking into account the calculated average lifetime risk and assuming a homogeneous exposure of the inhabitants (170,263) around the chemical site, 0.3 annual cases of lung cancer can be attributed to this PAH exposure. Furthermore, in the absence of major indoor PAH sources – such as tobacco smoking, cooking fumes and residential heating -outdoor PAHs can that the lung cancer risk due to these PAH exposures is not negligible and also substantially contribute to indoor PAH levels (Spengler et al 2001).

According to the WHO Air Quality Guidelines for Europe (WHO 2000) each country has to determine their own acceptable risk levels. However, the risk estimate for the study area was higher than 10^{-5}, the upper-bound excess lifetime cancer risk recommended by the WHO for carcinogens in drinking water (WHO 1993) and higher than the 10^{-6} risk which is the USEPA guideline (Robson 2007). We therefore conclude should be taken into account for health protection in the future.

Moreover, as it can be seen in Figure 2B, the maximum risk found was 1×10^{-3} in Site 1. Even though this risk corresponds to one episode, this result is higher than the recommended values and would correspond to a definite risk according to criteria used in similar risk assessment studies (Sexton et al. 2007).

Quantitative Risk Assessment (QRA) is a powerful tool to derive a quantitative estimate of risk that can be used to inform environmental legislation. However, QRA has also areas of uncertainty that should be taken into account. There are two main uncertainties in the case of PAHs: the TEF values, which were established from toxicological animal studies, and the value of BaP unit risk, which was extrapolated from the results of epidemiological studies with exposure to high concentrations, and can be biased in some cases, according to recent studies (Armstrong et al. 2004).

Finally, although the USEPA has demonstrated that the re-estimation of risk substituting the non-detected values with ½ LOD and the non-quantified values with ½ LOQ did not significantly affect risk assessment calculations by itself, the contribution of the compounds quantified in less than 15% of the samples can be overestimated. In such cases, the use of statistical imputation methodologies for risk estimation has been suggested (USEPA 2000).

4. CONCLUSIONS

In this study, 18 PAHs were determined in 153 matched samples of atmospheric air and particulate matter from three sampling locations around a chemical site. The results showed that PAH values were generally higher in low temperature periods than in high temperature periods, with higher individual PAH concentrations observed in the gas phase, especially for the most volatile PAHs.

Risk calculations showed that the contribution of the gas phase PAHs to the total risk should be taken into account, as well as the contribution of volatile PAHs such as FluT, and of the heaviest PAHs, like BaP or DahA, especially during high temperature periods.

The average estimated lifetime lung cancer risk for our study area was higher than the WHO and the USEPA recommended values, but lower than the threshold value of 10^{-3} considered a definite risk according to criteria used in similar risk assessment studies. Despite uncertainties associated with the sampling methodology and quantitative risk assessment calculations, our findings suggest that it would be prudent to take PAH concentrations in both gas and particle phases into account in future health risk legislation. The real risk values may otherwise be underestimated.

Acknowledgments

The authors wish to acknowledge the financial support of this study by the Department of Innovation, Universities and Enterprises of the Generalitat de Catalunya through project 2009 SGR 223 and the collaboration of the Departament de Medi Ambient i Habitatge of the Generalitat de Catalunya, especially its staff in the Tarragona local office for the sample collection.

None of the authors has any potential or actual competing financial interests.

REFERENCES

AEQT 2009. Public report 2009. Available: http://www.aeqt.com [accessed 1 December 2010].

Armstrong B, Hutchinson E, Unwin J, Fletcher T. 2004. Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: A review and meta-analysis. Environ Health Persp 112:970-978.

ATSDR (Agency for Toxic Substances and Disease Registry). 1995. Toxicological profile for polycyclic aromatic hydrocarbons. Available: http://www.atsdr.cdc.gov/ [accessed 17 March 2010].

ATSDR (Agency for Toxic Substances and Disease Registry). 2007. CERCLA Priority List of Hazardous Substances. Available: http://www.atsdr.cdc.gov/cercla/07list.html [accessed 22 June 2010].

Baek SO, Goldstone ME, Kirk PWW, Lester JN, Perry R. 1991. Phase distribution and particle-size dependency of polycyclic aromatic-hydrocarbons in the urban atmosphere. Chemosphere 22:503-520.

Bosetti C, Boffetta P, La Vecchia C. 2007. Occupational exposures to polycyclic aromatic hydrocarbons, and respiratory and urinary tract cancers: a quantitative review to 2005. Ann Oncol 18:431-446.

Boström CE, Gerde P, Hanberg A, Jernström B, Johansson C, Kyrklund T, et al. 2002. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. Environ Health Persp 110:451-488.

Cincinelli A, Del Bubba M, Martellini T, Gambaro A, Lepri L. 2007. Gas-particle concentration and distribution of n-alkanes and polycyclic aromatic hydrocarbons in the atmosphere of Prato (Italy). Chemosphere 68:472-478.

Dejmek J, Solansky I, Benes I, Lenicek J, Srám RJ. 2000. The impact of polycyclic aromatic hydrocarbons and fine particles on pregnancy outcome. Environ Health Persp 108:1159-1164.

ECRN (European Chemical Regions Network). 2010. http://www.ecrn.net/regions/cat.php [accessed 1 December 2010].

EEA (European Environment Agency). 1999. Criteria for EUROAIRNET - The EEA Air Quality Monitoring and Information Network. Technical report No. 12. Available: http://www.eea.eur

opa.eu/publications/TEC12 [accessed 1 December 2010].

EEC (European Economic Community). 2005. Directive 2004/107/EC of the European Parliament and of the Council relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Offi J Europ Comm L23.

Atmospheric gas-particle partitioning of polycyclic aromatic hydrocarbons in high mountain regions of Europe. Environ Sci Technol 36:1162-1168.

Gerde P, Muggenburg BA, Hoover MD, Henderson RF. 1993. Disposition of polycyclic aromatic-hydrocarbons in the respiratory-tract of the beagle dog .1. The alveolar region. Toxicol Appl Pharm 121:313-318.

IARC (International Agency for Research on Cancer). 2010. Some Non-heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures. Monogr Eval of Carcinog Risk Hum 92:765-771.

Larsen JC, Larsen PB. 1998. Chemical Carcinogens. In: Air Pollution and health (Herster RE, Harrison RM, eds). Cambridge: The Royal Society of Chemistry, 33-56.

Li Z, Mulholland JA, Romanoff LC, Pittman EN, Trinidad DA, Lewin MD, et al. 2010. Assessment of non-occupational exposure to polycyclic aromatic hydrocarbons through personal air sampling and urinary biomonitoring. J Environ Monit 12:1110-1118.

Lintelmann J, Fischer K, Karg E, Schroppel A. 2005. Determination of selected polycyclic aromatic hydrocarbons and oxygenated polycyclic aromatic hydrocarbons in aerosol samples by high-performance liquid chromatography and liquid chromatography-tandem mass spectrometry. Anal Bioanal Chem 381:508-519.

Liu HH, Yang HH, Chou CD, Lin MH, Chen HL. 2010. Risk assessment of gaseous/particulate phase PAH exposure in foundry industry. J Hazard Mater 181:105-111.

Morello-Frosch RA, Woodruff TJ, Axelrad DA, Caldwell JC. 2000. Air toxics and health risks in California: The public health implications of outdoor concentrations. Risk Anal 20:273-291.

Nisbet ICT, Lagoy PK. 1992. Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic-Hydrocarbons (PAHs). Regul Toxicol Pharm 16:290-300.

Perera FP, Li Z, Whyatt R, Hoepner L, Wang SA, Camann D, et al. 2009. Prenatal Airborne Polycyclic Aromatic Hydrocarbon Exposure and Child IQ at Age 5 Years. Pediatrics 124:E195-E202.

Ras MR, Borrull F, Marcé RM. 2009a. Pressurised liquid extraction of polycyclic aromatic hydrocarbons from gas and particulate phases of atmospheric samples. J Sep Sci 32:1051-1059.

Ras MR, Marcé RM, Cuadras A, Mari M, Nadal M, Borrull F. 2009b. Atmospheric levels of polycyclic aromatic hydrocarbons in gas and particulate

phases from Tarragona Region (NE Spain). Int J Environ Anal Chem 89:543-556.

Ravindra K, Bencs L, Wauters E, de Hoog J, Deutsch F, Roekens E, et al. 2006. Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. Atmos Environ 40:771-785.

Ravindra K, Sokhi R, Van Grieken R. 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmos Environ 42:2895-2921.

Robson MG, Toscano WA. 2007. Risk assessment for environmental health. 1st ed. Joboken: John Wiley & Sons, Inc.

Sexton K, Linder SH, Marko D, Bethel H, Lupo PJ. 2007. Comparative assessment of air pollution-related health risks in Houston. Environ Health Persp 115:1388-1393.

Spengler JD, McCarthy JF, Samet JM. 2001. Indoor Air Quality Handbook. 1st ed. New York: McGraw-Hill.

Srám RJ, Binková BB, Dejmek J, Bobak M. 2005. Ambient air pollution and pregnancy outcomes: A review of the literature. Environ Health Persp 113:375-382.

USEPA (U.S. Environmental Protection Agency). 1994. Amendments to 1990 Clean Air Act-List of 189 Hazardous Air Pollutants.

USEPA (U.S. Environmental Protection Agency). 1999. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS). Compendium Method TO-13, EPA//625/R-96/010b. Center for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency.

USEPA (U.S. Environmental Protection Agency). 2000. Assigning values to non-detected/non-quantified pesticide residues in human health food exposure assessments. Office of Pesticide Programs U.S. Environmental Protection Agency. Washington.

WHO (World Health Organization). 1993. Guidelines for drinking-water quality. Chemical aspects, 2n edition.

Available: http://www.who.int/water_sanitation_health/dwq/gdwq2v1/en [accessed 23 July 2010].

WHO (World Health Organization). 1998. Polycyclic aromatic hydrocarbons, selected non heterocyclic. Environmental health Criteria 202. Available: http://www.inchem.org/documents/ehc/ehc/ehc202.htm [accessed 19 May 2010].

WHO (World Health Organization). 2000. Air Quality Guidelines for Europe, 2n ed. World Health Organization. Regional Office for Europe. Copenhagen.

SUPPLEMENTAL MATERIAL

Supplemental Material, Table 1. Main method parameters tested by spiking different amounts of the standards in clean PUFs and QFFs and then extracted and analyzed in the optimized conditions. The table shows the average results for extraction of PUFs and QFFs.

PAHs	Recovery [a] (%, n=5)	Repeatability [b] (%RSD, n=5)	Reproducibility [c] (%RSD, n=5)	LOD [d] (ng m^{-3})	LOQ [e] (ng m^{-3})
Nap	90	1	3	0.016	0.033
AcPy	91	1	1	0.033	0.100
AcP	95	2	2	0.016	0.033
Flu	92	1	2	0.033	0.167
PA	98	2	2	0.033	0.067
Ant	97	1	1	0.033	0.100
FluT	91	5	7	0.033	0.067
Pyr	100	5	6	0.002	0.017
BaA	95	3	4	0.002	0.017
Chr	97	2	2	0.002	0.017
BbF	92	3	5	0.016	0.033
BjF	90	5	10	0.002	0.017
BkF	90	5	10	0.002	0.017
BeP	96	4	7	0.002	0.017
BaP	99	4	8	0.033	0.167
Ind	98	6	9	0.033	0.167
DahA	97	1	5	0.033	0.167
BghiP	98	6	6	0.033	0.167

[a] Recovery calculated as the percentage of the response obtained by the analysis of 5 PUFs and QFFs spiked with 1mL of standard target PAH solution of 1 ppm, compared with the responses obtained by direct injection of the same amount of standard under the same analytical conditions.

[b] Repeatability expressed as relative standard deviation (%RSD) for the analysis of PUFs and QFFs spiked with 1mL of standard target PAH solution of 1 ppm (n=5) on the same day.

[c] Reproducibility expressed as relative standard deviation (%RSD) for the analysis of PUFs and QFFs spiked with 1mL of standard target PAH solution of 1 ppm (n=5) on different days.

[d] Limits of detection (LODs) defined as the concentration equivalent to three times the noise of the quantifier ion, for 300 m^2 of sample volume.

[e] Limits of quantification (LOQs) defined as the lower calibration level for each compound, for 300 m^2 of sample volume.

Supplemental Material, Table 2. Daily PAH values, expressed in ng m^{-3}, obtained in Site 1 between the 2nd and the 16th of June 2008.

PAHs	2 Jun 08		3 Jun 08		4 Jun 08		10 Jun 08		11 Jun 08		12 Jun 08		16 Jun 08	
	Gas	PM	Gas	PM	Gas	PM	Gas	PM	Gas	PM	Gas	PM	Gas	PM
Nap	3.44	3.28	2.41	n.d.	3.53	n.d.	1.49	n.d.	n.d.	n.d.	2.10	n.d.	n.d.	n.d.
AcPy	2.21	2.52	1.53	n.d.	1.80	n.d.	0.98	n.d.	0.95	n.d.	1.32	n.d.	n.d.	n.d.
AcP	1.88	1.53	1.04	n.d.	1.09	n.d.	0.68	n.d.	n.d.	n.d.	0.71	n.d.	n.d.	n.d.
Flu	1.62	0.95	1.15	n.d.	1.35	n.d.	0.58	0.30	0.61	n.d.	0.68	n.d.	0.72	n.d.
PA	1.84	1.11	1.53	0.68	2.11	0.71	1.65	0.44	1.45	0.42	2.13	0.41	2.46	0.40
Ant	1.58	1.45	1.18	1.01	1.24	1.06	0.75	0.60	0.81	0.60	0.97	0.58	0.83	n.d.
FluT	0.81	0.88	0.63	0.39	0.70	0.41	0.51	0.24	0.61	0.24	0.88	0.21	0.94	0.22
Pyr	0.48	3.44	0.77	0.88	0.75	0.93	0.36	0.26	n.d.	0.29	0.58	0.28	0.70	0.26
BaA	1.11	2.67	0.91	0.88	0.99	0.93	0.62	0.47	n.d.	0.46	0.57	0.44	0.43	0.47
Chr	1.26	3.44	0.66	1.18	0.72	1.24	0.27	0.33	n.d.	0.30	0.53	0.30	0.33	0.33
BbF	0.84	2.67	0.91	0.71	1.12	0.75	1.56	0.51	n.d.	0.42	0.41	0.48	0.38	0.47
BjF/BkF	1.76	2.39	1.42	1.62	1.79	1.71	1.23	1.00	1.05	0.96	0.98	0.98	0.95	0.95
BeP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	n.d.	0.12	n.d.	0.09
BaP	1.02	1.36	0.82	0.82	1.11	0.86	0.52	0.48	0.59	0.45	0.51	0.45	n.d.	0.46
Ind	1.15	2.25	0.97	0.94	0.99	0.99	n.d.	0.49	0.62	0.51	0.52	0.59	0.45	0.58
DahA	5.34	1.86	1.07	1.10	1.16	1.16	n.d.	0.66	0.68	0.64	0.65	0.71	n.d.	0.70
BghiP	2.19	1.53	0.63	0.85	0.78	0.89	n.d.	0.43	0.46	0.43	0.40	0.56	n.d.	0.48
Total PAH	28.5	33.3	17.6	11.0	21.2	11.7	11.2	6.22	7.82	5.72	13.9	6.00	8.20	5.32

n.d., values under the limit of detection of each sample.

Supplemental Material, Table 3. Daily PAH values, expressed in ng m^{-3}, obtained in Site 1 between the 1st and the 16th of December 2008.

PAHs	1 Dec 08		2 Dec 08		9 Dec 08		10 Dec 08		11 Dec 08		15 Dec 08		16 Dec 08	
	Gas	PM	Gas	PM	Gas	PM	Gas	PM	Gas	PM	Gas	PM	Gas	PM
Nap	2.99	0.03	7.95	0.08	2.67	0.08	5.82	0.04	12.2	0.04	7.44	0.04	20.4	0.08
AcPy	1.43	n.d.	4.80	n.d.	1.55	n.d.	3.35	n.d.	8.63	n.d.	5.53	n.d.	9.03	n.d.
AcP	0.72	n.d.	1.81	0.04	5.77	0.04	1.33	0.03	3.70	0.03	1.72	0.04	2.52	n.d.
Flu	6.58	0.16	11.7	n.d.	6.41	n.d.	5.18	0.16	12.5	n.d.	14.4	n.d.	13.1	n.d.
PA	31.6	0.39	65.1	0.38	39.1	0.27	17.0	0.39	46.3	0.22	91.1	0.32	55.8	0.46
Ant	3.18	0.16	5.28	0.20	3.61	0.17	1.98	0.19	4.72	0.16	9.00	0.24	5.08	0.24
FluT	5.80	0.22	12.0	0.41	6.87	0.24	3.42	0.35	9.68	0.20	20.4	0.56	11.7	0.65
Pyr	3.96	0.55	9.11	0.55	5.41	0.47	2.44	0.60	6.44	0.41	15.5	0.76	8.07	0.86
BaA	0.78	0.34	1.09	1.02	1.17	0.48	0.64	1.85	1.38	0.26	1.09	0.73	1.17	0.58
Chr	0.65	0.55	1.25	0.95	1.03	0.38	0.07	0.11	1.53	0.26	1.26	1.88	0.99	1.22
BbF	n.d.	<LOQ	n.d.	<LOQ	n.d.	<LOQ	n.d.	<LOQ	n.d.	<LOQ	n.d.	<LOQ	n.d.	<LOQ
BjF/BkF	0.50	1.1	0.66	1.36	0.12	0.74	n.d.	0.44	n.d.	0.34	n.d.	1.93	n.d.	1.56
BeP	0.34	0.29	0.36	0.24	0.32	0.24	n.d.	0.15	n.d.	0.15	n.d.	0.38	n.d.	0.28
BaP	n.d.	0.73	n.d.	0.91	n.d.	0.84	n.d.	0.50	n.d.	0.36	n.d.	1.43	n.d.	1.53
Ind	n.d.	0.62	n.d.	0.72	n.d.	0.55	n.d.	0.29	n.d.	0.30	n.d.	0.89	n.d.	0.69
DahA	n.d.	n.d.	n.d.	0.41	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.34
BghiP	n.d.	0.66	n.d.	0.72	n.d.	0.65	n.d.	0.30	n.d.	0.31	n.d.	0.90	n.d.	0.85
Total PAH	58.5	5.54	121	7.74	74.1	4.91	41.3	5.25	107	2.89	167	9.73	128	9.06

n.d., values under the limit of detection of each sample
<LOQ, values under the limit of quantification of each sample

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.2.2. Chronic risk assessment of exposure to volatile organic compounds in the atmosphere near industrial sites

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

CHRONIC RISK ASSESSMENT OF EXPOSURE TO VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE NEAR INDUSTRIAL SITES

Noelia Ramírez[a], Anna Cuadras[b], Enric Rovira[b], Francesc Borrull[a]*, Rosa Maria Marcé[a]
[a] Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, Sescelades Campus, Tarragona 43007,Spain
[b] Observatory of Health and Environment of Tarragona, Agència de Protecció de la Salut, Departament de Salut. Generalitat de Catalunya,Tarragona, Spain

Abstract

This study focuses on characterising the risk of exposure to volatile organic compounds (VOCs) by means of inhalation in people living in the vicinity of the largest chemical site in the Mediterranean area. Eighty-six VOCs were initially selected for this study based on their adverse environmental and health effects. The monitoring campaign was conducted for 276 days in three different locations around the chemical site. The analytical method used for the characterisation was based on European standard method EN-14662-2, which consists of the active sampling of air for 24 h in charcoal tubes, followed by extraction with carbon disulfide and GC-MS analysis. Forty-four VOC compounds with toxicological data available concerning their carcinogenic and non-carcinogenic health effects were quantified during the monitoring campaign. None of the quantified VOCs showed average concentrations exceeding their chronic reference concentrations and, therefore, non-carcinogenic health effects are expected as a result of this exposure. However, the global average cancer risk due to VOC exposure in the area (3.3×10^{-4}) was found to be above the values recommended by the WHO and USEPA.The influence of the analytical method was also evaluated by comparing cancer risk estimates using a thermal desorption (TD) method based on method EN-14662-1. The results of the 24-h samples for the solvent extraction method were compared with the average of 12 daily samples of 2-h for the TD method for 24 sampling days. Although the global estimated lifetime cancer risk was statistically comparable for both methods, some differences were found in individual VOC risks.
To our knowledge, this is the first study that estimates the carcinogenic and non-carcinogenic risks posed by the inhalation of VOCs in people living near a chemical site of this size, and compares the estimated cancer risk obtained using two different standard analytical methods.

Keywords: Air quality; Cancer risk assessment; Non-cancer risk assessment; Volatile organic compounds.

1. INTRODUCTION

Because of their ubiquitous presence in the atmosphere and their significant impact on the environment and human health, volatile organic compounds (VOCs) are considered essential parameters for assessing the air quality in indoor and outdoor environments. Among the environmental effects of VOCs, the most relevant is the formation of tropospheric ozone (the main cause of photochemical smog formation) and secondary organic aerosols (the primary component of total aerosol mass) (Koppmann, 2008).

The chemical diversity of the VOC group is reflected in the diversity of the health effects that individual VOCs can cause, ranging from relatively inert VOCs with no known health effects to the highly toxic effects of reactive VOCs. In general, chronic health effects of VOCs can be classified as either non-carcinogenic or carcinogenic. The main non-carcinogenic chronic effects are irritative, sensory effects, damage to the liver, kidneys and central nervous system, asthma and other respiratory effects (Rumchev et al., 2007). The main carcinogenic effects are lung, blood (leukaemia and non-Hodgkin lymphoma), liver, kidney and biliary tract cancer (WHO, 2000). With regard to these carcinogenic effects, the International Agency for Research on Cancer (IARC) classifies benzene as a human carcinogen (Group 1) (IARC, 2011). Moreover, other VOCs also exhibit carcinogenic activity. For instance, trichloroethene, tetrachloroethene and 1,2-dibromo-ethane are considered to be probable carcinogens for humans (Group 2A, IARC), ethylbenzene, carbon tetrachloride and chloroform are possibly carcinogenic to humans (Group 2B, IARC), and dibromochloromethane and hexachlorobutadiene are weak carcinogens (Group 3, IARC).

Due to their low boiling points and high vapour pressures, the main exposure route to most VOCs is through inhalation and as more time is spent indoors than outdoors and because indoor environments are characterised by higher concentrations of pollutants, indoor environments are considered the most relevant source of VOC exposure. Although a variety of potential indoor sources of VOCs have been reported – such as environmental tobacco smoke, cooking, and cleaning and personal care products (Zhou et al., 2011) - recent studies have demonstrated that one of the main sources of indoor VOC concentrations is the infiltration of outdoor pollution into buildings (Esplugues et al, 2010; Loh et al., 2007).

Current air quality legislation restricts atmospheric VOC emissions, such as European Council Directive 1999/13/EC, which limits the emission of VOCs due to the use of organic solvents (European Commission, 1999) and 2008/50/EC, which recommends the monitoring of ozone precursor VOCs (European Commission, 2008).

Furthermore, most compounds listed in the United States Environmental Protection Agency (USEPA) Clean Air Act list of hazardous air pollutants are VOCs (USEPA, 1994). However, in European countries only the ambient concentration of benzene, limited to an annual average of 5 μg m^{-3}, is regulated (European Commission, 2008). Nevertheless, previous studies have demonstrated that in addition to benzene other VOCs carry significant weight in the characterisation of ambient chronic risk and should also be considered (McCarthy et al., 2009; Wu et al. 2009).

Today, many international agencies (e.g. the World Health Organization (WHO), the United States Environmental Protection Agency (USEPA), and the Unites States Food and Drug Administration (USFDA)) use quantitative risk assessment (QRA) as a basis for regulatory decisions about chemical mixtures. Cancer risk is typically estimated by lifetime cancer risk (LCR) which is presented as the increased probability of developing cancer as a result of a specific exposure (WHO, 2000). Non-cancer risk is assessed by the assumption of a threshold concentration for each toxicant and is expressed as a hazard ratio (HR, the ratio of a potential exposure to a chemical to the level at which no adverse effects are expected) (Robson and Toscano, 2007).

Air is a complex mixture in which VOC concentrations generally range from μg m^{-3} to ng m^{-3}. Therefore, efficient and sensitive sampling, preconcentration and analysis techniques are required to reliably determine atmospheric VOC concentrations. Of the sampling and preconcentration techniques proposed by official environmental agencies, the most commonly used are those based on enrichment onto solid sorbents followed either by thermal desorption (EN 14662-1, 2005; USEPA TO-17, 1999) or liquid desorption (EN 14662-2, 2005). Because the two methods use different adsorption sorbent and desorption processes, it is important to study how these can affect the risk estimates of an area.

The aim of this study is to characterise the risk of VOC exposure by inhalation in people living in urban and suburban areas near the largest chemical site in the Mediterranean area. To our knowledge, this is the first time that the non-carcinogenic and carcinogenic risks related to VOC inhalation has been estimated for people living around a chemical and petrochemical site of this size. To that end, eighty-six VOCs – most of them included in the USEPA priority list (USEPA, 1994) – were initially selected. The target VOCs were determined in three locations near the industrial site over two periods: from October 2008 to December 2008 and from October 2009 to May 2010. Furthermore, the uncertainties of risk assessment calculations were also discussed. Specifically, the influence of the analytical method used in the cancer risk estimates was evaluated by comparing the risk values obtained

using two different standard methods (EN 14662-1 and 14662-2).

2. EXPERIMENTAL

2.1. Study area

Because of its unique climate, location and the volume of emissions it receives, the Mediterranean atmosphere acts as a photochemical reactor with high levels of oxidants. As a consequence, the ozone and air quality limits are often exceeded in this region (Monks et al., 2009).

The largest chemical site in southern Europe and the Mediterranean region (ECRN, 2010) is located in the Tarragona area (Catalonia, north-western Spain). This chemical site is divided into two main areas: the North Industrial Complex, which has an area of 470 ha and includes an oil refinery and other chemical industries; and the South Industrial Complex, which occupies an area of 717 ha and contains several chemical and petrochemical plants. The total production of the two complexes is about 21 MT per year (AEQT, 2009). Atmospheric emissions of non-methane VOCs have been estimated at 3,100 T per year from the chemical site as a whole (PRTR, 2009).

To determine VOC risk, three sampling sites were selected on the basis of their proximity to the industrial complexes, and the prevailing winds (north-north-westerly in cold seasons and south-south-easterly in warm seasons, light annual average wind speeds (< 3 m s^{-1})). Figure 1 shows a map of the area studied, the location of the main city (Tarragona) and the three sampling sites. Site 1 is located in Perafort-Puigdelfí which is a semirural area less than 0.5 km east of the North Industrial Complex. Site 2, Tarragona-Bonavista, is a suburban area of Tarragona situated less than 1 km north of the South Industrial Complex and less than 0.5 km from a road with moderate traffic density (14,041 vehicles per day, Spanish Ministry of Public Works, 2007). Finally, Site 3 is also located in a suburban area – Vila-seca – less than 1 km from the west end of the South Complex and less than 1 km from a road (20,049 vehicles per day, Spanish Ministry of Public Works, 2007).

2.2. Sample collection

The monitoring campaign designed to determine the VOC risk of the chemical site was conducted over two periods: from October 2008 to January 2009 and from October 2009 to June 2010. A total of 276 samples were taken in both periods (91 in Site 1, 89 in Sites 2, and 96 in Site 3, respectively). Sampling was performed using the standard method for measuring benzene in air, EN-14662-2 (EN 14662-2, 2005) (method A). Samples were collected by means of active sampling in standard Orbo™-32 charcoal tubes (7 cm in length x 6-mm o.d., provided by Supelco) using a CPV-COV-S (MCV, Collbató, Spain) to pump air samples at a flow rate of between

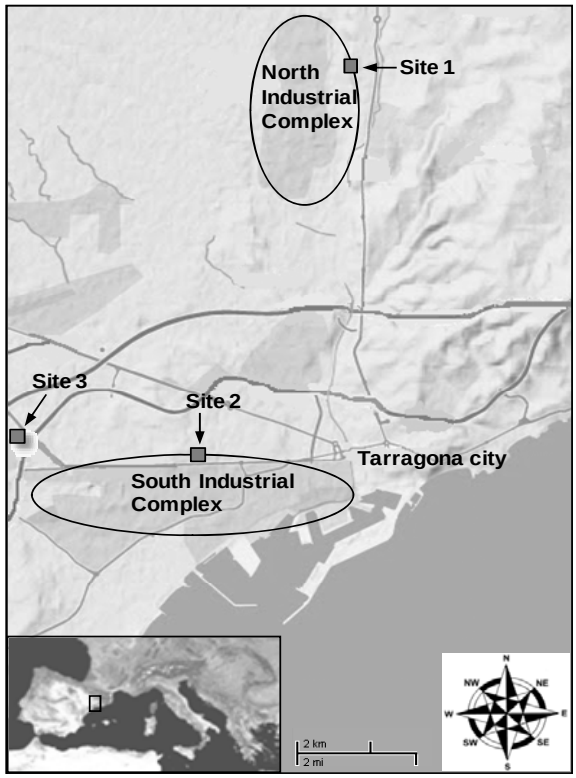


Figure 1. Map of the studied area showing the location of the main city (Tarragona), the North and South Industrial Complexes and the three sampling sites.

500 and 700 mL min^{-1} for 24 hours, thus collecting between 720 L and 1000 L of air. After sampling, the charcoal tubes were closed with PTFE caps, stored in hermetic glass jars at –20 °C and analysed no later than one week subsequent to collection.In order to determine the influence of the analytical method on the risk estimates, a thermal desorption method based on standard method EN 14662-1 (EN 14662-1, 2005) (method B) was simultaneously used for VOC monitoring during a period of 24 sampling days. A total of 288 samples were collected with this method corresponding to 2 h samples (12 per day) over eight days in each site, during the first period of sampling (from October 2008 to January 2009). Samples were taken with stainless-steel tubes (9 cm × 6.35 mm o.d. × 5 mm i.d.) filled with a multi-sorbent bed of Tenax TA-Carbograph 1TD (Markes International Limited, Llantrisant, UK). A MTS-32™ sequential tube sampler coupled with a constant flow sampling pump (FLEC Air Pump 1001, from Markes) was used to pump air samples at 22 mL min^{-1} for 2 hours and 2.64 L of

air were collected. Complete information about the development and optimisation of this sampling method can be found in a recent publication (Ramirez et al., 2010).

2.3. Chemical standards and reagents

The standards of the 85 target VOCs involved two mixtures of volatile organic compounds at 2000 mg L^{-1} (592/524 Volatile Organics Calibration Mix and EPA 524.2 Revision 4 Mix in methanol, from Supelco, Bellefonte, USA) and the individual standards of i-pentane, 1-pentene, n-pentane, 2-pentene (cis/trans mixture), isoprene, 1-hexene, n-hexane, i-octane, n-heptane, 1,4-dioxane, n-octane, (Sigma-Aldrich, Steinheim, Germany), 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, 1,2-diethylbenzene, 1,3-diethylbenzene, 1,4-diethylbenzene (Fluka, Buchs, Switzerland), 1-methylnaphthalene and 2-methylnaphthalene (Riedel-deHaën, Seelze, Germany). The minimal purity of the standards was 97%. Toluene-d_8 from Aldrich was used as an internal standard as recommended by EN 14662-2 (EN 14662-2, 2005).

The standards were diluted in methanol for gas chromatography with purity >99.9% (SDS, Peypin, France) and with a toluene-d_8 constant concentration of 5 mg L^{-1}. All the standards were prepared on the day of use and stored at 4°C in 10 ml Certan® capillary vials provided by Supelco. 99.999% pure helium gas and nitrogen were used for the chromatographic analysis and thermal desorption, respectively (Carburos Metálicos, Barcelona, Spain). Carbon disulfide from Sigma-Aldrich (purity 99.9% with less than 0.001% benzene) was used for the extraction of the analytes.

2.4. Analytical method

After sampling, each glass tube sample for method A was scored with a quartz blade (Orbo™ tube cutter, Supelco) and the charcoal from the adsorbing section (front section of the tube) was transferred to a 2-mL capped vial and the back-up section (back section of the tube) was transferred to another capped vial. These two sections were analysed separately.

To desorb the samples, 1 mL of extraction solution (5 ppm of internal standard diluted in carbon disulfide) was added to each sample vial. The sample vials were immediately capped with PTFE caps and shaken for 30 min. Immediately following the desorption period, 1 µl of sample extract was injected into the gas chromatograph. Samples whose back-up sections were found to have 5% or more analytes than the adsorbing section were discarded as recommended by EN 14662-2 (EN 14662-2, 2005).

A 6890N gas chromatograph and a 5973 inert mass spectrometer (Agilent Technologies, Palo Alto, USA) were used to separate and determine the

target VOCs using a Zebron ZB-5 capillary column (60 m, 0.32 mm, 1.0 µm, provided by Phenomenex, Le Pecq Cedex, France). Analyses were performed by injecting 1 µL of extract in a split/splitless port at 180C with a split of 5 mL min^{-1} and a helium flow rate of 1.2 mL min^{-1}. The oven temperature of the GC was initially maintained at 40 °C for 5 min, then raised to 140 °C at a rate of 6 °C min^{-1} and raised again to 220 °C at a rate of 15 °C min^{-1} and maintained at that temperature for 8 min. The GC-MS interface was set at 280 °C and the mass spectrometer acquired data in scan mode with an *m/z* interval from 35 to 280 and an electron impact energy of 70 eV.

Samples taken with method B were thermally desorbed in a Unity Thermal Desorption system connected to an Ultra A automatic sampler (both from Markes international Limited, Llantrisant, UK) and analysed using the chromatographic method described above. More detailed information about the optimisation and performance of method B has recently been published (Ramirez et al, 2010).

The guidelines for methods EN 14662-2 and EN 14662-1 (EN 14662-1, 2005; EN 14662-2, 2005) were followed for quality assurance purposes. The internal standard calibration method was used for the GC-MS quantification in method A and the external standard calibration was used in method B, with coefficients of determination values (r^2) higher than 0.996 for all target VOCs for both methods.

The limits of the detection (LODs) for method A ranged from 0.01 to 1 µg m^{-3} (for a sample preconcentration of 1 m^3), and from 4×10^{-4} to 0.4 µg m^{-3} for method B (for a sample pre-concentration of 2.64 L). The limits of quantification (LOQs) were between 0.05 and 2 µg m^{-3} for method A and between 0.002 and 0.45 µg m^{-3} for method B. Repeatability was < 13% RSD (n=5) for all target VOCs for method A and < 7% for method B and recoveries for most compounds were > 95% for both methods.

To detect possible background contamination, weekly field blanks were tested by placing a charcoal tube with broken ends into one of the sampler's channels, but without passing an air sample through it. With method B, blanks of the total process were checked by placing two blank tubes into the sequential tube sampler every sampling day without passing a sample through it. Signals of the target compounds in field blanks were taken into account when calculating sample concentrations. None of the samples showed VOC concentrations >5% in the back-up section compared to the respective adsorbing section; therefore, no samples were excluded from the study. More information about the method validation parameters and the quality assurance procedures employed can be found in a recent publication (Ramirez et al., 2010).

2.5. Risk assessment

The estimates for the non-cancer risk assessment were based on the comparison of the daily ambient concentrations with their respective chronic non-cancer inhalation level at which no adverse effects are expected for single VOCs. These levels are expressed as Reference Concentrations (RfCs) – used by the USEPA Integrated Risk Information System (IRIS) (IRIS, 2011); Minimum Risk Levels (MRLs) – used by the Agency for Toxic Substances and Disease Registry (ATSDR) (ATSDR, 2011); or Reference Exposure Levels (RELs) – used by the California Office of Environmental Health Hazard Assessment (OEHHA) (OEHHA, 2003). Therefore, the Hazard Ratio (HR) of each compound (i) was calculated by dividing its daily concentration (expressed in μg m^{-3}) by its corresponding Reference Concentration (RfC, also in μg m^{-3}):

$$HR_i = C_i / RfC_i \quad [1]$$

The reference concentrations for each VOC were taken first from IRIS and ATSDR, giving priority to the most recent available data. For reference concentrations not available from these agencies, those provided by OEHHA, the USEPA Health Effects Assessment Summary Tables (HEAST) or the USEPA provisional values were used (RAIS, 2009). The reference concentrations used in this study and their sources are listed in Table 1.

Cancer risk assessment was calculated for the carcinogenic VOCs detected in the samples, whose unit risk (UR) values have been established by an official agency. These URs were extracted from databases provided by the WHO (WHO, 2000), the IRIS (IRIS, 2011), the OEHHA (OEHHA, 2003), giving priority to the WHO and IRIS URs, in this order (see Table 1).

The lifetime cancer risk (LCR) attributable to inhalation exposures was calculated by multiplying each UR estimate value by the daily concentrations (in μg m^{-3}) of each compound (i):

$$LCR_i = C_i \times UR_i \quad [2]$$

The UR of each compound corresponds to excess lifetime cancer risk calculated as a result of the continuous exposure to an agent at a concentration of 1 μg m^{-3} over a lifetime of 70 years (IRIS, 2011). In this study, the individual cancer risk of each VOC was assumed to be additive, and therefore, the global lifetime cancer risk was considered as the sum of the LCRs of the individual compounds.

To determine the risk of the industrial area, the risk values of the three sampling sites were considered together. For risk assessment calculations, VOC concentrations under the LODs and the LOQs were considered as half the LOD or half the LOQ, in accordance with USEPA criteria (USEPA, 2000). The acceptance of these criteria provides a background risk for

Table 1. Non-cancer reference concentrations, cancer unit risks of the VOCs found during the monitoring campaign and their carcinogenic classifications in the IARC.

VOCs	Non-cancer		Cancer		
	Chronic conc. ($\mu g\ m^{-3}$)	Source	Group IARC	Unit risk $(\mu g\ m^{-3})^{-1}$	Source
n-Pentane	1000	PPRTV	-	-	-
Methyl-tercbutylether	2520	ATSDR	3	2.6×10^{-7}	OEHHA
n-Hexane	700	IRIS	-	-	-
Methacrylonitrile	0.7	HEAST	-	-	-
Chloroform	98	ATSDR	2B	2.3×10^{-5}	IRIS
1,1,1-Trichloroethane	5000	IRIS	3	-	-
1,2-Dichloroethane	2430	ATSDR	2B	2.6×10^{-5}	IRIS
Benzene	9.6	ATSDR	1	6.0×10^{-6}	WHO
Carbon tetrachloride	100	IRIS	2B	6.0×10^{-6}	IRIS
2-Nitropropane	20	IRIS	2B	-	-
1,2-Dichloropropane	4	IRIS	3	1.0×10^{-5}	OEHHA
Trichloroethene	600	OEHHA	2A	4.3×10^{-7}	WHO
1,4-Dioxane	3600	ATSDR	2B	7.7×10^{-6}	OEHHA
Methylmethacrylate	700	IRIS	3	-	-
Cis-1,3-Dichloropropene	31.8	ATSDR	2B	4.0×10^{-6}	IRIS
Trans-1,3-Dichloropropene	31.8	ATSDR	2B	4.0×10^{-6}	IRIS
Toluene	5000	IRIS	3	-	-
1,1,2-Trichloroethane	-	-	3	1.6×10^{-5}	IRIS
Ethylmethacrylate	300	PPRTV	-	-	-
Dibromochloromethane	-	-	3	2.7×10^{-5}	OEHHA
1,2-Dibromoethane	9	IRIS	2A	6.0×10^{-4}	IRIS
Tetrachloroethene	271	ATSDR	2A	5.9×10^{-6}	OEHHA
Chlorobenzene	1000	OEHHA	-	-	-
1,1,1,2-Tetrachloroethane	-	-	3	7.4×10^{-6}	IRIS
Ethylbenzene	1300	ATSDR	2B	2.5×10^{-6}	OEHHA
m,p-Xylene	217	ATSDR	3	-	-
Bromoform	-	-	3	1.1×10^{-6}	IRIS
Styrene	852	ATSDR	2B	-	-
o-Xylene	217	ATSDR	3	-	-
1,1,2,2,-Tetrachloroethane	-	-	3	5.8×10^{-5}	OEHHA
1,2,3-Trichloropropane	0.3	IRIS	2A	-	-
Isopropylbenzene	400	IRIS	-	-	-
Bromobenzene	60	IRIS	-	-	-
1,3,5-Trimethylbenzene	6	PPRTV	-	-	-
1,2,4-Trimethylbenzene	7	PPRTV	-	-	-
1,2,3-Trimethylbenzene	5	PPRTV	-	-	-
1,4-Dichlorobenzene	60	ATSDR	2B	1.1×10^{-5}	OEHHA
1,2-Dichlorobenzene	200	HEAST	3	-	-
Hexachloroethane	-	-	2B	4.0×10^{-6}	IRIS
1,2-Dibromo-3-chloropropane	0.2	IRIS	2B	2.0×10^{-3}	OEHHA
1,2,4-Tricholorobenzene	200	HEAST	-	-	-
Naphtalene	3.7	ATSDR	2B	8.7×10^{-5}	WHO
Hexachlorobutadiene	-	-	3	2.2×10^{-5}	IRIS

ATSDR (Agency for Toxic Substances and Disease Registry) (ATSDR, 2011); HEAST (Health Effects Assessment Summary Tables) (RAIS,2009); IRIS (Integrated Risk Information System) (IRIS, 2011); PPRTV (Provisional Peer Reviewed Toxicity Values of IRIS) (RAIS,2009); OEHHA (Office of Environmental Health Hazard Assessment) (OEHHA, 2003); WHO (World Health Organization) (WHO, 2000).

each non-detected and non-quantified VOC.

Moreover, the corresponding attributable annual number of cases in the population around the chemical site were calculated as: population exposed (number of inhabitants) × global lifetime cancer risk (number of cases per population) / 70 (years of exposure). The exposed population (170,263 inhabitants, Statistical Institute of Catalonia, 2008) was defined based on the proximity to the industrial site and the prevailing winds.Furthermore, in order to ascertain how the analytical method employed might influence cancer risk estimates, some parameters were evaluated for both official methods on 24 days (8 days at each sampling site) during the first monitoring period. The following parameters were compared for each carcinogenic compound detected in the samples: the number of quantified samples; the background LCR considered as the estimated risk assuming half of the MDL for non-detected samples; and average LCR. Moreover, the global cancer risk obtained for each method was also statistically compared.

3. RESULTS AND DISCUSSION

Seventy-two of the 86 target VOCs initially selected for this study were detected during the monitoring campaign. Of these 72 VOCs detected, toxicological data for non-cancer reference concentrations and/or cancer UR were only available for 44; therefore, these VOCs were selected for risk assessment estimations.

The remainder of the VOCs detected can be classified as uncertain risk compounds because there was insufficient data to ascertain risk and they were therefore excluded from the risk estimates. However, their detection in the samples should be taken into account for future research. Data about the 42 VOCs excluded from the risk study is shown in the supplementary material section, in Table 1S.

3.1. VOC distribution

Table 2 summarises the average, minimum and maximum concentrations of the VOCs considered for the risk assessment estimations. The sampling period and the number of samples in each site, as well as the number of samples in which each compound was quantified are also indicated in the table. In general, the most often quantified compounds (>75%) were benzene, carbon tetrachloride, toluene, ethylbenzene, m,p-xylene, styrene and o-xylene. Other VOCs such as n-pentane, chloroform, 2-nitropropane, tetrachloroethene, 1,3,5 trimethylbenzene and 1,2,4-trimethylbenzene were detected in more than 50% of the samples.

The highest maximum concentrations were found at Site 2 and correspond to n-pentane (34.2 μg m^{-3}), toluene (26.2

Table 2. Target VOCs (in chromatographic elution order) found during the campaign and considered for the risk estimations, showing their average, minimum and maximum concentrations at each sampling site, expressed in μg m^{-3}, and percent of detected samples.

VOCs	Site 1			Site 2			Site 3			% Quant. samples
	Aver.	Min	Max	Aver.	Min	Max	Aver.	Min	Max	
n-Pentane [b]	2.06	n.d.	6.30	1.73	<LOQ	34.2	0.85	n.d.	n.d.	60.1
Methyl-tercbutylether [a]	0.01	n.d.	0.50	0.05	n.d.	0.6	n.d.	n.d.	n.d.	3.6
n-Hexane [a,b]	1.06	n.d.	10.70	0.39	n.d.	4.8	0.31	n.d.	7.1	35.5
Methacrylonitrile	n.d.	n.d.	0.20	n.d.	n.d.	n.d.	0.24	n.d.	4.5	9.4
Chloroform [a]	0.65	n.d.	1.50	0.52	n.d.	1.3	2.29	n.d.	129.7	59.1
1,1,1-Trichloroethane [a]	0.09	n.d.	0.70	0.04	n.d.	0.8	0.09	n.d.	0.6	10.1
1,2-Dichloroethane [c]	0.03	n.d.	1.50	0.21	n.d.	2.8	0.07	n.d.	3.6	6.2
Benzene [a,b,c]	1.50	n.d.	6.40	1.37	<LOQ	3.7	0.48	n.d.	2	80.1
Carbon tetrachloride [a]	1.29	0.8	2.30	0.99	0.6	2.3	0.37	n.d.	2.5	77.2
2-Nitropropane [a]	0.50	n.d.	1.40	1.31	0.5	4.9	0.20	n.d.	1.9	59.8
1,2-Dichloropropane [a]	0.05	n.d.	0.70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.8
Trichloroethene [a,c]	0.74	n.d.	2.20	0.67	n.d.	3	0.28	n.d.	3	46.0
1,4-Dioxane [a]	0.01	n.d.	1.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
Methylmethacrylate [a]	1.25	n.d.	14.40	0.05	n.d.	0.6	n.d.	n.d.	<LOQ	22.8
Cis-1,3-dichloropropene	0.20	n.d.	4.50	0.03	n.d.	0.6	n.d.	n.d.	n.d.	3.3
Trans-1,3-dichloropropene	0.14	n.d.	2.70	0.06	n.d.	0.8	n.d.	n.d.	n.d.	3.6
Toluene [a,b,c]	2.61	0.3	8.30	4.26	1.00	26.2	1.12	n.d.	6.7	93.8
1,1,2-Trichloroethane [a]	0.01	n.d.	0.60	0.01	n.d.	0.4	n.d.	n.d.	n.d.	0.7
Ethylmethacrylate	n.d.	n.d.	n.d.	0.02	n.d.	0.7	n.d.	n.d.	n.d.	1.1
Dibromochloromethane	0.01	n.d.	0.60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7
1,2-Dibromoethane	0.01	n.d.	0.60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7
Tetrachloroethene [a,c]	0.67	n.d.	1.00	0.57	n.d.	0.2	0.05	n.d.	0.6	67.0
Chlorobenzene [a]	0.13	n.d.	1.10	0.34	n.d.	1.1	n.d.	n.d.	<LOQ	19.9
1,1,1,2-Tetrachloroethane	0.01	n.d.	0.70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
Ethylbenzene [a]	1.91	0.7	5.70	1.85	0.5	14.3	0.46	n.d.	3.1	77.5
1,2,3-Trichloropropane	0.01	n.d.	0.70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
m,p-Xylene [a,b]	1.22	0.7	2.80	1.13	0.6	2.9	0.48	n.d.	2.9	77.2
Bromoform [a]	0.01	n.d.	0.70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
Styrene [a,c]	1.25	0.2	4.20	1.21	n.d.	2.8	0.34	n.d.	3.7	75.0
o-Xylene [a,b]	0.96	n.d.	2.00	0.82	0.4	1.6	0.35	n.d.	2.3	76.1
1,1,2,2-Tetrachloroethane [a]	0.01	n.d.	0.70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
Isopropylbenzene [a]	0.34	n.d.	0.80	0.23	n.d.	0.8	n.d.	n.d.	<LOQ	31.2
Bromobenzene	0.51	n.d.	1.10	0.13	n.d.	0.7	n.d.	n.d.	0.1	25.0
1,3,5-Trimethylbenzene [b]	0.61	n.d.	0.90	0.45	0.3	1.00	0.21	n.d.	1.4	64.9
1,2,4-Trimethylbenzene [b]	0.62	n.d.	1.60	0.78	0.4	1.5	0.28	n.d.	2.3	68.5
1,2,3-Trimethylbenzene [b]	0.03	n.d.	0.90	0.21	n.d.	18.6	0.08	n.d.	1.3	5.1
1,4-Dichlorobenzene [a]	0.04	n.d.	0.80	0.03	n.d.	0.4	n.d.	n.d.	n.d.	3.6
1,2-Dichlorobenzene	0.04	n.d.	0.80	0.01	n.d.	0.4	n.d.	n.d.	n.d.	2.9
Hexachloroethane [a]	0.01	n.d.	0.70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
1,2-Dibromo-3-chloropropane	0.01	n.d.	0.80	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
1,2,4-Trichlorobenzene	0.02	n.d.	1.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7
Naphthalene [a,c]	0.33	n.d.	1.40	0.45	n.d.	1.9	0.02	n.d.	1.7	19.2
Hexachlorobutadiene	0.01	n.d.	0.85	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
Sampling period	07-10-2008/04-12-2008 20-10-2009/29-12-2009			05-11-2008/05-12-2008 19-01-2010/31-03-2010			06-12-2008/09-01-2009 09-04-2010/17-06-2010			
Number of samples	91			89			96			

Table 2 (cont.)

[a] Compounds included in the USEPA List of Hazardous Air Pollutants (USEPA, 1994).
[b] Ozone precursors recommended for measurement by the Directive 2008/50/EC (European Commission, 2008).
[c] Compounds included as hazardous organic pollutants in the WHO Air Quality Guidelines (WHO, 2000).
n.d., values under the limit of detection of each sample.
< LOQ, values under the limit of quantification of each sample.

μg m^{-3}), ethylbenzene (14.3 μg m^{-3}) and 1,2,3-trimethylbenzene (18.6 μg m^{-3}). metacrylate (14.4 μg m^{-3}) at Site 1 and chloroform at Site 3 (129.7 μg m^{-3}) were also high. It is worth mentioning that the average concentration of benzene at all three sites did not exceed the 5 μg m^{-3} established as the annual average threshold limit (European Commission, 2008), which was exceeded on only one day at Site 1 (6.4 μg m^{-3}).

The VOC concentrations found in this study were comparable with those measured in other industrial and suburban sites in Spain (Pérez-Rial et al., 2010). However, the average concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) were below those reported in previous studies in the main city of the area (Ras-Mallorquí et al. 2009) and in other areas with intensive street traffic (Buczynska et al., 2009).

3.2. Non-cancer risk assessment

Thirty-seven quantified VOCs have estimated reference values for non-cancer effects (see Table 1). Figure 2 shows the average, maximum, minimum, 25^{th}, 50^{th} (median) and the 75^{th} percentile HR for these compounds.

The maximum concentrations of n-hexane (10.7 μg m^{-3}) and methyl-

The average HRs were less than 1 for all the studied VOCs, which means that their concentrations were commonly below the level of concern. However, five VOCs showed maximum concentrations over their reference value: 1,2-dibromo-3-chloropropane, 1,2,3-trichloropropane, methacrylo-nitrile, 1,2,3-trimethylbenzene and chloroform. It is also worth mentioning that four compounds presented average HR values of over 0.1, which can also be considered of potential concern (McCarthy et al., 2009). However, among these VOCs only benzene was quantified in more than 15% of the samples.

3.3. Cancer risk assessment

Figure 3 shows the average, maximum, minimum, 25^{th}, 50^{th} (median) and 75^{th} percentile of the individual LCRs for the 23 VOCs found in the samples that showed a cancer potential value (see UR values in Table 1). A LCR of 10^{-6} (recommended by USEPA (Robson, 2007) was used for reference in this study and is also indicated in Figure 3. In accordance with a previous study (Sexton et al., 2007), compounds with an attributable cancer risk of over 10^{-4}

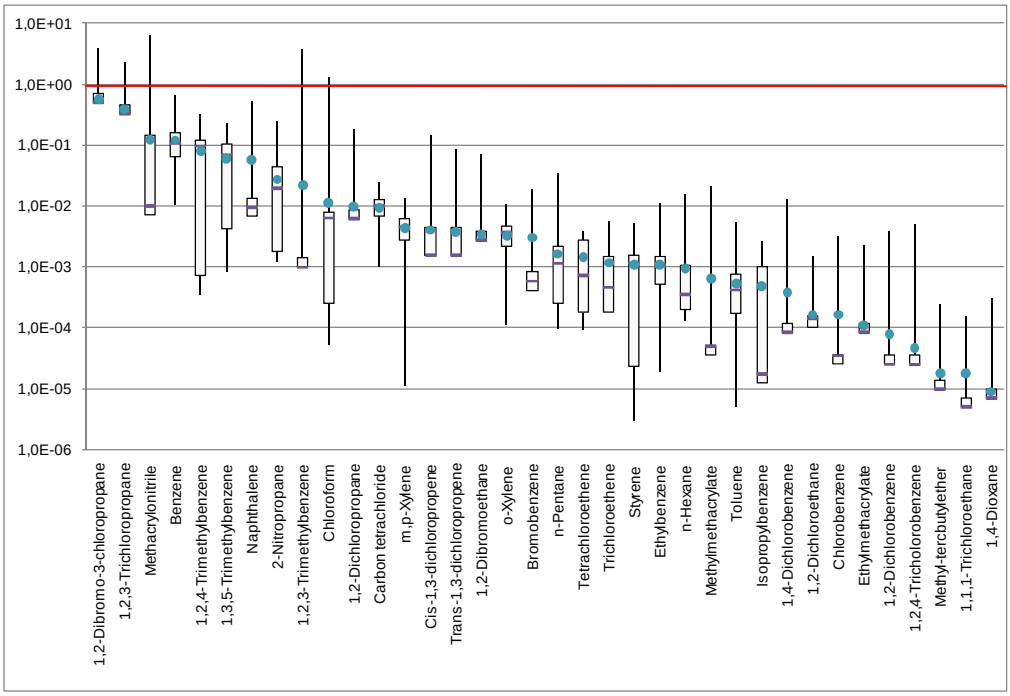


Figure 2. Percentile distributions for hazard ratios for the VOCs detected with non-cancer reference concentrations. For each individual VOC, the box plot represents the 25th and 75th percentile of the hazard ratio and the horizontal line inside the box represents the median. The bottom and top vertical lines indicate the minimum and the maximum hazard ratios and the circle symbol the average hazard ratio.

can be considered as a "definite risk", between 10^{-5} and 10^{-4} as a "probable risk" and between 10^{-5} and 10^{-6} as a "possible risk".

In this study, the carcinogenic VOCs were grouped into three different categories depending on their LCRs and the samples quantified for each compound: group A compounds were quantified in over 15% of the samples, whose average LCR is above the 10^{-6} (1 additional case per 1,000,000 people exposed) benchmark; group B compounds were quantified in fewer than 15% of the samples with average LCR above 10^{-6}; and group C compounds with LCRs below 10^{-6} were either quantified or not in 15% of the samples.

Group A includes chloroform (2.5×10^{-5}, probable risk), naphthalene (1.9×10^{-5}, probable risk), benzene (6.9×10^{-6}, possible risk), carbon tetrachloride (5.6×10^{-6}, possible risk), ethylbenzene (3.5×10^{-6}, possible risk) and tetrachloroethylene (2.3×10^{-6}, possible risk).

Group B includes 1,2-dibromo-3-chloropropane, 1,2-dibromoethane, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane. As mentioned earlier, these compounds were quantified in fewer

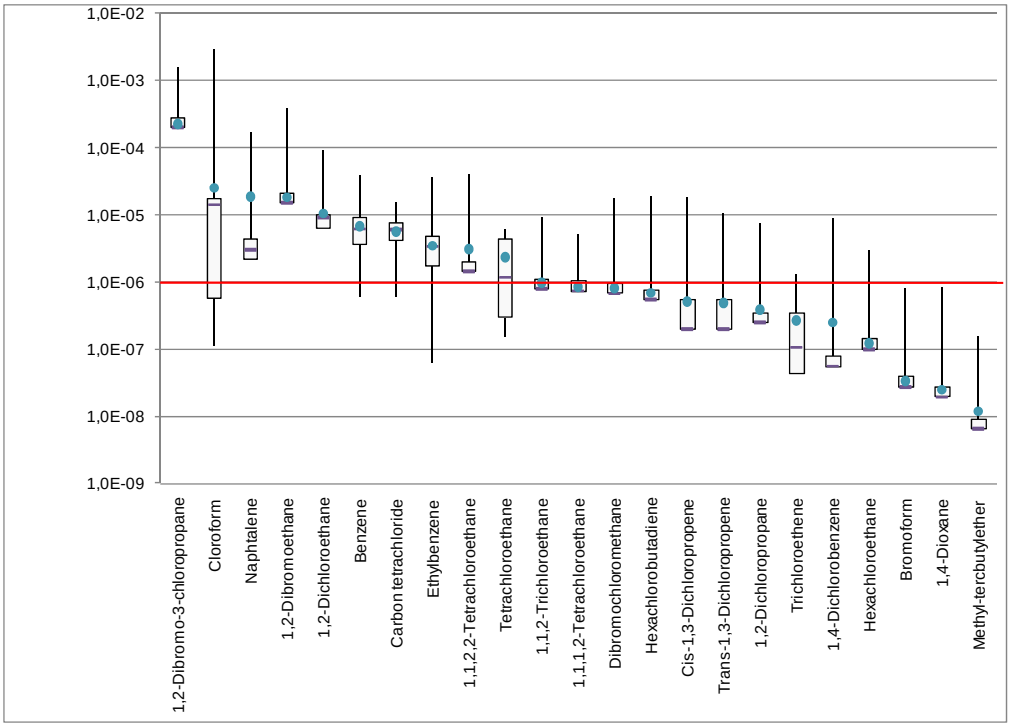


Figure 3. Percentile distribution of individual LCRs for the quantified VOCs with cancer potential values. The box plot of each individual VOC represents the 25th and 75th percentile of the LCRs and the horizontal line inside the box indicates the median LCR. The bottom and top lines indicate the minimum and the maximum LCRs, and the circle symbol the average LCR.

than 15% of the samples and therefore their risk values reflect the distribution of ½ LOD rather than ambient concentrations. For instance, 1,2-dibromo-3-chloropropane (LCR= 2.3×10^{-4}) was only determined in one of the samples throughout the course of the entire campaign. Lower LODs would help to reduce the uncertainty in ambient risk estimates, especially for compounds with very high URs.The remainder of the VOCs detected were included in group C (LCRs below 10^{-6}), and their risk values did not pose a relevant health concern. This group included the least quantified compounds such as 1,4-dichloro-benzene (2.5×10^{-7}), quantified in 4% of the samples, and compounds quantified in most of the samples, such as trichloroethene (2.7×10^{-7}), found in 46% of the samples.

The average, P25 and P75 lifetime cancer risks for the global study were 3.3×10^{-4} (3.3 additional cases per 10,000 people exposed), 2.6×10^{-4} and 3.5×10^{-4}, respectively. This represents the estimated risk above the baseline lifetime cancer risk in the absence of atmospheric VOC exposure. Taking into account the calculated average lifetime cancer risk and assuming exposure of

the inhabitants (170,263) around the chemical site, 0.8 (0.6-0.9) annual cases of cancer can be attributed to this VOC exposure.

The results obtained at each site showed similar estimated cancer risks at all three locations: Site 1, 3.4×10^{-4} (2.7×10^{-4} - 3.6×10^{-4}); Site 2, 3.2×10^{-4} (2.7×10^{-4} - 3.5×10^{-4}); and Site 3, 3.2×10^{-4} (2.3×10^{-4} - 3.4×10^{-4}). Previous studies estimating the overall cancer risk of different atmospheric contaminants have reported similar health risk values (Loh et al., 2007; Morello-Frosch et al., 2000; Wu et al., 2009). The estimated risk of this study was higher than the USEPA guideline (10^{-6}), and exceeded 10^{-5}, which is the upper-bound excess lifetime cancer risk recommended by the WHO for carcinogens in drinking water (WHO, 1993). Therefore, the average cancer risk attributed to this VOC exposure is not negligible and should be taken into account for future health risk legislation.

In a recent study the excess lifetime cancer risk attributable to exposure to polycyclic aromatic compounds (PAHs) from the same chemical site was estimated as 1.2 per 10,000 people exposed (Ramírez et al., 2011). Assuming accumulative cancer risks, the global cancer risk estimate for VOCs (3.4×10^{-4}) should be added to those found for PAHs (1.2×10^{-4}). Although neither the individual compounds of VOCs or PAHs revealed a definite risk in either study, the global lifetime cancer risk in this area is clearly high. Therefore, these risks are not negligible and can help to prioritise risk management decisions in a socially responsible and beneficial way for the protection against illness in the future. According to the WHO Air Quality Guidelines for Europe (WHO, 2000) each country has to determine their own acceptable risk levels. In fact, acceptable risk levels should be justifiable based on expected public health, environmental and socio-economic impacts (Assante-Duah, 2002).

3.4. Uncertainties and limitations of risk estimates

QRA can appropriately be regarded as a valuable tool for public health and environmental decisions. However, there are also some limitations and uncertainties inherent to QRA and the overall risk estimates that should be taken into account.

First, the analytical method chosen can play an important role in the quantification of the samples, and therefore in the estimated risk (Assante-Duah, 2002). Table 3 shows the most relevant cancer risk calculation parameters for the methods compared in this study: enrichment into charcoal tubes and liquid desorption (method A, 24 h samples) and enrichment into Tenax TA-Carbograph 1TD tubes and subsequent thermal desorption (method B, average of 12 daily samples of 2 h each). These parameters were calculated for each detected carcinogenic compound over

Table 3. Main risk calculation parameters for the detected carcinogenic compounds for both methods: % of quantified samples; limit of detection (LOD), average daily concentrations (expressed in μg m^{-3}); background LCR (risk estimated considering ½ LOD in the non detected samples); average LCR; and the range of the global LCR estimated for each method.

	Method A					Method B				
VOCs	% Quant. samples	LOD (μg m^{-3})	Aver. daily concen. (μg m^{-3})	Back-ground LCR [a]	Aver. LCR [a]	% Quant. samples	LOD (μg m^{-3})	Aver. daily concen. (μg m^{-3})	Back-ground LCR [a]	Aver. LCR [a]
Methyl-tercbutylether	8	0.05	0.45	$6.5x10^{-9}$	$1.9x10^{-8}$	8	0.04	0.52	$4.9x10^{-9}$	$1.2x10^{-8}$
Chloroform	50	0.01	3.23	$1.2x10^{-7}$	$3.8x10^{-5}$	96	0.02	0.48	$2.2x10^{-7}$	$1.0x10^{-5}$
1,2-Dichloroethane	13	0.50	1.96	$6.5x10^{-6}$	$1.5x10^{-5}$	58	0.004	1.36	$5.2x10^{-8}$	$2.2x10^{-5}$
Benzene	100	0.20	1.64	$6.0x10^{-7}$	$9.8x10^{-6}$	100	0.16	5.57	$4.9 x10^{-7}$	$3.3x10^{-5}$
Carbon tetrachloride	100	0.50	1.23	$1.5x10^{-6}$	$7.4x10^{-6}$	96	0.02	0.72	$5.7x10^{-8}$	$4.1x10^{-6}$
Trichloroethene	67	0.20	1.67	$4.3x10^{-8}$	$5.0x10^{-7}$	92	0.004	0.22	$8.6x10^{-10}$	$8.4x10^{-8}$
1,4-Dioxane	0	0.05	nd	$1.9 x10^{-7}$	-	79	0.30	0.54	$1.2x10^{-6}$	$4.0x10^{-6}$
Tetrachloroethene	71	0.05	0.16	$1.5x10^{-7}$	$7.8x10^{-7}$	96	0.002	0.47	$5.9x10^{-9}$	$2.6x10^{-6}$
Ethylbenzene	100	0.05	1.99	$6.3x10^{-8}$	$5.0x10^{-6}$	96	0.04	3.01	$4.8x10^{-8}$	$7.1x10^{-6}$
1,4-Dichlorobenzene	0	0.01	nd	$5.5x10^{-8}$	-	29	0.004	0.06	$2.2x10^{-8}$	$2.2x10^{-7}$
Naphthalene	0	0.05	nd	$2.2x10^{-6}$	-	17	0.04	0.64	$1.7x10^{-8}$	$1.6x10^{-5}$
Total LCR [a] Average (Min.-Max.)	$7.9x10^{-5}$ ($2.3x\ 10^{-5}$ – $7.1x\ 10^{-4}$)					$9.9 x\ 10^{-5}$ ($2.2x\ 10^{-5}$ – $4.4x10^{-4}$)				

a period of 24 sampling days from October 2008 to January 2009. In general, method B resulted in more compounds detected in the samples except for benzene, carbon tetrachloride, and ethylbenzene, whose results were ca. 100% for both methods.This higher number of compounds detected in these samples may indicate that more confident risk estimations can be obtained when using method B.

In general, background LCR values for method A were higher than those obtained for method B because the LODs for method B were generally lower (ranging from 0.002 μg m^{-3} to 0.30 μg m^{-3} for method B and from 0.01 μg m^{-3} to 0.50 μg m^{-3} for method A). This background risk is especially relevant for the VOCs detected in fewer than 15% of the samples, in which overall risk can be overestimated, especially when using method A. The average LCR for each carcinogenic VOC and total LCR was estimated for both methods. As Table 3 shows, the estimated individual LCRs may differ depending on the method used. For instance, the estimated average LCR for benzene was 9.8 x 10^{-6} with method A, whereas with method B it was 3.3 x 10^{-5}. Similarly, the estimated risk for trichloroethene was 5.0 x 10^{-7} with method A and 8.4 x 10^{-8} with method B. Despite the differences in the individual LCR estimates, the global LCR estimated for both methods was statistically

comparable (p=0.05). Since chronic risk is assessed using the average global daily concentrations (Robson, 2007), both methods can generate similar risk estimates. However, the differences for the individual VOCs should not be underestimated and further research should be directed toward exploring such differences.

Other important QRA uncertainties come from the limited and incomplete available toxicological information. For non-cancer risk estimates, HR calculations are useful for health endpoints, but do not provide an estimated probability of effects and the chronic reference benchmarks are often derived from No-Observed-Adverse-Effect Levels (NOAEL) or Lowest-Observed-Adverse-Effect Levels (LOAEL) with their associated uncertainty factors. For cancer risk, UR values are estimated from occupational studies in humans and from toxicological studies in animals, and are usually determined for adults with body weights of 70 kg and inhalation rates of 20 m^3 h^{-1}. Therefore, these toxicological data do not account for the wide variability of the exposed population. Moreover, only 54% of the 86 VOCs determined in this study had RfC or UR. For instance, styrene and 2-nitropropane (Group 2B, IARC) and 1,2,3-trichloropropane (Group 2A, IARC) do not have a certain estimated UR, and hence were excluded from the cancer risk estimate.

Furthermore, the risks of the individual compounds were considered accumulative in this study. However, some authors have suggested that possible mixture-related effects, such as, antagonistic, synergistic, potentiating or additive effects may occur in complex mixtures such as industrial air (Sterner 2010). Because of the lack of information about these mixture-related effects, they could not be considered in this study.

Finally, although the USEPA has demonstrated that the re-estimation of risk by replacing non-detected values with ½ LOD and the non-quantified values with ½ LOQ does not significantly affect risk assessment calculations in itself, the contribution of the compounds quantified in fewer than 15% of the samples may be overestimated. In this case, guidance of the risk decisions by statistical imputation methods for risk estimations have been suggested (USEPA, 2000).

4. CONCLUSIONS

In this study, 86 VOCs were selected for the risk characterisation of the largest chemical site in the Mediterranean area. Of these, 44 VOCs with quantifiable health effects were found in some of the 276 samples of atmospheric air from three sampling locations around the chemical site. For non-carcinogenic effect calculations, all the quantified VOCs showed average concentrations below their chronic reference concentrations; therefore no adverse health effects are expected as

a result of this exposure. For cancer effects, although none of the individual VOCs presented average LCRs over the definite lifetime cancer risk (10^{-4}), the global cancer risk of the area was above this benchmark. The VOCs that most contributed to the global risk were chloroform, naphthalene, benzene, carbon tetrachloride, ethylbenzene and tetrachloroethylene.

The comparison of risk estimated using two different analytical methods showed that the analytical method employed may play an important role in the results obtained. Some differences in individual VOC concentrations and LCRs were found when determining the target VOCs by solvent desorption and by thermal desorption. However, global estimated cancer LCR was statistically comparable in both methods.

Despite the uncertainties and limitations associated with risk estimates, this study demonstrates that VOCs in addition to benzene should be taken into account in future regulatory approaches because they can affect air pollution and the distribution of cancer and non-cancer health risks.

Acknowledgments

The authors wish to acknowledge the financial support for this study provided by the Department of Innovation, Universities and Enterprises of the Generalitat de Catalunya through project 2009 SGR 223 and the collaboration of the Departament de Territori i Sostenibilitat of the Generalitat de Catalunya, and especially its staff in the Tarragona local office for the sample collection.

REFERENCES

Assante-Duah, K. 2002. Public Health Risk Assessment for human exposure to chemicals. The Nederlands: Kluwer Academic Publishers, Dordrecht.

ATSDR (Agency for Toxic Substances and Disease Registry). http://www.atsdr.cdc.gov/substances/indexAZ.asp#B Accessed March 15, 2011

Buczynska, A.J., Krata, A., Stranger, M., Godoi, A.F.L., Kontozova-Deutsch, V., Bencs, L., Naveau, I., Roekens, E., Van Grieken, R. Atmospheric BTEX-concentrations in an area with intensive street traffic. Atmos Environ 2009; 43(2):311-318.

ECRN (European Chemical Regions Network). http://www.ecrn.net/regions/cat.php Accessed December 1, 2010.

EN 14662-1 - Ambient air quality - Standard method for measurement of benzene concentrations - Part 1: Pumped sampling followed by thermal desorption and gas chromatography, 2005.

EN 14662-2 - Ambient air quality - Standard method for measurement of benzene concentrations - Part 2: Pumped sampling followed by solvent desorption and gas chromatography, 2005.

Esplugues, A., Ballester, F., Estarlich, M., Llop, S., Fuentes-Leonarte, V., Mantilla, E., Iniguez, C. Indoor and outdoor air concentrations of BTEX and determinants in a cohort of one-year old children in Valencia, Spain. Sci Total Environ 2010; 409(1):63-69.

European Commission. Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations. Off. J. Eur. Communities L13; 29/03/1999: 1-25.

European Commission. Directive 2008/50/EC of the European parliament and of the council of 21 May 2008 on ambient air quality and cleaner air for Europe. Off. J. Eur. Communities L152/1; 11/06/2008:1-44.

IARC (International Agency for Research on Cancer). List of classifications by alphabetical order. Available at: http://monographs.iarc.fr/ENG/Classification/index.php Accessed May 14, 2011

IRIS (Integrated Risk Information System). http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.showSubstanceList Accessed March 15, 2011

Koppmann, R. (Ed.), 2007. Volatile Organic Compounds in the Atmosphere. Blackwell Publishing Ltd, Oxford.

Loh, M.M., Levy, J.I., Spengler, J.D., Houseman, E.A., Bennett, D.H. Ranking cancer risks of organic hazardous air pollutants in the United States. Environ Health Perspect 2007; 115(8):1160-1168.

McCarthy, M.C., O'Brien, T.E., Charrier, J.G., Hather, H.R. Characterization of the Chronic Risk and Hazard of Hazardous Air Pollutants in the United States Using Ambient Monitoring Data. Environ Health Perspect 2009; 117(5):790-796.

Monks, P.S., Granier, C., Fuzzi, S., et al. Atmospheric composition change - global and regional air quality. Atmos Env 2009; 43(33):5268-5350.

Morello-Frosch, R.A., Woodruff, T.J., Axelrad, D.A., Caldwell, J.C. Air toxics and health risks in California: The public health implications of outdoor concentrations. Risk Anal 2000; 20(2):273-291.

OEHHA (Office of Environmental Health Hazard Assessment) http://oehha.ca.gov/risk/ChemicalDB/index.asp Accessed March 15, 2011

Pérez-Rial, D., López-Mahia, P., Tauler, R. Investigation of the source composition and temporal distribution of volatile organic compounds (VOCs) in a suburban area of the northwest of Spain using chemometric methods. Atmos Environ 2010; 44(39):5122-5132.

PRTR-España. Spanish Register of Emission and Pollutant Sources. http://www.en.prtr-es.es/ Accessed April 30, 2011.

RAIS (The Risk Assessment Information System) http://rais.ornl.gov/tools/profile.php Accessed March 15, 2011

Ramírez, N., Cuadras, A., Rovira, E., Borrull, F., Marcé, R.M. Comparative study of solvent extraction and thermal desorption methods for determining a wide range of volatile organic compounds in ambient air. Talanta 2010; 82(2):719-727.

Ramírez, N., Cuadras, A.M., Rovira, E., Marcé, R.M., Borrull, F. Risk Assessment Related to Atmospheric Polycyclic Aromatic Hydrocarbons in Gas and Particle Phases near Industrial Sites. Environ Health Perspect 2011, DOI: 10.1289/ehp.1002855.

Ras-Mallorquí, M.R., Marcé-Recasens, R.M., Borrull-Ballarín, F. Determination of volatile organic compounds in urban and industrial air from Tarragona by thermal desorption and gas chromatography-mass spectrometry. Talanta 2007; 72(3):941-950.

Robson M.G., Toscano, W.A., 2007. Risk assessment for environmental health. Wiley and Sons inc., New York.

Rumchev, K., Brown, H., Spickett, J. Volatile organic compounds: Do they present a risk to our health? Rev Environ Health 2007; 22(1):39-55.

Sexton, K., Linder, S.H., Marko, D., Bethel, H., Lupo, P.J. Comparative assessment of air pollution-related health risks in Houston. Environ Health Perspect 2007; 115(10):1388-1393.

Sterner, O., 2010. Chemistry, Health and Environment., 2nd. Ed. Wiley-Blackwell Verlag, Weinheim.

USEPA (United States Environmental Protection Agency). The Clean air Act Amendments of 1990 List of Hazardous Air Pollutants. Available at: http://www.epa.gov/ttnatw01/orig189.html Accessed December 17, 2010.

USEPA (United States Environmental Protection Agency). Compendium Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes. EPA/625/R-96/010b, 1999.

USEPA (U.S. Environmental Protection Agency). 2000. Assigning values to nondetected/non-quantified pesticide residues in human health food exposure assessments. Office of Pesticide Programs U.S. Environmental Protection Agency. Washington.

WHO (World Health Organization), 2000. Air Quality Guidelines for Europe, 2n ed. Regional Office for Europe, Copenhagen. Available at: http://www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf Accessed February 28, 2011

Wu, C.F., Wu, S.Y., Wu, Y.H., Cullen, A.C., Larson, T.V., Williamson, J., Liu, L.J.S. Cancer risk assessment of selected hazardous air pollutants in Seattle. Environ Int 2009; 35(3):516-522.

Zhou, J.A., You, Y., Bai, Z.P., Hu, Y.D., Zhang, J.F., Zhang, N. Health risk assessment of personal inhalation exposure to volatile organic compounds in Tianjin, China. Sci Total Environ 2011; 409(3):452-459.

SUPPLEMENTARY MATERIAL

Supplementary Material, Table S1. Target VOCs excluded from the risk study, showing their average, minimum and maximum concentrations at each sampling site, expressed in μg m^{-3}, and percent of detected samples.

VOCs	Perafort			Bonavista			Vilaseca			%Quant. Sampl.
	Aver.	Min	Max	Aver.	Min	Max	Aver.	Min	Max	
i-Pentane [b]	4.45	<LQM	18.7	3.6	n.d.	22.4	1.67	n.d.	7.6	66
1-Pentene [b]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.7	n.d.	5.7	3
Diethyl ether	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
2-Trans-pentene [b]	n.d.	n.d.	n.d.	0.09	n.d.	3.1	n.d.	n.d.	n.d.	3
Isoprene [b]	0.1	n.d.	1.4	0.09	n.d.	7.7	n.d.	n.d.	<LQM	2
2-Cis-pentene [b]	0.02	n.d.	1.0	0.03	n.d.	7.8	n.d.	n.d.	n.d.	1
1,1-Dichloroethylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
1-Hexene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
Trans-1,2-dichloroethene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
1,1-Dichloroethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
Cis-1,2-dichloroethylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LQM	0
Methylacrilate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
2,2-Dichloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
Bromochloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
Tetrahydrofuran	0.06	n.d.	0.8	0.01	n.d.	0.7	n.d.	n.d.	<LQM	2
1-Chlorobutane	n.d.	n.d.	n.d.	0.01	n.d.	0.5	n.d.	n.d.	<LQM	1
1,1-Dichloropropene	0.02	n.d.	0.8	n.d.	n.d.	n.d.	0.03	n.d.	1.6	1
i-Octane [b]	0.09	n.d.	6.3	0.12	n.d.	10.4	0.19	n.d.	1.7	8
n-Heptane [b]	0.58	n.d.	2.3	1.1	<LQM	10.8	0.38	n.d.	3.6	53
Dibromomethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
Bromodichloromethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
1,3-Dichloropropane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
n-Octane [b]	0.19	n.d.	1.4	0.33	n.d.	0.15	0.21	n.d.	1.8	35
1,4-Dichloro-2-butene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
n-Propylbenzene	0.3	n.d.	0.8	0.36	n.d.	0.6	n.d.	n.d.	<LQM	28
2-Chlorotoluene	0.01	n.d.	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	<LQM	0
4-Chlorotoluene	0.04	n.d.	0.7	0.04	n.d.	0.4	n.d.	n.d.	<LQM	4
3-Ethyltoluene	0.05	n.d.	0.5	0.57	<LQM	0.36	0.32	n.d.	8.4	29
4-Ethyltoluene	0.12	n.d.	0.4	0.59	n.d.	32.9	0.17	n.d.	0.9	51
2-Ethyltoluene	0.04	n.d.	0.3	0.42	<LQM	35.4	0.01	n.d.	0.3	34
Pentachloroethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
tert-Butylbenzene	0.33	n.d.	0.8	0.29	n.d.	0.6	0.08	n.d.	1.1	45

Table S1 (cont.)

1,3-Dichlorobenzene	0.01	n.d.	0.8	0.06	n.d.	0.7	n.d.	n.d.	n.d.	3
sec-Butylbenzene	0.14	n.d.	0.7	0.09	n.d.	0.3	n.d.	n.d.	<LQM	11
p-Isopropyltoluene	0.39	n.d.	1.5	0.29	n.d.	2.2	0.1	n.d.	1.3	46
1,3-Diethylbenzene	0.01	n.d.	0.2	0.42	n.d.	36.6	n.d.	n.d.	<LQM	5
1,4-Diethylbenzene	0.01	n.d.	0.6	0.45	n.d.	36.4	0.2	n.d.	3.1	13
n-Butylbenzene	0.23	n.d.	0.6	0.11	n.d.	4.1	0.03	n.d.	0.2	20
1,2-Diethylbenzene	n.d.	n.d.	<LQM	0.41	n.d.	36.3	n.d.	n.d.	<LQM	0.4
1,2,3-Trichlorobenzene	0.02	n.d.	0.99	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4
2-Methylnaphtalene [a,c]	n.d.	n.d.	0.3	0.36	n.d.	32.4	0.28	n.d.	7.5	2
1-Methylnaphtalene [a,c]	0.05	n.d.	3.8	n.d.	n.d.	<LQM	0.41	n.d.	12.2	3

[a] Compounds included in the USEPA List of Hazardous Air Pollutants (USEPA, 1994).

[b] Ozone precursors recommended for measurement by the Directive 2008/50/EC (European Commission, 2008).

[c] Compounds included as hazardous organic pollutants in the WHO Air Quality Guidelines (WHO, 2000). Available toxicological information of these compounds: 1,1-diethylether (RfC 200 μg m^{-3} (IRIS, 2011)); Methylacrilate, Group 3 (IARC, 2011); Bromodichloromethane, Group 2B (IARC, 2011), UR=3.7 × 10^{-5} (OEHHA, 2003), Pentachloroethane, Group 3 (IARC, 2011).

References

European Commission. Directive 2008/50/EC of the European parliament and of the council of 21 May 2008 on ambient air quality and cleaner air for Europe. Off. J. Eur. Communities L152/1; 11/06/2008:1-44.

IARC (International Agency for Research on Cancer). List of classifications by alphabetical order. Available at: http://monographs.iarc.fr/ENG/ Classification/index.php Accessed May 14, 2011.

IRIS (Integrated Risk Information System). http://cfpub.epa.gov/ncea/iris/index.cfm? fuseaction =iris.showSubstanceList Accessed March 15, 2011.

OEHHA (Office of Environmental Health Hazard Assessment) http://oehha.ca.gov/risk/ ChemicalDB/index.asp Accessed March 15, 2011.

USEPA (United States Environmental Protection Agency). The Clean air Act Amendments of 1990 List of Hazardous Air Pollutants. Available at: http://www.epa.gov/ttnatw01/orig189.html Accessed December 17, 2010.

WHO (World Health Organization), 2000. Air Quality Guidelines for Europe, 2n ed. Regional Office for Europe, Copenhagen. Available at: http://www. euro.who.int/data/assets/ pdf_file/0005/74732/E71922.pdf Accessed February 28, 2011.

3.2.3. Discussion of results

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

The results presented in these studies demonstrate the presence of airborne PAHs and VOCs in the surroundings of the chemical site, and, therefore, the potential human exposure to these atmospheric contaminants in this area.

Regarding the results obtained from the PAH study, the most abundant PAHs around the chemical site were the most volatile ones, the highest concentrations of which were found in the gas phase. As expected, the airborne gas phase contained the most volatile PAHs, such as Nap, Flu, FluT, PA and Pyr. However, less volatile PAHs were also found in the gas phase, especially during high temperature periods. Additionally, temperature appeared to have a considerable influence on PAH values because the highest concentrations of PAHs occurred at low temperature periods. Furthermore, the heaviest PAHs were more equally distributed in both phases at low temperatures than in high temperature periods. As mentioned before, the three monitoring sites are suburban and rural areas near the chemical site and roads with moderate traffic and PAH concentrations can reflect both traffic intensity and industrial activities. Regarding the monitoring sites, the highest average concentrations of PAHs in the particle phase were registered in Perafort-Puigdelfí, the sampling site closest to the refining area. The average levels of PAHs found in this study for both phases (9.3-68.6 ng m^{-3}) were higher than those found in the air and particulate phases of the main city of the area, Tarragona (4.2-14.3 ng m^{-3}) [1], and in other European cities, such as Toulouse in France (12.3-21.6 ng m^{-3}) [2], but similar to those found in other industrial sites in Europe, such as in Italy (25.6-59.4 ng m^{-3}) [3] and lower than those found in a Petrochemical complex in Belgium (90.6-137 ng m^{-3}) [4]. Regarding the PAH lung cancer risk estimates, the compounds that most contributed to the total risk were BaP (19-45%), DahA (24-67%) and FluT (2-32%). The contribution of the gas phase PAHs to the risk ranged from between 34% and 86% and, therefore, the important contribution of the PAHs present in this phase to the estimated lung cancer risk has been confirmed.

Concerning VOC concentrations, BTEX was found in most of the samples, as well as carbon tetrachloride and styrene. The maximum concentrations of VOCs were found in Tarragona-Bonavista, although the average total VOC concentrations were similar to those found in Perafort-Puigdelfí (28.8 and 26.6 µg m^{-3}, respectively). Average VOC concentrations were higher than the average found in previous studies in Tarragona, but lower than the maximum concentrations found in this city during periods of high traffic intensity when the figures increased up to 306 µg m^{-3} [5-7]. Moreover, VOC concentrations were similar to those recently found in a suburban industrial area in northern Spain [8]. Concerning the VOC cancer risk estimates, it should be pointed out that some of the compounds with higher risk estimates were quantified in very few samples. For instance, 1,2-dibromo-3-chloropropane, which presents the highest

individual estimated cancer risk (LCR=2.3 × 10^{-4}), was only determined in one of the samples. Therefore, we want to highlight with confidence the contribution of the VOCs classified as Group A in the study, quantified in more than 15% of the samples and whose average LCR were above 10^{-6} (more than 1 additional case per 1,000,000 people exposed). Regarding the non-cancer effects of VOCs, none of the quantified compounds showed average concentrations higher than their chronic reference concentrations and, therefore, no adverse health effects are expected as a result of this exposure.

Quantitative Risk Assessment (QRA) has been demonstrated as a powerful tool for risk calculations. However, QRA presents some limitations and uncertainties that have been discussed in the studies. Some remarkable uncertainties of QRA come from the limited data available and the uncertainty of TEF, UR and RfC values, which were established from toxicological animal studies and which can vary depending on the official agency.

Another relevant limitation of risk estimates is the analytical methodology used in the monitoring campaigns. This limitation is especially relevant for the compounds which were non-detected and non-quantified in the samples. Their values were substituted for ½LOD or ½LOQ, respectively, according to the USEPA guidelines [9]. For these compounds, LOD and LOQ values provide a background risk, which can lead to overestimating the exposure risk. To further evaluate the influence of the analytical method in the study of VOCs, the main parameters for cancer risk estimates were compared using two different standard analytical methods for determining VOCs over 24 sampling days during the first period of sampling. Since the TD method provided lower limits of detection and was able to quantify more VOCs in the samples, this analytical method was thought to provide more accurate risk estimates. As seen in the study, some differences were found in the LCRs of the individual VOCs, and therefore, further investigation is needed in this respect.

Besides the limitations and uncertainties mentioned before, several important conclusions regarding risk estimates can be drawn from the studies presented in this section. As regards the average cancer estimates for both studies, a similar risk was found for both families of contaminants (1.2 and 3.4 additional cases per 10,000 people exposed to PAHs and VOC exposure, respectively). This means that there is an estimated cumulative risk of 4.6 additional cases per 10,000 people related to inhalation of PAHs and VOCs in this area. Although none of the individual PAHs or VOCs presented average LCRs over the definite lifetime cancer risk (LCR > 10^{-4}) considered by Sexton et al. [10], the global cancer risk was over this benchmark. Considering the population exposed and an homogenous exposure of the inhabitants for 70 years of life, an average of 1.1 annual cases of cancer can be attributed to the exposure to these atmospheric contaminants (0.3 cases for PAH and 0.8 cases for VOC exposure).

In conclusion, both studies have demonstrated that the estimated risks by inhalation of PAHs and VOCs for people living near the chemical site is not negligible and, therefore, should be taken into account when risk management and policy decisions are made in the future. In the case of PAHs, as mentioned before, only BaP in the PM_{10} fraction is regulated in Europe [11]. However, in the PAH study it was demonstrated that besides BaP, other PAHs contribute significantly to the estimated risk. Furthermore, the results obtained also demonstrate that the contribution of the gas phase PAHs should not be underestimated. In the case of VOCs, only annual benzene emissions are regulated to an annual average of 5 μg m^{-3}. However, the results obtained in the VOC study showed that other compounds besides benzene have a high contribution to risk and should be taken into account when considering the effects on human health.

References

[1] M.R. Ras, R.M. Marcé, A. Cuadras, M. Mari, M. Nadal, F. Borrull, Int. J. Environ. Anal. Chem. 89 (2009) 543.
[2] S. Dejean, C. Raynaud, M. Meybeck, J.P. Massa, V. Simon, Environ. Monitor. 148 (2009) 27.
[3] A. Cincinelli, M. Del Bubba, T. Martellini, A. Gambaro, L. Lepri, Chemosphere 68 (2007) 472.
[4] K. Ravindra, L. Bencs, E. Wauters, J. de Hoog, F. Deutsch, E. Roekens, N. Bleux, P. Berghmans, R. Van Grieken, Atmos. Environ. 40 (2006) 771.
[5] M.R. Ras-Mallorquí, R.M. Marcé-Recasens, F. Borrull-Ballarín, Talanta 72 (2007) 941.
[6] M.R. Ras, R.M. Marcé, F. Borrull, Sci. Total Environ. 407 (2009) 4312.
[7] M.R. Ras, R.M. Marcé, F. Borrull, Environ. Monit. Assess. 161 (2010) 389.
[8] D. Pérez-Rial, P. López-Mahia, R. Tauler, Atmos. Environ. 44 (2010) 5122.
[9] USEPA, Assigning values to non-detected/non-quantified pesticide residues in human health food exposure assessments. Office of Pesticide Programs U.S. Environmental Protection Agency. Washington, 2000.
[10] K. Sexton, S.H. Linder, D. Marko, H. Bethel, P.J. Lupo, Environ. Health Perspect. 115 (2007) 1388.
[11] Directive 2004/107/EC, Off. J. Eur. Commun. L23 (2005) 3.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.3. Personal care products in indoor and outdoor atmospheres

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

The studies presented in the two previous sections focused on VOCs of PAHs, contaminants which are widely-studied and whose effects on health and the environment are quite well-known. However, new contaminants are receiving increasing attention by the scientific community because of their presence in different environmental matrices, and the potential bioaccumulation and health effects of some of them. These are the so-called emerging organic contaminants (EOCs) and consist of a broad range of new kinds of organic contaminants continuously introduced into the environment by anthropogenic activities. Because of the increasing relevance of these compounds in environmental analytical chemistry, from now on the studies presented in this Thesis will focus on the determination of several groups of EOCs in different environmental matrices.

The study presented in this section focuses on the development of an analytical method for determining some groups of personal care products (PCPs) in atmospheric samples. As mentioned in the introduction, the active ingredients of PCPs include several families of organic compounds used as additives in a wide range of consumer products. The atmosphere is one of the main routes of exposure and diffusion of the most volatile PCPs. However, only a few studies have focused on the determination of PCPs in air. Among the volatile PCPs, the most studied are synthetic musks fragrances. Since their first determination in 1999 in indoor and outdoor air in Norway by Kallenborn et al. [1], the presence of synthetic musks has been reported in different indoor [2-4] and outdoor environments [5]. As they are persistent in the environment, the long-range transport of synthetic musks has caused them to be found in remote non-anthropogenic areas such the Arctic [6]. Other PCPs determined in air matrices are p-hydroxybenzoic esters (parabens) [7] and siloxanes [8]. However, there is no information about the occurrence of any insect repellent compounds in air. Although there is a lack of information about the health effects of most PCPs, it should be pointed out that some of them, such as parabens and synthetic musks, are considered endocrine-disrupting chemicals by several authors [9].

The analytical methods used for the determination of PCPs in air are based typically on the collection of air in high-volume samplers followed by sample preparation methods that commonly involve multiple steps. Atmospheric PCPs are usually trapped in PUFs or XAD-2 resins or combinations of both sorbents. After the sampling, samples are desorbed with organic solvents using a Soxhlet [10] or pressurised liquid extraction technique (PLE) [3]. Typically a clean-up step is also needed prior to the GC-MS analysis, using chromatographic columns of silica, alumina or florisil [1,5,7,10]. Besides the fact that these methods take long periods of time, the sample manipulation and use of organic solvents increase the risk of background contamination because of the presence of the PCPs in the environment. Recently, a high throughput method for determining

synthetic musks in air based on active sampling in Tenax followed by desorption with 100 µL of acetone and further headspace SPME extraction was developed by Regueiro el al. [2].

In section 3.1, the applicability of methods involving enrichment into solid sorbents followed by TD prior to GC-MS for determining VOCs was demonstrated. As mentioned before, this analytical method provides enhanced sensitivity because the entire sample is analysed. Although TD methods have been widely-used for determining volatile contaminants, their application for semi-volatile compounds is scarce.

Therefore, to extend the application of TD, the purpose of the study presented in this section was to develop a TD-GC-MS method for the simultaneous determination of semi-volatile PCPs. Fourteen PCPs were selected for this study: 6 polycyclic musks (cashmeran, celestolide, phantolide, traseolide, galaxolide and tonalide), 3 nitro musks (musk xylene, musk moskene and musk ketone), 4 parabens (methyl, ethyl, propyl and butyl paraben) and 1 insect repellent (*N,N*-diethyl-*m*-toluamide, DEET). Three kinds of fillings for the sorbent tubes and traps were tested for trapping the target PCPs: Carbograph 1TD, Tenax TA, and two-sorbents tubes with a mixture of Tenax TA and Carbograph 1TD.

The optimised method was applied for the determination of the target PCPs in different indoor atmospheres (a chemical laboratory, a classroom, a secretary's office, a medical centre, a pharmacy, a hairdresser's and a flower shop) and two outdoor environments (one urban and one suburban). Because of their use in consumer products, the presence of these PCPs is especially important in indoor environments. Previous studies have determined synthetic musks and parabens in indoor environments, such as kindergartens [3], sport centres [4] and houses [7]. The presence of these fragrances has also been determined near a cosmetics plant [11], but there is no information concerning these compounds in outdoor air. Hardly any information can be found in the literature about the presence of parabens in the atmosphere [12] and, as previously mentioned, there is no information about DEET in indoor and outdoor samples.

A paper with the results obtained in this study has been published in the *Journal of Chromatography A* 1217 (2010) 4430-4438.

References

[1] R. Kallenborn, R. Gatermann, S. Planting, G.G. Rimkus, M. Lund, M. Schlabach, I.C. Burkow, J. Chromatogr. A 846 (1999) 295.
[2] J. Regueiro, C. García-Jares, M. Llompart, J.P. Lamas, R. Cela, J. Chromatogr. A 1216 (2009) 2805.

[3] H. Fromme, T. Lahrz, M. Piloty, H. Gebhart, A. Oddoy, H. Ruden, Indoor Air 14 (2004) 188.
[4] A. Sofuoglu, N. Kiymet, P. Kavcar, S.C. Sofuoglu, Indoor Air 20 (2010) 515.
[5] A.M. Peck, K.C. Hornbuckle, Atmos. Environ. 40 (2006) 6101.
[6] Z.Y. Xie, R. Ebinghaus, C. Temme, O. Heemken, W.G. Ruck, Environ. Sci. Technol. 41 (2007) 5654.
[7] R.A. Rudel, D.E. Camann, J.D. Spengler, L.R. Korn, J.G. Brody, Environ. Sci. Technol. 37 (2003) 4543.
[8] A. Kierkegaard, M.S. McLachlan, J. Chromatogr. A 1217 (2010) 3557.
[9] P.D. Darbre, P.W. Harvey, J. Appl. Toxicol. 28 (2008) 561.
[10] A.M. Peck, K.C. Hornbuckle, Environ. Sci. Technol. 38 (2004) 367.
[11] D.H. Chen, X.Y. Zeng, Y.Q. Sheng, X.H. Bi, H.Y. Gui, G.Y. Sheng, J.M. Fu, Chemosphere 66 (2007) 252.
[12] R.A. Rudel, L.J. Perovich, Atmos. Environ. 43 (2009) 170.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.3.1. Development of a thermal desorption-gas chromatography-mass spectrometry method for determining synthetic musks in water samples

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

DEVELOPMENT OF A THERMAL DESORPTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY METHOD FOR DETERMINING PERSONAL CARE PRODUCTS IN AIR

Noelia Ramírez, Rosa Maria Marcé, Francesc Borrull
Department of Analytical Chemistry and Organic Chemistry
Universitat Rovira i Virgili, Marcel·lí Domingo s/n
Sescelades Campus, Tarragona 43007, Spain

Abstract

This study describes the development of a new analytical method for determining 14 personal care products (PCPs) - nine synthetic musks, four parabens and one insect repellent - in air samples. The method is based on active sampling on sorbent tubes and thermal desorption - gas chromatography - mass spectrometry analysis, and is rapid, sensitive and drastically reduces the risk of sample contamination. Three kinds of tubes and traps were tested, those filled with Tenax TA being the most suitable for this study. Method validation showed good repeatability and reproducibility, low detection limits (between 0.03 ng m^{-3} for DPMI and 12.5 ng m^{-3} for propyl paraben) and good linearity for all compounds. Stability during storage indicated that samples must be kept refrigerated at 4 °C and analysed within one week of collection.

The applicability of the technique to real samples was tested in different indoor and outdoor atmospheres. The total PCP values for indoor air ranged from 135 ng m^{-3} in a pharmacy to 2838 ng m^{-3} in a hairdresser's, whereas the values for outdoor air ranged from 14 ng m^{-3} for a suburban environment to 26 ng m^{-3} for an urban environment. In general, the most abundant synthetic musks were galaxolide (5.9 ng m^{-3} - 1256 ng m^{-3}), musk xylene (1.6 ng m^{-3} - 766 ng m^{-3}) and tonalide (1.1 ng m^{-3} –138 ng m^{-3}). Methyl and ethyl paraben (2.4 ng m^{-3} - 313 ng m^{-3} and 1.8 - 117 ng m^{-3}, respectively) were the most abundant parabens. Although thermal desorption methods have been widely used for determining volatile organic compounds, they are rarely used with semi-volatile compounds. This study thus demonstrates that the thermal desorption method performs well with semi-volatile compounds and, for the first time, that it can be used for determining PCPs.

Keywords: Thermal desorption; personal care products; synthetic musks; parabens; insect repellent; air analysis

1. INTRODUCTION

Personal care products (PCPs) include a broad range of compounds widely used as additives in cosmetic, household, food and pharmaceutical products among others. Because of their widespread use, they are commonly found in environmental matrices such as water, biota, sediments and even air

[1]. Recent research suggests that some groups of PCPs are potentially harmful to the environment and human health [1-4]. Because of their adverse effects and the high hydrophobicity of some of them, which indicates potential bioaccumulation [3], some PCPs are regarded as emerging organic contaminants [5].

Although in recent years several studies have focused on detecting PCPs and their degradation products in environmental matrices [1,2,6-8], few studies have dealt with air matrices [5,9,10]. Synthetic musk fragrances, preservatives (p-hydroxybenzoic esters, parabens) and insect repellents are some of the PCPs which, because of their physical and chemical properties and their possible sources of emission, can be found in air matrices.

Synthetic musk fragrances are added in high quantities to scent a wide variety of consumer products. There are three types of synthetic musk fragrance: nitro, polycyclic and macrocyclic. The nitromusks were the first to be produced but their use has been drastically reduced in recent decades due to their accumulation in environmental matrices [11]. Nowadays, the polycyclic musk fragrances are the most widely used, especially galaxolide (HHCB) and tonalide (AHTN), which are included in the US Environmental Protection Agency's (EPA) High Production Volume (HPV) list [12]. These compounds have been detected in indoor air [13-16] and outdoor air [15,17,18] and their presence in Arctic samples suggests that atmospheric transport plays an important role in dispersing these fragrances throughout the global environment [19]. Although synthetic musks are produced to replace the more expensive natural musks, polycyclic and nitromusks are not structurally or chemically similar to natural ones and are lipophilic, persistent chemicals which biomagnify throughout the food chain [11,20]. Synthetic musks have been found in human adipose tissue, breast milk and blood and inhibit the activity of multidrug efflux transporters responsible for multixenobiotic resistance in muscle among other effects. Although polycyclic musks have not shown mutagenic potential in different tests, general data on their toxicological properties are scant [21,22].

p-Hydroxybenzoic esters (parabens) are the most common preservatives and antimicrobial agents used in personal care, pharmaceutical and food products. The most widely used are methyl paraben and propyl paraben, but ethyl, isopropyl, butyl and benzyl paraben are also commonly used. Although there is no clear evidence of their bio-accumulation, parabens have been detected in human tissue, including breast tumours [23,24], and have endocrine activity [25]; therefore, they are considered endocrine disrupting chemicals (EDCs). However, there is little information regarding either their presence in air or their

toxicity and their absorption into the human body through the skin or the respiratory system [10,26].

Finally, DEET is the most commonly used insect repellent. It has been widely detected in aquatic systems, but the processes controlling its environmental effects have not been well-studied and there is no information about its presence in atmospheric samples. Information about DEET toxicity is also scarce but there is evidence that it is slightly toxic to aquatic invertebrates, fish and birds [1].

Several analytical methods for determining PCPs in air have been developed in the last decade. Samples have typically been collected by active sampling in high volumes (ranging from 2 to 100 m^3) using polyurethane foams, XAD-2 resins or combinations of both these sorbents [13,18,19,26]. The samples were then solvent extracted with organic solvents by Soxhlet extraction, sonication or pressurised liquid extraction (PLE). A clean-up step with chromatographic columns of deactivated silica, silica/alumina (2:1) or florisil is commonly needed before the analysis. The typical analytical techniques were GC-MS by EI for musks and GC-MS by NCI for nitromusks [1]. Parabens should be derivatized prior to GC analysis [10]. These methods are time-consuming and require the samples to be manipulated, which means that there is a high risk of samples being contaminated by the presence of the PCPs in the environment.

Recently, Regueiro et al. [17] developed a new method for determining synthetic musks in which they collected 5 m^3 of air in 25 mg of Tenax, added 100 µl of acetone to the sorbent, and extracted musks using a headspace SPME with a DVB/CAR/PDMS fibre. However, thermal desorption methods (TD) have yet to be applied to determining PCPs in air. These methods, widely used for volatile target compounds, have recently been successfully used to determine semi-volatile com-pounds such as polycyclic aromatic hydrocarbons [27].

The aim of this study is to develop a TD-GC-MS method for determining three families of PCPs (synthetic musks, parabens and insect repellents) in air samples. The TD method is rapid and simple, and provides enhanced sensitivity because the whole sample is analysed. It also reduces the risk of sample contamination because a minimal manipulation of the sample is required. Furthermore, parabens can be directly determined by this method and there is no need for derivatization prior to GC-MS analysis. The applicability of the technique in real samples was tested in different indoor and outdoor atmospheres.

2. EXPERIMENTAL

2.1. Chemical standards

Promochem Iberia (Barcelona, Spain) supplied the six polycyclic musks: 6,7,-

dihydro-1,1,2,3,3-pen-tamethyl-4(5H)-indanone (DPMI, cashmeran), 4-acetyl-1,1-dimethyl -6-*tert*-butyl-indane (ADBI, celestolide), 6-acetyl-1,1,2,3,3,5-hexa-methylindane (AHMI, phantolide), 5-acetyl-1,1,2,6-tetramethyl-3-iso-propylindane (ATII, traseolide), 1,3,4,7,8 – hexahydro - 4,6,6,7,8,8 – hexamethylcyclopenta - (γ) -2-benzopy-ran (HHCB, galaxolide) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2, 3,4-tetra-hydronaphthalene (AHTN, tonalide). The nitro musk fragrances 2,4,6-trinitro -1, 3 - dimethyl - 5 - tert - butylbenzene (musk xylene) and 1,1,3,3,5-penta-methyl-4,6-dinitroindane (musk mos-kene) were purchased as 100 µg m^{-3} solutions in acetonitrile from Sigma-Aldrich (Steinheim, Ger-many) and Riedel de Haën (Seelze, Germany), respectively. The standards were also 4-aceto-3,5-di methyl-2,6-dinitro-tert-butyl-benzene (musk ketone) from Fluka (Buchs, Switzerland) and 4-hydroxybenzoic acid methyl ester (methyl paraben), 4-hydro-xybenzoic acid ethyl ester (ethyl paraben), 4-hydroxybenzoic acid propyl ester (propyl paraben), 4-hydroxybenzoic acid butyl ester (butyl paraben) and *N,N*-diethyl-*m*-toluamide (DEET) from Aldrich. Table 1 shows the main characteristics (formula name, boiling point, vapour pressure and molecular structure) of the target compounds.

The individual standard solutions of the synthetic musks were prepared in acetone and the mixture with the rest of the PCPs was prepared in methanol. The solvents were GC grade with purity >99.9% (SDS, Peypin, France). All the standards were prepared on the day of use, and stored at 4 °C in 10 ml Certan© capillary vials provided by Supelco. Nitrogen gas of 99.999 % purity was used to activate the thermal desorption sorbent tubes and 99.999% pure helium gas was used for the chromatographic analysis (both gases from Carburos Metálicos, Barcelona, Spain).

2.2. Sampling tubes and cryogenic traps

Cartridges for thermal desorption were stainless-steel tubes (Markes Inter-national Limited, Llantrisant, UK, length: 9 cm × 6.35 mm o.d. × 5 mm i.d.). Three kinds of cartridge package were tested in this study: Carbograph 1TD, Tenax TA and a mixture of Tenax TA and Carbograph 1TD. These three kinds of cartridge were respectively used in combination with three kinds of cryogenic trap (also from Markes): a high boiler trap (filled with Carbograph 1 TD, glasswool and quartz particles), a Tenax trap (filled with Tenax TA) and a General Purpose Hydrophobic trap (filled with Tenax TA and Carbograph 1TD).

Before each use, tubes were conditioned by thermal cleaning under a nitrogen flow rate of 100 ml min-1 (Tenax TA and Tenax TA/Carbograph 1TD tubes: 335 °C for 30 min, Carbograph 1TD tubes: 380 °C for 30 min). After conditioning, the tubes were sealed with Swagelok end caps

Table 1. Formula name, boiling point, vapor pressure and molecular structure of the target PCPs.

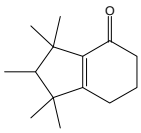
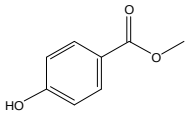
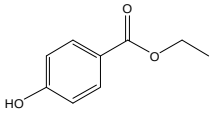
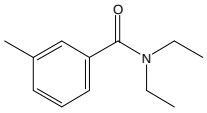
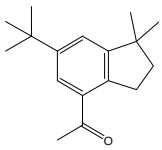
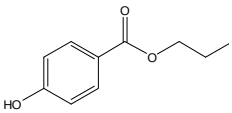
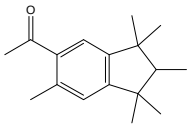
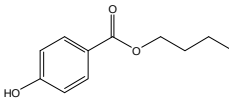
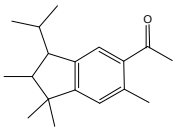
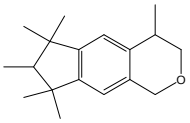
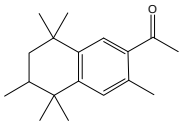
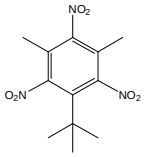
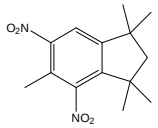
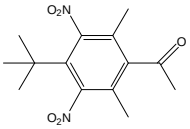
No.	Compound	Formula name	B.p. (°C)	Vapor pressure (mm Hg)	Molecular structure
1	Cashmeran (DPMI)	6,7,-Dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone	286.1	2.69×10^{-3}	
2	Methyl paraben (MeP)	4-Hydroxybenzoic acid methyl ester	265	5.55×10^{-3}	
3	Ethyl paraben (EtP)	4-Hydroxybenzoic acid ethyl ester	297.5	7.6×10^{-4}	
4	DEET	*N,N*-Diethyl-*m*-toluamide	297.5	1.35×10^{-3}	
5	Celestolide, Crisolide (ADBI)	4-Acetyl-1,1-dimethyl-6-*tert*-butylindane	309	6.5×10^{-4}	
6	Propyl paraben (PrP)	4-Hydroxybenzoic acid propyl ester	294	3.56×10^{-2}	
7	Phantolide (AHMI)	6-Acetyl-1,1,2,3,3,5-hexamethylindane	336.6	1.11×10^{-4}	
8	Butyl paraben (BuP)	4-Hydroxybenzoic acid butyl ester	309	3.56×10^{-4}	
9	Traseolide, Fixolide (ATII)	5-Acetyl-1,1,2,6-tetramethyl-3-isopropyl-indane	350	4.56×10^{-5}	

Table 1 (cont.)

10	Galaxolide, Abbalide, Pearlide (HHCB)	1,3,4,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran	326	4.14×10^{-4}	
11	Tonalide (AHTN)	7-Acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene	356.8	2.86×10^{-5}	
12	Musk Xylene (MX)	2,4,6-Trinitro-1,3-dimethyl-5-*tert*-butylbenzene	392.3	5.23×10^{-6}	
13	Musk Moskene (MM)	1,1,3,3,5-Pentamethyl-4,6-dinitroindan	351.1	8.49×10^{-5}	
14	Musk Ketone (MK)	4-Aceto-3,5-dimethyl-2,6-dinitro-*tert*-butylbenzene	369	1.22×10^{-5}	

fitted with PTFE ferrules and stored in hermetically sealable glass jars with desiccant material in order to prevent any ambient contamination of the sorbents.

2.3. Sampling

Air samples were collected by active air sampling with a constant flow air sampling pump (FLEC Air Pump 1001, from Markes) at a flow rate of 100 mL min^{-1}.

Samples were taken from seven indoor environments (a chemical laboratory, a classroom, a secretary's office, a medical centre, a pharmacy, a hairdresser's and a flower shop) and two outdoor environments (one urban, in a city centre, and one suburban, on the outskirts of a city).

The volume and the period sampled varied depending on the characteristics of each atmosphere. The indoor samples were taken over 8 hours coinciding with the working hours of each place, except for the hairdresser's where the samples were taken over 2 hours because of the high levels of PCPs expected. The outdoor samples were taken over 24 hours.

After collection, samples were immediately sealed with Swagelok end caps fitted with PTFE ferrules, stored at 4 °C in hermetically sealable glass jars with desiccant material and analysed

within seven days of collection.

2.4. Thermal desorption GC-MS analysis

Thermal desorption of the analytes retained on the tubes was performed in a Unity Thermal Desorption system combined with an Ultra A autosampler (both from Markes). The optimised thermal desorption conditions for the Tenax TA tubes and trap were: pre-purge for 1 minute at room temperature, tube desorption at 320 °C for 15 minutes using helium carrier gas at 100 mL min^{-1} in splitless mode, trapping at 0 °C and finally trap desorption at 320 °C for 10 min with a split of 5 mL min^{-1}.

Table 2. Target PCPs with quantifier ions, qualifier ions (with their percent abundaces in brackets) and the time windows used for the SIM detection.

No.	Compound	Quantifier ion	Qualifiers	Time window (min)
1	DPMI	191	206 (60), 192 (14)	4.00-5.50
2	MeP	121	152 (30), 93 (12)	5.50-7.00
3	EtP	121	138 (21), 65 (12)	5.50-7.00
4	DEET	119	190 (48), 91 (35)	7.00-7.60
5	ADBI	229	244 (45), 173 (20)	7.60-7.95
6	PrP	121	138 (60), 93 (11)	7.95-8.50
7	AHMI	229	244 (24), 187 (10)	8.50-9.00
8	BuP	121	138 (90), 65 (20)	9.00-9.85
9	ATII	215	258 (15), 173 (16)	9.85-10.15
10	HHCB	243	213 (15), 258 (10)	10.15-11.00
11	AHTN	243	258 (28), 159 (20)	10.15-11.00
12	MX	282	283 (15), 128 (13)	11.00-12.20
13	MM	263	264 (15), 278 (10)	11.00-12.20
14	MK	279	294 (20), 280 (15)	12.20-20.33

Separation and detection were performed in a 6890N gas chromatograph and 5973 *inert* mass spectrometer (Agilent Technologies. Palo Alto, USA), using a Zebron ZB- 50 capillary column (30 m, 0.25 mm, 0.25 µm, provided by Phenomenex, Le Pecq Cedex, France). For the GC-MS analysis, the helium carrier gas flow was 2 mL min^{-1} and the temperature program was as follows: initial temperature 100 °C, 30 °C min^{-1} to 170 °C, then at 5 °C min^{-1} to 190 °C and then at 15 °C min^{-1} to 290 °C and held for 4 min.

The GC-MS interface was set at 290 °C. MS-detector acquired in the selective

ion monitoring mode (SIM) operating at an electron impact energy of 70 eV. Table 2 shows the quantification ions, the qualifier ions and the time windows used for the SIM detection.

Quantification was done via an external standard method in which microlitre quantities (ranging from 1 to 5 µL) of the corresponding standard solution were loaded into the cartridges using a conventional GC syringe. The tubes were attached to a Calibration Solution Loading Rig (Markes) and purged for 5 minutes with a Helium stream of 100 ml min^{-1} to evaporate the solvent and to ensure the repeatability of the injection. After this, the tubes were sealed with Difflok caps and then immediately analysed.

3. RESULTS AND DISCUSSION

3.1. Method optimisation

The chromatographic separation of the 14 PCPs was done in a midpolarity phase capillary column coated with a 50% diphenyl/50% dimethyl polysiloxane. This kind of coating allows a high column flow rate (2 mL min^{-1} in this study) without compromising the resolution of the compounds. As a result, the 14 analytes were resolved in about 13 min (Figure 1A). The chromatogram (Figure 1B) also shows the separation of the four HHCB enantiomers (4S, 7S, t_R=10.25 min; 4S, 7R, t_R= 10.31 min; 4R, 7S, t_R= 10.71 min; 4R, 7R, t_R=10.80 min). The HHCB was quantified in real samples by integrating the 4S and 7R/S isomers peaks. These were chosen because of their high chromatographic signal and the fact that they are the diastereoisomers responsible for the musky odour [28].

Finally, it is worth noting the good shape of the paraben peaks, which were directly spiked in the thermal desorption tubes without any previous derivatization. This implies that the TD method is more effective than previous direct injection and SPME methods, which need the paraben hydroxylic group to be derivatized prior to the analysis [26,29].

For the thermal desorption of the target compounds, the suitability of three kinds of sorbent tubes combined with three kind of cryogenic traps were tested. The optimal desorption conditions of each tube and each trap were determined to yield the maximal recovery of the analytes, taking into account the time of the whole analysis and without exceeding the desorption conditions recommended for the sorbents. Tests were performed by spiking the sorbent tubes with the highest calibration level (20 ng).

The optimal conditions for each combination of cartridge/trap are shown in Table 3. Due to the relatively high boiling points of the analytes (between 265 and 392 °C), the sorbent tubes were packed with Carbograph 1TD and the high boiler cryogenic trap during the initial tests. Carbograph 1TD

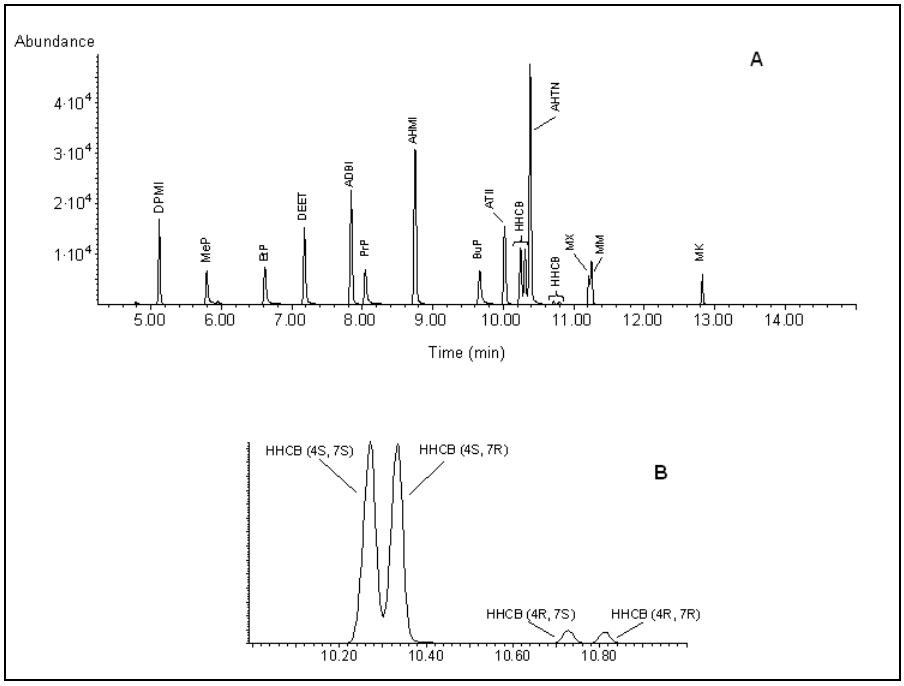


Figure 1. Chromatogram of 5 ng of PCP standard mixture spiked on a Tenax tube (A) and the peaks of the HHCB diastereoisomers (B).

is a hydrophobic sorbent which resists high temperatures, so it can be used in the thermal desorption of semi-volatile compounds [30]. Although this combination allows desorption temperatures of 370 °C, splits of at least 30 mL min^{-1} are needed to achieve complete analyte desorption from the trap. This high split significantly compromised method detection limits raising them to µg m^{-3} levels. Given that PCPs in air have been found at ng m^{-3} levels, this combination was discarded. The second series of tests used a combination of Tenax TA and Carbograph 1TD. Tenax TA sorbent is weaker than Carbograph 1 TD, and analytes can be easily removed with low splits. However, Tenax degrades at temperatures higher than 320 °C.

The optimal desorption conditions (Table 3) were set at 320 °C combined with the maximal desorption flow recommended by the manufacturer (100 mL min^{-1}). Carry-over was checked by performing a second desorption of a sorption tube spiked with the highest calibration level. The peak areas found in the second analysis were higher than 20% for most analytes. Hence, this combination was also discarded for the study. Finally, tests with the tubes and the trap filled with Tenax TA at the optimised desorption conditions showed, for the highest calibration level, a carry-over of less than 1% for all

Table 3. Optimised thermal desorption conditions for the three cartridges and traps tested in this sudy.

	Carbograph 1TD	Carbograph 1TD/ Tenax TA	Tenax TA
Pre-purgue (min)	1	1	1
Tube desorption			
Temperature (°C)	370	320	320
Time (min)	15	15	15
Flow (mL min^{-1})	100	100	100
Trap temperature (°C)	0	0	0
Split (mL min^{-1})	splitless	splitless	splitless
Trap desorption			
Temperature (°C)	370	320	320
Time (min)	10	10	10
Flow (mL min^{-1})	32	7	7
Split (mL min^{-1})	30	5	5

analytes. Consequently, the Tenax TA sorbent for the tube and the trap was chosen as the best option.

Blank signals and the artifacts of the Tenax tubes were tested by analyzing the 10 freshly cleaned sorbent tubes involved in this study. Two blank signals coincided with the retention time and the quantifier ion of two target compounds: methyl paraben and propyl paraben. The average blank concentrations (0.07 ±0.01 ng for methyl paraben and 0.51±0.03 ng for propyl paraben) were included in the calibration curves of these parabens. However, it is worth pointing out that the extensive use of PCPs as additives in a wide range of consumer products meant that there was a high risk that the samples were contaminated. Therefore, the deter-mination of trace PCPs requires special precautions throughout the analytical procedure. The method developed in this study already drastically reduces the potential contamination risk because the sample is directly analyzed after the sampling step; nevertheless, further precautions were taken such as using PCP-free gloves and tissues and storing the samples in sealable glass jars. It is also worth noting that the thermal desorption of semi-volatile compounds can cause memory effects in the instrumentation due to either the partial desorption of the analytes from the trap or their accumulation in the transfer lines, whose temperature can only be raised to 200 °C [27]. Thus, it is important not to overload the sampling tube with high amounts of standards and to check the blanks after sample analysis if high concentrations have been determined.

To set the sample volume, samples were taken by connecting two freshly cleaned Tenax tubes in series. For the indoor samples, tests were performed in a hairdresser's, whose indoor environment had the highest concentrations of the target PCPs. Several flow rates (ranging between 1000 mL min^{-1} and 50 mL min^{-1}) and sampling volumes of air (ranging from 500 L and 25 L) were tested. Some analytes, especially parabens, appeared in the second tube when sampling at high flows and high volumes of air. Therefore, the sampling flow rate was fixed at 100 ml min^{-1} and a maximal volume of 100 L of air could be preconcentrated in this environment without significant loss of analytes. At this volume, only three PCPs were found in the second tube: methyl paraben, ethyl paraben and HHCB in concentrations of 4.3, 4.9 and 0.4% of their respective concentrations in the first tube. For the outdoor samples the preconcentrated volume was increased to 144 L (24 hours of sampling) due to the low levels of PCPs expected in these environments. No analyte was detected in the second tube for the outdoor samples.

3.2. Method validation

The linearity was measured by loading sampling tubes with different amounts of PCPs (between 0.01 and 20 ng). The coefficient of determination (r^2) values were higher than 0.999 for polycyclic musks and higher than 0.990 for all analytes. The results of the other instrumental parameters are summarised in Table 4. The instrumental repeatability was tested by spiking five Tenax tubes with a low calibration level and with a midpoint calibration level (0.5 ng and 5 ng per analyte). The five tubes of each calibration level were analysed the same day. The RSDs for the 14 target compounds ranged between 2.3% and 4.7% for the low calibration level and 1.4% and 3.9% for the midpoint calibration level (n=5).

Similarly, the instrumental reproducibility was tested by analysing five replicates of each calibration level on different days. The RSDs for the instrumental reproducibility ranged between 2.8% and 5.4% for the low calibration level and between 1.6% and 4.3% for the high calibration level.

For target compounds without blank signals, the instrumental limits of detection (LODs) were determined as the concentrations corresponding to three times the noise signal of the quantifier ion. For target compounds which present a signal in the blank (methyl and propyl paraben), the LODs were determined as the average of the blank signal of each target ion plus three times the standard deviation of this signal (n=10). In all cases the instrumental limits of quantification (LOQs) were fixed as the lowest calibration level. As Table 4 shows, the synthetic musks generally have the lowest LODs and LOQs. The LODs ranged between 0.004 ng for ATII and

Table 4. Instrumental parametres: retention time (t_R), repeteability and reproducibility between days at a low and a mid point calibration level and the instrumental limit of detection and limit of quantification, expressed in ng.

No.	Compound	t_R (min)	Repeatability (%RSD, n=5)		Reproducibility (%RSD, n=5)		LOD (ng)	LOQ (ng)
			0.5 ng	5 ng	0.5 ng	5 ng		
1	DPMI	5.17	3.3	2.4	3.6	2.5	0.005	0.01
2	MeP	5.85	4.1	2.8	5.3	3.1	0.1	0.2
3	EtP	6.68	4.5	3.2	5.5	4.3	0.05	0.1
4	DEET	7.25	2.8	2.2	2.8	2.3	0.02	0.1
5	ADBI	7.92	3.2	2.4	3.5	2.8	0.01	0.03
6	PrP	8.11	2.6	1.7	2.9	2.5	0.3	0.8
7	AHMI	8.83	3.0	2.3	3.3	3.0	0.01	0.03
8	BuP	9.75	3.7	2.8	4.1	3.3	0.01	0.10
9	ATII	10.1	4.4	3.1	4.9	3.6	0.004	0.01
10	HHCB	10.36	2.5	1.8	2.7	2.2	0.005	0.01
11	AHTN	10.46	4.7	3.9	5.4	3.8	0.1	0.2
12	MX	11.3	2.3	1.4	2.8	1.6	0.01	0.05
13	MM	11.34	3.5	1.9	3.8	2.3	0.02	0.05
14	MK	12.89	3.6	2.4	4.1	2.9	0.005	0.01

0.3 ng for propyl paraben and the LOQs between 0.01 ng for DPMI, ATII, HHCB and MK and 0.8 ng for propyl paraben.

The main method parameters are summarised in Table 5.

The method repeatability was determined by sampling three sorbent tubes connected in parallel at the same time and under the same conditions. Method repeatability ranged between 2.1% RSD for ATII and 18.2% for AHTN and MK in indoor samples (pharmacy sample, n=3) and between 3.0% for ADBI and 18.5% for MK in outdoor samples (urban sample, n=3).

Table 5 also shows the method detection and quantification limits (MDLs and MQLs) for indoor and outdoor samples. For the indoor samples (sampling 8 h, 48 L) the MDLs ranged between 0.08 ng m^{-3} and 6.25 ng m^{-3} and the MQLs ranged between 0.2 ng m^{-3} and 16.7 ng m^{-3}. In the case of the outdoor samples (sampling 24 h, 144 L) the MDLs ranged between 0.03 ng m^{-3} and 2.1 ng m^{-3} and the MQLs between 0.07 ng m^{-3} and 5.6 ng m^{-3}. Previous studies for synthetic musks showed MDLs and MQLs ranging from 0.005 ng m^{-3} to 10 ng m^{-3} [13-17]. It is worth noting that the preconcentration volumes in these studies were between 1 m^3 and 108 m^3 of air, that is, 10 to 1000-fold higher than in the present

Table 5. Method parametres for the outdoor and the indoor samples: method repeatability (expresed as %RSD, n=3), and the method detection limit (MDL) and method quantification limit (MQL), expressed in ng m^{-3}.

		Indoor samples			Outdoor samples		
No.	**Compound**	**Method repeatability[a] (%RSD, n=3)**	**MDL[b]**	**MQL[b]**	**Method repeatability* (%RSD, n=3)**	**MDL[c]**	**MQL[c]**
1	DPMI	11.5	0.1	0.1	n.d.	0.03	0.07
2	MeP	14.5	2.1	4.2	10.1	0.7	1.4
3	EtP	9.8	1.0	2.1	6.4	0.3	0.7
4	DEET	15.3	0.4	2.1	n.d.	0.1	0.7
5	ADBI	2.3	0.2	0.6	3.0	0.07	0.2
6	PrP	16.6	6.3	16.7	n.d.	2.1	5.6
7	AHMI	15.2	0.2	0.6	4.2	0.07	0.21
8	BuP	16.5	0.6	2.1	n.d.	0.2	0.7
9	ATII	2.1	0.08	0.2	n.d.	0.03	0.07
10	HHCB	13.7	0.1	0.2	11.3	0.03	0.07
11	AHTN	18.2	2.1	4.2	6.3	0.7	1.4
12	MX	6.9	0.2	1.0	8.6	0.07	0.3
13	MM	n.d.	0.4	1.0	n.d.	0.1	0.3
14	MK	18.2	0.1	0.2	18.5	0.03	0.07

n.d.: analyte not detected in the samples

[a] The Method repeatability was tested in the pharmacy, for the indoor samples, and in the urban environment, for the outdoor samples.

[b] Limits of detection and quantification for indoor samples calculated for a sampling volume of 48 L.

[c] Limits of detection and quantification for outdoor samples calculated for a sampling volume of 144 L.

study. However, the MDLs and MQLs obtained were similar. Although preconcentration volumes for synthetic musks in Tenax was higher in other studies than those used in this study (over 10 m^3 for 25 mg of sorbent without the breakthrough of any analyte [17]) the presence of parabens meant that we had to use lower sampling volumes.

3.3. Stability during storage

To investigate stability during storage, nine freshly cleaned Tenax tubes were filled with 5 ng of PCP standard solution, sealed with Swagelok end caps fitted with PTFE ferrules, stored at 4 °C in hermetically sealable glass jars with desiccant material for 3, 7 and 14 days and then analysed. The responses of the PCPs in the stored tubes were compared with the responses of three tubes filled with 5 ng of standard solution and immediately analysed. After 3 days of storage all the analytes showed recoveries above 98% (n=3, %RSD between 0.5% and 5.4%). After one week of storage synthetic musks and DEET recoveries were above 95%

and the lower value was 92.6% for butyl paraben (n=3, %RSD between 0.4% and 8%). However, after two weeks of storage the recoveries of the parabens had considerably decreased and ranged from 78.6% to 85.1%. Recoveries for the remaining compounds were above the 90% (n=3, %RSD between 0.4 and 8.1%). These results indicate that the samples should be analysed within one week of collection.

3.4. Analysis of outdoor and indoor samples

The method developed was used to analyze indoor and outdoor air samples. Figure 2 shows the SIM chromatograms of one indoor sample, the hairdresser's sample, and one outdoor sample, the urban sample.

Table 6 shows the concentrations of the PCPs detected in the seven indoor environments and the two outdoor environments. As expected, the indoor PCP concentrations were higher than the outdoor ones (from 4 to 1000-fold). The hairdresser's showed the highest values with a total PCP concentration of 2838 ng m^{-3}. The other indoor environments showed total PCP values of between 99.5 ng m^{-3} for the laboratory and 551 ng m^{-3} for the classroom. In the case of the outdoor environments, the concentrations of PCPs in urban air were approximately double those obtained in suburban air except for ethyl paraben, whose concentration was similar in both environments.

Figure 3 represents the distribution of PCPs in the samples. HHCB was the most abundant compound and appeared in all real samples and at the highest concentrations, ranging from 1256 ng m^{-3} in the hairdresser's to 5.9 ng m^{-3} in suburban air. Musk xylene and AHTN were also present in all the samples with a maximal concentration in the hairdresser's air of 766 ng m^{-3} and 138 ng m^{-3}, respectively. The most abundant paraben was methyl paraben, which was also detected in all the samples with a maximal concentration of 313 ng m^{-3} in the hairdresser's. Although methyl paraben is commonly used in combination with propyl paraben, in the samples propyl paraben was only found in the pharmacy and in the hairdresser's. It should also be noted that DEET was only found at a low concentration (2.5 ng m^{-3}) in the pharmacy air probably because it is present in the formulations of commercial insect repellents. On the other hand, musk moskene was not found in any sample. This agrees with the prohibition in European countries regarding the use of musk moskene in cosmetics [31].

As mentioned above, little previous work has focused on the determination of PCPs in air [13-15,17-19,26], but those that have been carried out confirm the findings in this study, i.e. that the most abundant synthetic musk are HHCB,AHTN and musk xylene and

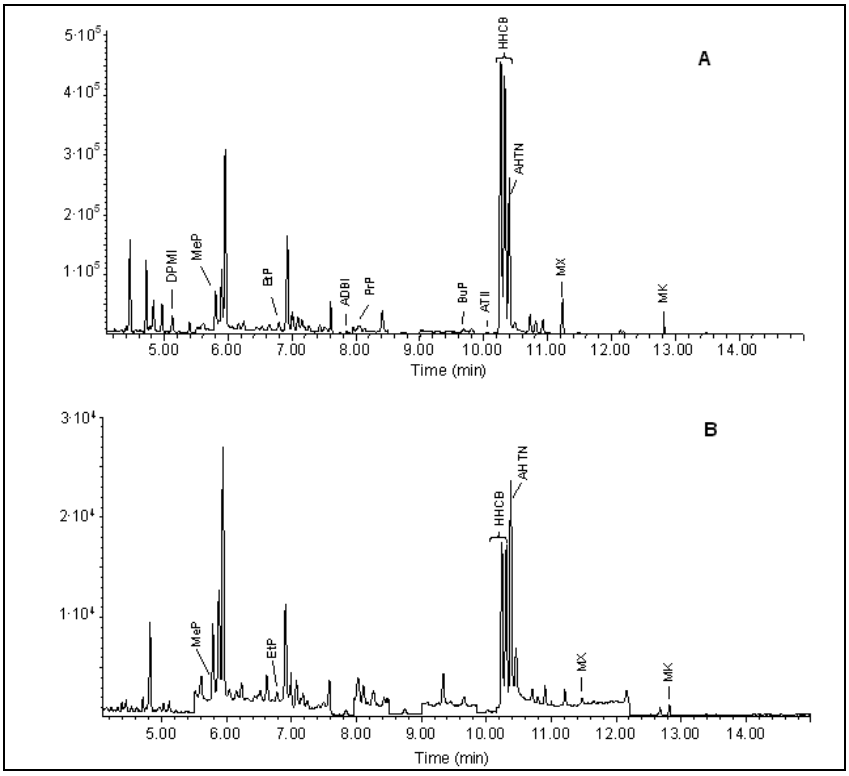


Figure 2. Chromatograms of two real samples: an indoor sample (hairdresser's, A) and an urban outdoor sample (B). The target PCPs found in the samples are marked.

that the most abundant paraben is methyl paraben. However, the advantage of this study in comparison with earlier work is the high sensitivity of the TD method developed. This facilitated both PCP detection from lower volumes of air with shorter sampling times and allowed monitoring of PCPs in less contaminated environments such as outdoor air.

4. CONCLUSIONS

In this study, a thermal desorption-GC-MS method was success-fully developed for determining 14 PCPs in air samples. As far as we know, this is the first method for analyzing PCPs in air that is based on thermal desorption and it has been demonstrated that it efficiently traps and quantitatively desorbs semi-volatile PCPs. The suitability of three kinds of cartridge/trap with different sorbent combinations was tested and it was found that the Tenax TA sorbent was the most appropriate for this study. The method is rapid, sensitive and significantly reduces the risk of sample contamination. Furthermore, parabens can be directly determined by this method without derivatization prior to

Table 6. Concentrations of the target PCPs found in the real samples, expressed in ng m^{-3}.

No.	Compound	Indoor samples							Outdoor samples	
		Laboratory	Pharmacy	Flower shop	Classroom	Secretary's office	Medical centre	Hair-dresser's	Urban	Sub-urban
1	DPMI	<MQL	0.4	2.1	10.8	0.3	10.3	35.3	n.d.	<MQL
2	MeP	20.4	24.9	25.6	15.5	13.9	31.9	313.5	6.2	2.4
3	EtP	<MQL	8.7	14.9	n.d.	7.1	16.0	116.6	1.9	1.8
4	DEET	n.d.	2.5	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	<MQL
5	ADBI	<MQL	0.7	n.d.	0.6	0.5	0.8	7.7	<MQL	0.1
6	PrP	<MQL	17.5	<MQL	n.d.	<MQL	<MQL	85.2	<MQL	<MQL
7	AHMI	<MQL	0.5	0.3	0.7	0.7	<MQL	<MQL	<MQL	0.2
8	BuP	<MQL	9.6	7.9	5.0	<MQL	<MQL	47.3	<MQL	<MQL
9	ATII	<MQL	0.6	<MQL	0.4	n.d.	1.2	3.4	n.d.	n.d.
10	HHCB	65.2	47.1	176.4	374.0	321.6	86.3	1256	10.5	5.9
11	AHTN	7.5	5.3	46.1	43.0	11.8	10.7	138.1	2.4	1.1
12	MX	6.4	15.7	2.9	95.3	55.6	22.7	766.5	4.0	1.6
13	MM	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
14	MK	n.d.	1.9	2.5	5.2	4.9	4.3	68.4	1.5	0.8
Total PCPs		99.5	135.2	278.6	550.6	426.8	184.2	2838	26.5	14.0

n.d.: values under the method detection limit of each sample
<MQL: values under the method quantification limit of each sample

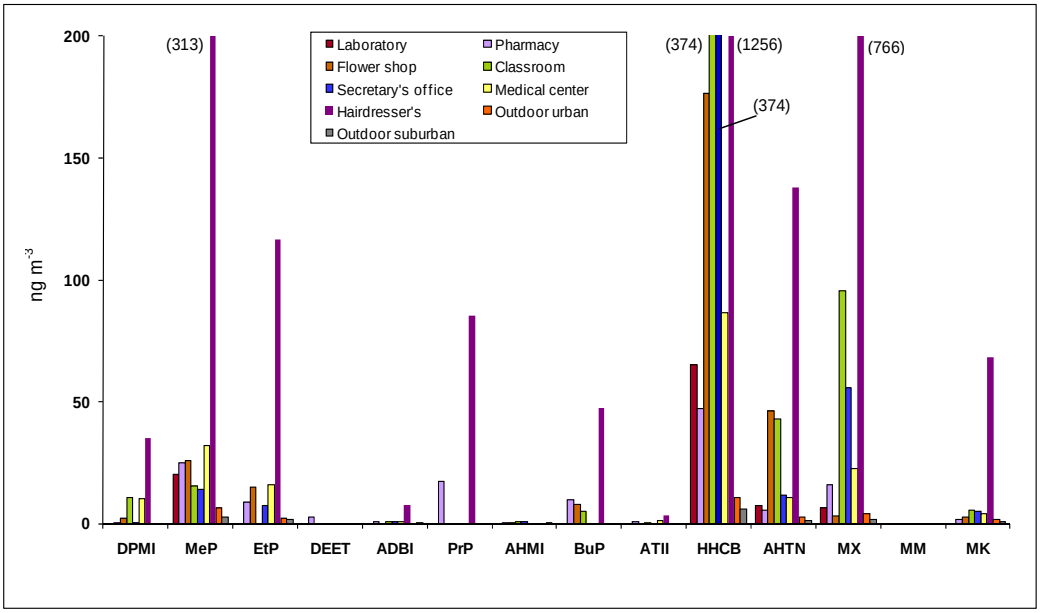


Figure 3. Concentrations of the target PCPs found in the real samples.

GC-MS analysis.

The applicability of the technique in real samples was tested in different indoor and outdoor atmospheres. The method showed enough sensitivity to detect the PCPs with short periods of sampling, even in outdoor environments. The most abundant synthetic musks in the samples were HHCB, AHTN and musk xylene and the most abundant parabens were methyl and propyl paraben. The presence of these PCPs in air and the high values detected in some indoor environments indicate that air is an important source and means of transporting these compounds in the environment.

Acknowledgments

The authors wish to acknowledge the financial support provided to this study by the Spanish Ministry of Science and Innovation through projects CTM-2008-06847-C02-01.

REFERENCES

[1] A.M. Peck, Anal. Bioanal. Chem. 386 (2006) 907.
[2] K. Bester, J. Chromatogr. A 1216 (2009) 470.
[3] F.A. Caliman, M. Gavrilescu, Clean-Soil Air Water 37 (2009) 277.
[4] F.B. Antwi, L.M. Shama, R.K.D. Peterson, Regul. Toxicol. Pharmacol. 51 (2008) 31.

[5] Z.Y. Xie, R. Ebinghaus, Anal. Chim. Acta 610 (2008) 156.
[6] V. Matamoros, E. Jover, J.M. Bayona, Anal. Bioanal. Chem. 393 (2009) 847.
[7] M. Pedrouzo, F. Borrull, R.M. Marce, E. Pocurull, J. Chromatogr. A 1216 (2009) 6994.
[8] A. Nieto, F. Borrull, R.M. Marce, E. Pocurull, J. Chromatogr. A 1216 (2009) 5619.
[9] C. Garcia-Jares, J. Regueiro, R. Barro, T. Dagnac, M. Llompart, J. Chromatogr. A 1216 (2009) 567.
[10] R.A. Rudel, L.J. Perovich, Atmos. Environ. 43 (2009) 170.
[11] C. Sommer, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part X, vol.3, Springer-Verlag, Heidelberg, 2004, p. 1.
[12] High Production Volume (HPV) Chemical List Database, US EPA, June 8, 2003 (http://www.epa.gov/chemrtk/index.htm). Accessed on: 11th January 2010
[13] R. Kallenborn, R. Gatermann, S. Planting, G.G. Rimkus, M. Lund, M. Schlabach, I.C. Burkow, J. Chromatogr. A 846 (1999) 295.
[14] H. Fromme, T. Lahrz, M. Piloty, H. Gebhart, A. Oddoy, H. Ruden, Indoor Air 14 (2004) 188.
[15] D.H. Chen, X.Y. Zeng, Y.Q. Sheng, X.H. Bi, H.Y. Gui, G.Y. Sheng, J.M. Fu, Chemosphere 66 (2007) 252.
[16] R. Kallenborn, R. Gatermann, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part X, vol.3, Springer-Verlag, Heidel-berg, 2004, p. 85.
[17] J. Regueiro, C. Garcia-Jares, M. Llompart, J.P. Lamas, R. Cela, J. Chromatogr. A 1216 (2009) 2805.
[18] A.M. Peck, K.C. Hornbuckle, Atmos. Environ. 40 (2006) 6101.
[19] Z.Y. Xie, R. Ebinghaus, C. Temme, O. Heemken, W.G. Ruck, Environ. Sci. Technol. 41 (2007) 5654.
[20] F. Balk, D. Salvito, H. Blok, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part X, vol.3, Springer-Verlag, Heidelberg, 2004, p. 311.
[21] T. Luckenbach, D. Epel, Environ. Health Perspect. 113 (2005) A803.
[22] H. Brunn, N. Bitsch, J. Amberg-Muller, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part X, vol.3, Springer-Verlag, Heidelberg, 2004, p. 259.
[23] P.D. Darbre, A. Aljarrah, W.R. Miller, N.G. Coldham, M.J. Sauer, G.S. Pope, J. Appl. Toxicol. 24 (2004) 5.
[24] M.G. Soni, G.A. Burdock, S.L. Taylor, N.A. Greenberg, Food Chem. Toxicol. 39 (2001) 513.
[25] E.J. Routledge, J. Parker, J. Odum, J. Ashby, J.P. Sumpter, Toxicol. Appl. Pharmacol. 153 (1998) 12.
[26] R.A. Rudel, D.E. Camann, J.D. Spengler, L.R. Korn, J.G. Brody, Environ. Sci. Technol. 37 (2003) 4543.
[27] E. Wauters, P. Van Caeter, G. Desmet, F. David, C. Devos, P. Sandra, J. Chromatogr. A 1190 (2008) 286.
[28] R. Gatermann, S. Biselli, H. Huhnerfuss, G.G. Rimkus, S.

Franke, M. Hecker, R. Kallenborn, L. Karbe, W.A. Konig, Arch. Environ. Contam. Toxicol. 42 (2002) 447.

[29] J. Regueiro, E. Becerril, C. Garcia-Jares, M. Llompart, J. Chromatogr. A 1216 (2009) 4693.

[30] Markes, Themal Desoption Technical Support Note 53, 2008.

[31] Council directive 98/62/EEC (1998) Off J Europ Comm L253: 20.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

The results presented in this section describe the development and optimisation of a method based on the active enrichment into solid sorbents followed by TD-GC-MS for determining semi-volatile PCPs in air samples. As mentioned in the paper, this is the first time, to our knowledge, that a TD method has been developed for the determination of airborne PCPs.

As stated in the introduction, TD has not been extensively used for the extraction of high boiling point compounds because of several limitations of the technique. One of the main precautions that should be taken into account when developing TD methods for determining semi-volatile organic contaminants is the possible memory effects that can be present, either in the instrumentation transfer lines or in the sorbent tubes and traps. The TD equipment used in this study was a Markes^{TM} (see Figure 1.18 in the introduction), whose transfer lines can only be heated to 200 °C. However, the boiling points of the target PCPs ranged from 265 °C and 369 °C and therefore condensation of these compounds and other less volatile organic air contaminants can occur in the transfer lines. This possible condensation of semi-volatile compounds can be avoided when small amounts of them are loaded. For instance, Wauters et al. [1] avoided these memory effects and limited the highest calibration level of 16 PAHs to 1 ng. Therefore, in our study, the highest calibration level for the PCPs was set at 20 ng and no memory effects were observed.

Furthermore, in order to avoid memory effects in the sorbent tubes and traps, the suitability of three sorbent fillings was tested. The first experiments were performed with tubes filled with Carbograph 1TD combined with traps filled with the same sorbent and quartz glass. This sorbent allows high desorption temperatures (up to 370 °C) and is recommended by the manufacturer for the trapping and desorption of high boiling point organic compounds [2]. However, Carbograph 1TD is quite a retentive sorbent and high splits were needed for the quantitative desorption of the analytes from the cryogenic trap, causing a decrease in the method sensitivity. Next, the suitability of sorbent tubes and traps filled with Tenax TA and Carbograph 1TD was tested. This combination of sorbents was successfully applied for the determination of VOCs (see Section 3.1). However, Tenax TA degrades at temperatures higher than 320 °C, and this temperature was not enough for the quantitative desorption of the analytes from this combination of sorbents. Finally, tubes and traps filled only with Tenax TA were tested that showed the highest efficiency and were chosen for the study. Tenax TA is a medium-strength sorbent which is able to trap the target PCPs as well as providing their quantitative desorption at 320 °C. Regarding blank signals, two blank peaks in the clean Tenax TA tubes coincided with the retention time and the quantifier ion of methyl and propyl paraben and were taken into account in the LOD and LOQ calculations of these parabens.

Regarding the chromatographic separation, it is worth mentioning the fast separation and high resolution power of the chromatographic column (50% diphenyl/50% dimethyl polydimethylsiloxane) that allows the separation of the target compounds in less than 15 minutes. This even provided the separation of the 4 galaxolide estereoisomers, which can not be separated in a more apolar GC column, such as 5% diphenyl/95% dimethyl polydimethylsiloxane [3].

The method developed presents some analytical advantages in comparison with the high-volume sampling methods used for the determination of atmospheric PCPs reported in previous studies [3,4]. Firstly, because of the high sensitivity of the TD method, the process requires a lower flow rate (100 mL min^{-1}) and lower volume of sample (between 12 L and 48 L for indoor samples and 144 L for outdoor samples). Therefore, shorter periods of sampling (between 2 hours and 8 hours for indoor samples, and 24 hours for outdoor samples) are needed. Sampling volumes of air in high-volume sampling are typically 300 m^3 and sampling periods last at least 24 hours. The shorter sampling times of the TD method avoid some of the drawbacks of high-volume samplers mentioned before, such as the blow-off of the most volatile organic contaminants. Moreover, after sampling, the sorbent tubes are thermally desorbed directly and injected in the GC in one single step, avoiding further manipulation of the sample and drastically decreasing the risk of background contamination. Since the whole sample is analysed, LODs were at ng m^{-3} levels, ranging from 0.08 ng m^{-3} to 6.25 ng m^{-3} for indoor samples and from 0.03 ng m^{-3} to 2.1 ng m^{-3} for outdoor samples. As seen in the paper, previous studies reported LODs ranging from 0.001 to 10 ng m^{-3} for preconcentration volumes 10 to 1000 times higher than those in our study [3,5,6].

Another important advantage of the method developed was the good shapes of the chromatographic peaks of parabens, as seen in the chromatograms shown in the paper. This allows the GC-MS analysis of the parabens without the need for derivatization prior to injection. One possible explanation for these good shapes may be the effcient preconcentration effect of the cryogenic trap. Finally, it is worth mentioning the high portability of the sorbent tubes in comparison to high-volume samplers. This allowed sampling in a wide range of atmospheric environments and easy storage of the sorbent tubes. In this study, it was found that Tenax tubes can be stored at 4 °C for one week without the degradation of the target analytes.

Regarding the PCP concentrations, the synthetic musks galaxolide, tonalide and musk xylene were found in all of the samples. Among them, galaxolide was the most abundant which matches other studies [5,7]. Methyl paraben was the most widely-detected paraben and DEET was only found in the pharmacy at a low concentration, probably because of the presence of this insect repellent as an ingredient in some

pharmaceutical products. Regarding the kind of samples, outdoor concentrations of total PCPs were, as expected, 4 to 1000 times lower than those found in indoor samples. It is also worth mentioning that the musk moskene was not found in any of the samples, which follows the prohibition of its use in cosmetics in European countries by the 2008 amendments of the European directive 76/768/EEC [8]. The PCP concentrations found in this study match those found in previous and later studies. For instance, Sofuoglu et al. [7] recently found average concentrations of galaxolide of 267 ng m^{-3} in a primary school and of 144 ng m^{-3} in a sports centre in Turkey. Furthermore, some recent studies determined emissions of synthetic musks from landfills and WWTPs with concentrations of up to 344 µg m^{-3} of HHCB. Therefore these facilities should be considered as an additional PCP emission source into the atmosphere [9-11].

In light of the results presented in this study, the enrichment into solid sorbents followed by TD-GC-MS analysis has been demonstrated as a valuable alternative method to high volume sampling, for determining semi-volatile PCPs in air samples. The method is rapid, highly sensitive and minimises the risk of external contamination of the samples.

References

[1] E. Wauters, P. Van Caeter, G. Desmet, F. David, C. Devos, P. Sandra, J. Chromatogr. A 1190 (2008) 286.
[2] Markes, Thermal Desorption Tehcnical Support Note 53, 2008.
[3] R. Kallenborn, R. Gatermann, S. Planting, G.G. Rimkus, M. Lund, M. Schlabach, I.C. Burkow, J. Chromatogr. A 846 (1999) 295.
[4] R.A. Rudel, D.E. Camann, J.D. Spengler, L.R. Korn, J.G. Brody, Environ. Sci. Technol. 37 (2003) 4543.
[5] H. Fromme, T. Lahrz, M. Piloty, H. Gebhart, A. Oddoy, H. Ruden, Indoor Air 14 (2004) 188.
[6] D.H. Chen, X.Y. Zeng, Y.Q. Sheng, X.H. Bi, H.Y. Gui, G.Y. Sheng, J.M. Fu, Chemosphere 66 (2007) 252.
[7] A. Sofuoglu, N. Kiymet, P. Kavcar, S.C. Sofuoglu, Indoor Air 20 (2010) 515.
[8] Council Directive 98/62/EEC, Off. J. Eur. Commun. L253 (1998) 20.
[9] N. Upadhyay, Q. Sun, J.O. Allen, P. Westerhoff, P. Herckes, Water Res. 45 (2011) 1071.
[10] I. Weinberg, A. Dreyer, R. Ebinghaus, Atmos. Environ. 45 (2011) 935.
[11] I. Weinberg, A. Dreyer, R. Ebinghaus, Environ. Pollut. 159 (2011) 125.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.4. Personal care products in environmental waters

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

Besides the atmosphere, another important pathway of PCPs into the environment is through the aquatic systems. After the human use of consumer products containing PCPs, these compounds can be absorbed by the body and excreted or rinsed off and enter the environmental waters directly via waste waters or through effluents of waste water treatment plants (WWTPs). Therefore, one of the main pathways of PCPs into the environment is through urban and industrial WWTP effluents. PCPs have previously been detected in WWTP waters [1,2] and also in surface waters [3,4]. Biological WWTPs are able to degrade the most polar PCPs and almost quantitative removals have been reported for compounds such as parabens [5]. However, more lipophilic PCPs that exhibit low biodregradability, such as synthetic musks, are only partially removed by conventional WWTPs [6]. Furthermore, some additional oxidised degradation products of PCPs can also be formed during the waste water treatments [4,7] and can enter the environment later.

Among the sample preparation techniques, solid-phase extraction (SPE) has been the most commonly-used for extracting PCPs from environmental waters [8,9]. However, as mentioned in the previous section, one of the main problems that analysts should consider when determining PCPs is the risk of background contamination of the samples and extracts because of the ubiquitous presence of PCPs in the environment. Therefore, methods that reduce the sample preparation steps, and minimise the use of organic solvents and the manipulation of the sample should be developed. In this sense, adsorptive techniques such as solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) followed by TD minimise the risk of this external contamination.

Hence, the focus of the studies included in this section was the development of sensitive and environmentally friendly methods that are capable of determining PCPs in water samples and reducing the risk of background contamination. As discussed in section 3.3, TD techniques applied for the determination of PCPs are a reliable alternative to LD techniques. Following this research line, we have developed two methods based on stir bar sorptive extraction (SBSE) with stir bars coated with polydimethylsiloxane (PDMS) followed by TD and GC-MS analysis. SBSE is a solventless extraction technique which allows the direct extraction and preconcentration of the analytes from the aqueous matrices. Furthermore, in combination with TD, it provides enhanced sensitivity without the use of any organic solvent. It is also worth mentioning that for the TD of the stir bars, we used Markes^{TM} TD equipment which is normally used for desorption of sorbent tubes, as mentioned in the introduction (see Figure 1.18 in the introduction). After the SBSE process, the stir bars were placed in an empty stainless-steel tube and put in the Ultra auto-sampler for desorption. To our knowledge, these studies represent the first time that TD equipment with these characteristics has been used to desorb stir bars.

In the first study we developed a SBSE-TD-GC-MS method for the determination of 9 synthetic musks (6 polycyclic musks and 3 nitromusks) in water samples. Synthetic musks are quite hydrophobic compounds that present high affinity for the polydimethylsiloxane (PDMS) phase of commercial stir bars. In the second study, the SBSE-TD-GC-MS method was optimised for the simultaneous determination of 14 PCPs (the 9 synthetic musks of the first study and 5 parabens) and one PCP degradation product (the main degradation product of the galaxolide, the galaxolidone). Parabens are more polar and present low affinity for the PDMS phase. To overcome this, one of the easiest possibilities is the derivatization of the polar analytes to enhance their recoveries. Therefore, in order to increase the affinity of the parabens for the PMDS phase of stir bars, they were in situ acetylated prior to the extraction. In this study, not only were the derivatization conditions optimised in order to obtain the best recoveries of the parabens, but also the influence of the addition of the derivatizing agents on the extraction efficiency of the musks was studied.

In both studies, the main parameters of SBSE extraction were optimised. These included the size of the stir bar, volume of sample, the salting-out effect, temperature and time of extraction, pH influence and the addition of an organic modifier. Although SBSE has previously been used for the determination of some PCPs in environmental waters [1,10], the first study presented here was, to our knowledge, the first that determined synthetic musks using SBSE followed by TD.

The optimised methods were applied for the determination of the target PCPs in several kinds of water samples: influent and effluent from urban and industrial WWTPs, effluent from a reverse osmosis (RO) treatment plant, and three river waters. The results obtained from the first study was published in the *Journal of Chromatography A* 1218 (2011) 156-161. A paper with the results of the second study has been submitted for publication in *Talanta*.

References

[1] M. Pedrouzo, F. Borrull, R.M. Marcé, E. Pocurull, J. Chromatogr. A 1216 (2009) 6994.
[2] K. Bester, Chemosphere 57 (2004) 863.
[3] N.R. Sumner, C. Guitart, G. Fuentes, J.W. Readman, Environ. Pollut. 158 (2010) 215.
[4] K. Bester, J. Environ. Monit. 7 (2005) 43.
[5] I. González-Mariño, J.B. Quintana, I. Rodríguez, R. Cela, Rapid Commun. Mass Spectrom. 23 (2009) 1756.
[6] S.L. Simonich, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part O, vol. 5, Springer-Verlag, Heidelberg, 2005, p. 79.

[7] V. Matamoros, E. Jover, J.M. Bayona, Anal. Bioanal. Chem. 393 (2009) 847.
[8] A.M. Peck, Anal. Bioanal. Chem. 386 (2006) 907.
[9] M. Pedrouzo, F. Borrull, R.M. Marcé, E. Pocurull, Trends Anal. Chem. 30 (2011) 749.
[10] A.R.M. Silva, J.M.F. Nogueira, Anal. Bioanal. Chem. 396 (2010) 1853.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.4.1. Development of a stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry method for determining synthetic musks in water samples

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

DEVELOPMENT OF A STIR BAR SORPTIVE EXTRACTION AND THERMAL DESORPTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY METHOD FOR DETERMINING SYNTHETIC MUSKS IN WATER SAMPLES

Noelia Ramírez, Rosa Maria Marcé, Francesc Borrull
Department of Analytical Chemistry and Organic Chemistry
Universitat Rovira i Virgili, Marcel·lí Domingo s/n
Sescelades Campus, Tarragona 43007, Spain

Abstract

This study presents the development of an analytical method for determining 9 synthetic musks in water matrices. The developed method is based on stir bar sorptive extraction (SBSE), coated with polydimethylsiloxane, and coupled with a thermal desorption-gas chromatography-mass spectrometry system (TD-GC-MS). SBSE can efficiently trap and desorb the analytes providing low limits of detection (between 0.02 ng L^{-1} and 0.3 ng L^{-1}). Method validation showed good linearity, repeatability and reproducibility for all compounds. Furthermore, the limited manipulation of the sample required in this method implies a significant decrease of the risk of external contamination of the samples.

The performance of the method in real samples was evaluated by analysing biological waste water treatment plant (WWTP) influent and effluent samples, reverse osmosis treatment plant effluents and river waters. The most abundant musk was galaxolide with values up to 2069 ng L^{-1} and 1432 ng L^{-1} in the influent and effluent of urban WWTP samples, respectively. Cashmeran, Pantolide and Tonalide were also detected in all the matrices with values up to 94 ng L^{-1}, 26 ng L^{-1} and 88 ng L^{-1}, respectively. Although in Europe the use of nitromusks in cosmetics is prohibited, musk xylene and musk ketone were detected both in the WWTP and in the river samples.

As far as we know, this is the first time than a SBSE method coupled with TD is applied for the determination of synthetic musks in water samples.

Keywords: Stir bar sorptive extraction (SBSE); Thermal desorption (TD); Gas chromatography-mass spectrometry (GC-MS); Synthetic musks; Water samples.

1. INTRODUCTION

Synthetic musks are commonly used as fragrances in a wide range of consumer products such as detergents, cosmetics and other personal care products. These fragrances comprise a broad range of different compounds, including the polycyclic, nitro and macrocyclic musks. Most commonly used are the polycyclic musks, especially galaxolide (HHCB) and tonalide (AHTN), added to the majority of household and cosmetic products.

However, polycyclic and nitro musks are not structurally or chemically similar to the natural ones and have a lipophylic nature, causing them to bioaccumulate in sediments, sludge and biota and biomagnify throughout the food chain [1,2]. Consequently, these compounds have even been found in human tissues, such as adipose tissue, breast milk and blood [3-5].

The main route of exposure of synthetic musks into the environment is through waste water effluent [6]. Since these fragrances are only partially biodegradable and are not completely eliminated by waste water treatment plants (WWTPs) determination in waste waters and in natural water samples is of major importance [7]. The long-range transport and persistence of synthetic musks, as well as, their exchange between air and water matrices, has caused them to be found in remote non-anthropogenic areas such as the Great Lakes [8,9] and Arctic waters [10]. Their presence has also been reported in fish, mussel and crustacean [11,12]. Furthermore, due to their widespread use and the detection of these compounds in natural waters, several authors have suggested the use of polycyclic musks as chemical markers of anthropogenic pollution [13,14].

Several analytical methods for determining synthetic musk compounds in water samples have been developed in the last years, most of them based on GC-MS analysis. One of the most commonly used sample preparation technique is solid-phase extraction (SPE), for which different sorbents, have been successfully tested in previous studies [1,15]. However, due to the widespread use of synthetic musks they can be found in solvents and laboratory equipment, which can contaminate the samples. Therefore, analytical methods that can reduce the risk of the background musk contamination should be developed. In this respect, the use of sorptive methods coupled with thermal desorption - such as solid-phase micro extraction (SPME) and stir bar sorptive extraction (SBSE) - drastically reduces the risk of contamination. These techniques are solventless sample enrichment methods, which allow the direct extraction of the analytes, implying the minimal manipulation of the sample and avoiding the use of organic solvents, with enhanced sensitivity. Furthermore, the combination of the extraction and the concentration of the analytes in one step also reduces the time of sample preparation. Indeed, SPME methods have been previously developed for the detection of fragrances in aquatic matrices [16-18]. However, SBSE is a more powerful extraction technique, with higher preconcentration capacity as the amount of sorbent is 50-250-fold higher than in SPME fibre. Since the development of SBSE in 1999 by Baltussen et al. [19], this extraction

technique has been successfully applied for the analysis of trace environmental pollutants in different matrices [20-22].

As far as we know, only one SBSE method with liquid desorption has been recently developed for determining four synthetic musks in water [22]. Therefore, the aim of this study is to propose a method based on SBSE followed by TD-GC-MS for determining nine synthetic musks in water samples. After the extraction step, stir bars were place in empty stainless-steel tubes and thermally desorbed in a TD equipment designed to desorb sorbent tubes for air analysis. To the best of our knowledge, a SBSE method is for the first time combined with a thermal desorption system for determining these fragrances in water samples. The applicability of the method to real samples was tested by analysing biological waste water treatment plant influent and effluent samples, reverse osmosis treatment plant effluents and river waters.

2. EXPERIMENTAL

2.1. Chemical standards

The six polycyclic musks: 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (DPMI, cashmeran), 4-acetyl-1,1-dimethyl-6-*tert*-butylindane (ADBI, celestolide), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI, phantolide), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane (ATII, traseolide), 1,3,4,7,8-hexahydro-4,6,6,7,8,8 - hexamethyl-cyclopenta-(γ)–2-benzopyran (HHCB, galaxolide) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4 – tetrahydro-naphthalene (AHTN, tonalide), were supplied by Promochem Iberia (Barcelona, Spain). The nitro musks fragrances 2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene (musk xylene), 1,1,3,3,5-pentamethyl-4,6-dinitroindane (musk moskene) were purchased as 100 mg L^{-1} solutions in acetonitrile from Sigma-Aldrich (Steinheim, Germany) and Riedel de Haën (Seelze, Germany), respectively, and 4-aceto-3,5-dimethyl-2,6-dinitro-*tert*-butylbenzene (musk ketone) from Fluka (Buchs, Switzerland). Table 1 shows the formula name of the target compounds and the logarithm of the octanol-water constant (K_{OW}) predicted from the software SRC-KowWIN (Syracuse Research Corp., Syracuse, New York, USA).

Individual standard solutions of synthetic musks were prepared in acetone and the mixtures prepared in methanol. The solvents were GC grade with purity >99.9% (SDS, Peypin, France). Helium gas and nitrogen gas of purity 99.999% (Carburos Metálicos, Barcelona, Spain) were used for the thermal desorption and the chromatographic analysis. Ultra-pure water was obtained using a Mili-Q water purification system (Millipore, Bedford, MA, EEUU).

Table 1. Formula name, log $K_{OW,}$ retention times t_R and quantifier and qualifier ions of the target musk compounds

No.	Compound	Formula name	Log K_{ow}[a]	t_R (min)	Quantifier ion	Qualifiers
1	Cashmeran (DPMI)	6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone	4.9	5.12	191	206 (60), 192 (14)
2	Celestolide (ADBI), Crisolide	4-acetyl-1,1-dimethyl-6-*tert*-butylindane	6.6	7.84	229	244 (45), 173 (19.5)
3	Phantolide (AHMI)	6-acetyl-1,1,2,3,3,5-hexamethylindane	6.7	8.75	229	244 (24), 187 (9.5)
4	Traseolide (ATII), Fixolide	5-acetyl-1,1,2,6-tetramethyl-3-isopropyl-indane	6.7	10.02	215	258 (15), 173 (16)
5	Galaxolide (HHCB), Abbalide, Pearlide	1,3,4,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran	5.9	10.25	243	213 (15), 258 (10)
6	Tonalide (AHTN)	7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene	5.7	10.38	243	258 (27.5), 159 (20)
7	Musk Xylene (MX)	2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene	4.8	11.22	282	283 (15), 297 (10)
8	Musk Moskene (MM)	1,1,3,3,5-pentamethyl-4,6-dinitroindan	5.8	11.26	263	264 (15), 278 (10)
9	Musk ketone (MK)	4-aceto-3,5-dimethyl-2,6-dinitro-*tert*-butylbenzene	4.3	12.83	279	294 (20), 280 (15)

[a] Log K_{ow} values predicted from SRC-KowWin software.

2.2. Sample collection

Four representative water types were sampled to test the performance of the method in real samples: the influent and effluent of two urban waste water treatment plants (WWTPs), which collect wastewater from ca. 120.000 inhabitants, respectively; the effluent of a reverse osmosis plant (RO) located after the secondary treatment of one of the studied urban plants; and samples from the Ebro River. Samples were collected in amber glass bottles, pre-cleaned overnight with chromic mixture and subsequently rinsed with Milli-Q water and HPLC grade isopropanol. After collection, samples were filtered using a 0.45 µm nylon filter (Whatman, Maidstone, UK), stored at 4 °C and analysed within a week.

2.3. Stir bar sorptive extraction

Extractions were carried out with polydimethylsiloxane (PDMS) coated stir bars (20 mm length × 0.5 mm film thickness, from Gerstel (Mülheim an der Ruhr, Germany)), which correspond to approximately 48 µL of PDMS phase. Before each use, stir bar were conditioned by thermal cleaning at 300 °C for 3 hours, in a pure Helium stream of 100 mL min^{-1}. Stir bars were stored in cleaned 2 mL vials until their use.

For the extraction procedure, a cleaned stir bar was placed in a 250 mL vial containing 100 mL of water, immediately capped and stirred at 900 rpm for 4 hours at 25 °C and pH 7. One hundred millilitres of river and reverse osmosis effluent samples were directly extracted, whereas urban WWTP influent and effluent samples were

diluted with Milli-Q water before extraction (5 mL of sample into 100 mL of total volume).

After 4 hours of extraction, stir bars were magnetically removed, rinsed with ultra-pure water, dried with a lint-free tissue and placed inside a thermally cleaned stainless-steel tube for the thermal desorption.

2.4. Thermal desorption GC-MS analysis

Thermal desorption of the musks retained on the stir bars was performed in a Unity Thermal Desorption system combined with a Ultra A autosampler (both from Markes International Limited, Llantrisant, UK). Stir bars were placed in empty stainless-steel tubes for thermal desorption (9 cm length × 6.35 mm o.d. × 5 mm i.d., also from Markes). Prior to the analysis, the empty tubes were thermally cleaned at 300 °C for 15 min and then stored in a hermetical glass jar under nitrogen atmosphere. The optimised thermal desorption conditions for the stir bar were: pre-purge for 1 minute at room temperature, stir bar desorption at 300 °C for 15 minutes using helium carrier gas at 100 mL min^{-1}, in splitless mode, trapping at 0 °C. The trap was then desorbed at 320 °C for 10 min with a split of 5 mL min^{-1}.

Separation and detection were performed in a 6890N gas chromatograph and 5973 *inert* mass spectrometer (Agilent Technologies. Palo Alto, USA), using a Zebron ZB- 50 capillary column (30 m × 0.25 mm × 0.25 µm) provided by Phenomenex (Le Pecq Cedex, France). For the GC-MS analysis, the helium carrier gas flow was 2 mL min^{-1} and the temperature program was as follows: initial temperature 100 °C, 30 °C min^{-1} to 170 °C, then at 5 °C min^{-1} to 190 °C and then at 15 °C min^{-1} to 290 °C and held for 4 minutes. The GC-MS interface was set at 290 °C. The MS-detector acquired in the selective ion monitoring mode (SIM) operating at an electron impact energy of 70 eV. The GC-MS parameters of the target musks were optimised in a previous paper [23]. Table 1 shows the retention times and the quantifier and qualifier ions used for the SIM detection.

3. RESULTS AND DISCUSSION

3.1. Method optimisation

As previously stated, the GC-MS parameters for these 9 synthetic musks were optimised in a prior study [23]. It is worth mentioning that the use of a midpolarity phase capillary column (a 50% diphenyl / 50% dimethylpoly-siloxane) provided the resolution of the compounds in about 13 min, even with the separation of the 4 HHCB diastereoisomers. HHCB was quantified by integrating the signals of 4S and 7R/S isomer peaks, which are the diastereoisomers responsible of the characteristic musky odour [24]. Following the previous optimisation of

the GC-MS conditions, this study has focused on the optimisation of the SBSE parameters.

3.1.1. SBSE extraction

In the SBSE technique the extraction is an equilibrium process dependent on the amount of the PDMS phase, the volume of aqueous sample and the partitioning coefficients of the compounds between the PDMS phase and the aqueous phase that are correlated with the octanol-water distribution coefficients (K_{ow}) [19,21]. Therefore, the first parameters fixed were the size of the stir bar and the volume of sample. In order to have high sensitivity, the sample volume was fixed at 100 mL. Therefore, a suitable size of stir bar (20 mm length x 0.5 µm film thickness, with ca. 48 µL of PDMS coating) was selected for this study. The calculated theoretical recoveries for 100 mL of sample using this stir bar ranged from 90.5% for musk ketone to 100% for the most apolar synthetic musks, such as AHMI and ATII. Regarding the stirring rate, although the increase of the stirring speed can accelerate the extraction, it also reduces the lifetime of the stir bar [25]. Hence, a medium level stirring rate of 900 rpm was used.

Once the amount of organic phase, the volume of sample and the stirring rate were fixed, the influence of other factors, which play an important role in the efficiency of the SBSE extraction, was studied. A screening 2^3 factorial design was used to study the influence of the salting-out effect, the time and the temperature on the SBSE extraction, involving 8 randomised experiments performed in duplicate. Statistical analysis was carried out with Statgraphics-Plus 5.1 (Magnugistic, Rockville, MD, USA). All experiments were run using 100 mL solutions of the target musks at a concentration of 70 ng L^{-1} in Milli-Q water.

The influence of an addition inert salt (NaCl) at 0% (no addition), and 20% levels was studied. Salt increases the ionic strength of the solution, which can decrease the solubility of the analytes in the aqueous phase and promote their transference to the organic phase [22]. Although in general for polar analytes with K_{ow}>3.5 the addition of salt reduces the extraction efficiency [26,27], the opposite effect for apolar compounds, such as polycyclic aromatic hydrocarbons, has been also described [28].

Extraction temperature was studied at 25 °C and 60 °C. A high temperature helps to reach the equilibrium faster but also decreases the K_{ow} partition coefficient and the lifetime of the PDMS extraction phase [25]. However, other studies have reported opposite results [29,30]. Finally, the SBSE extraction time was studied at 3 hours and 12 hours. Extraction time is one of the most important parameters and should be optimised in every application. The optimal extraction time can vary from several minutes to

hours or 1-2 days depending on the physical and chemical properties of the analytes, the partition coefficient between the volume of sample and the volume of the organic phase (β) and the experimental conditions [21]. As an example, the calculated standardised effects for the three factors and the two-factor interactions for DPMI, HHCB and MK are shown in the Pareto charts in Figure 1. The standardised effect is obtained by dividing the estimated effect by its standard error. The vertical line indicates the statistically significant bound at the 95% confidence level. As it can be seen in Figure 1, temperature was the most important factor for the musks. Moreover, temperature was

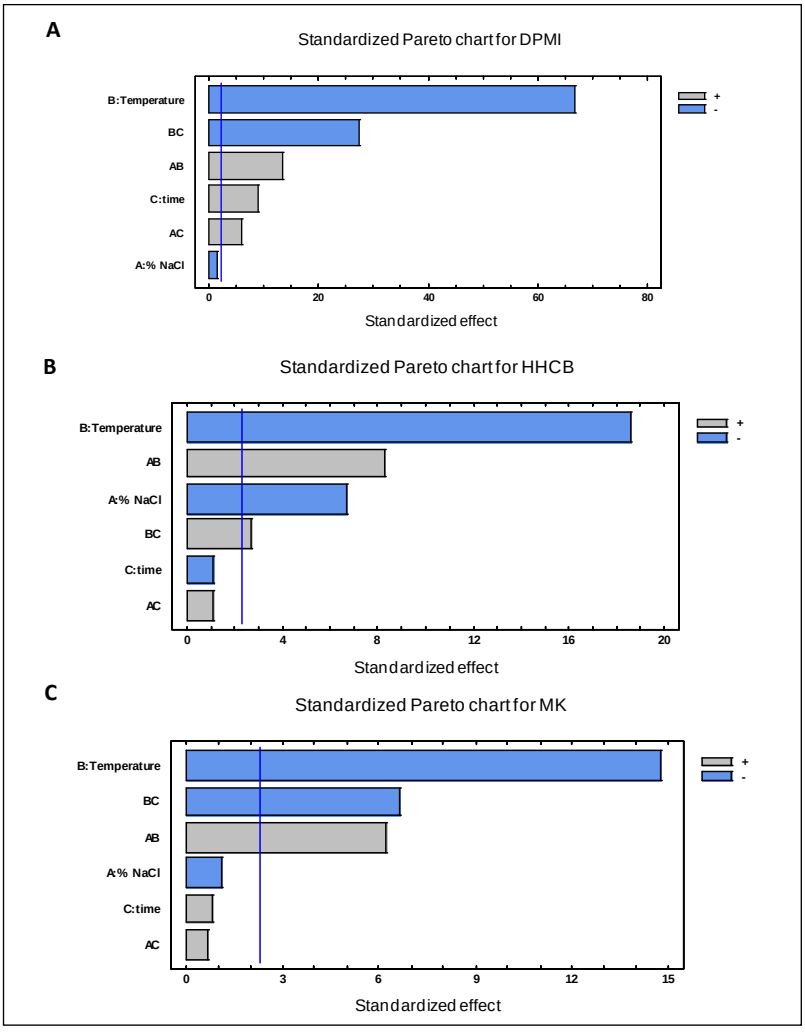


Figure 1. Standarised Pareto charts for the mean effects and two-factor interactions of the factorial design for three representative synthetic musks: (A) DPMI, (B) HHCB and (C) MK.

the only significant factor for MK (Figure 1C). For all the target musks, increasing the temperature from 25 °C and 60 °C had a negative effect in the extraction. Possible explanations can be the vaporisation of part of the analytes at high temperatures (vapour pressures from 2.69×10^{-3} for DPMI to 5.23×10^{-6} for MX) and/or the decrease of the partition coefficient at high temperatures. Furthermore, the addition of 20% NaCl had a negative effect for all the musks except DPMI and MK whose salting-out effect was not significative. The decrease of extraction efficiency with the addition of NaCl can be explained by the increase of the solution viscosity, which slows down the interaction kinetics of the analytes. Finally, the extraction time did not have an important role at the two levels studied (3 and 12 hours), being statistically significant only for DPMI although it has a slightly positive effect for most compounds except for HHCB, which had reduced extraction at the higher time level.

Concerning the two-factor interactions, the effect of NaCl-temperature interaction (AB) was significant for all the target compounds. Therefore, the effect of increasing the temperature in the extraction process is different depending on the amount of NaCl added. However, the effect of NaCl-time interaction (AC) was only important for ADBI and the temperature-time interaction (BC) for DPMI and HHCB.

Taking into account the results of the screening multifactorial design, the subsequent tests were done at 25 °C without the addition of salt in the solution over 3 hours of extraction.

Next, the influence of pH was evaluated, at pH 2.0, 7.0 and 10.0. As for previous studies [31,32], the efficiency of the extraction decreased under acidic conditions but no significant effect of sample pH was observed at neutral and basic pH (results not shown). Therefore, neutral pH was selected in order to avoid the PDMS-phase degradation.

The addition of organic modifiers, such as MeOH, can also favour the extraction of apolar analytes by reducing their adsorption to the vial glass walls. However, the presence of the organic modifier also increases the solubility of the apolar compounds in the solution, decreasing the extraction efficiency. In order to determine this effect, 10% MeOH was added to the samples. No significant variations in the analytes responses were observed, hence, the addition of MeOH was rejected in the sample analysis.

After the rest of the conditions were fixed, different extraction times were studied in order to find the best compromise between sample preparation time and extraction efficiency. Results showed that the equilibrium was reached between 4 and 5 hours for most compounds (4 hours for the polycyclic musks and 5 hours for the nitro musks).

Consequently, as a compromise 4 hours extraction time was selected for the musks determination.
The final conditions for the stir bar extraction of the synthetic musks in the samples are summarised in Table 2.

3.1.2. Stir bar thermal desorption

Polycyclic musks are semi-volatile compounds with relatively high boiling points (between 286 and 392 °C). A previous study showed that relatively high temperatures (320 °C), longer times of desorption (15 min) and high helium flows (100 mL min^{-1}) were needed for the quantitative recovery of these analytes in Tenax TA [23]. PDMS is a weaker sorbent than Tenax TA and desorption temperatures up to 300 °C and desorption flows up to 100 mL min^{-1} are recommended by the manufacturer in order to avoid the degradation of the stir bar coating. Hence, in this study different desorption temperatures (from 275 to 300 °C), times (from 5 to 20 min) and flows (from 30 to 100 mL min^{-1}) were tested for recovery of analytes from the PDMS stir bar. Carry-over of all analytes was under 1% when appliying the maximal recommended desorption temperature (300 °C) and flow rate (100 mL min^{-1}) for 15 min. Higher desorption times did not show significant improvement in the recoveries. Once desorbed from the stir bar, analytes were focused in a Tenax TA cryogenic trap at 0 °C The optimised stir bar thermal desorption conditions are summarised in Table 2. The conditions of the trap desorption step were optimised in a previous work [23].

3.1.3. Control of blanks

The extensive use of synthetic musks as fragrances in a wide range of consumer products means a high risk of contamination. Therefore, special precautions are required through the whole analytical procedure. The SBSE procedure developed in this study reduces the potential contamination risk because the aqueous sample is directly extracted by the stir bar, which is then analysed by thermal desorption. Even so, further precautions were taken. In this respect, all the glassware used for the sampling and the extraction step was cleaned overnight with chromic mixture and then rinsed five times with Milli-Q water and three times with HPLC grade isopropanol. Furthermore, musk-free gloves were used and the samples were prepared in a fume cupboard. In addition, the thermal desorption tubes were conditioned at 300 °C for 10 min and then stored in sealable glass jars under nitrogen atmosphere, as described above (section 2.4.). Despite these precautions, signals of HHCB corresponding to 0.010±0.007 ng (n= 5) were found in blanks of 100 mL of pure Milli-Q water.
It should be also taken into account that the thermal desorption of semi-volatile compounds can cause memory

Table 2. Optimised conditions for the stir bar extraction and thermal desoprtion.

Stir bar extraction	
Sample volume	100 mL
Stirring speed	900 rpm
Temperature	25 °C
% NaCl	0
Time	4 hours
Use of organic modifier	No
pH	7
Stir bar thermal desorption	
Temperature	300 °C
Time	15 min
Flow	100 mL min^{-1}
Trap temperature	0 °C
Split	splitless

effects in the instrumentation, either in the cryogenic trap (due to the partial desorption of the analytes) or in the transfer lines (whose temperature can only be raised to 200 °C and may cause the accumulation of the less volatile compounds) [23,33]. To avoid these memory effects, in this study the influent and effluent samples from the WWTPs were diluted before the extraction (5 mL of sample diluted to 100 mL with Milli-Q water) and the maximal calibration level was fixed at 20 ng of each compound per sample.

3.2. Method validation

The main method parameters for the optimised SBSE method were tested by spiking different amounts of the standards (from 0.001 to 200 ng L^{-1}) in 100 mL of Milli-Q water and in each kind of sample. Linearity was good for all the target musks with coefficient of determination (r^2) values higher than 0.999.

Table 3 shows the main method parameters in 100 mL of Milli-Q water. Experimental recoveries of the synthetic musks were analysed at low and midpoint calibration levels (5 ng L^{-1} and 100 ng L^{-1}, respectively, n=3). To calculate recoveries the response obtained by the SBSE method was compared with the response obtained by spiking the same amount of standard in a tube filled with thermally cleaned deactivated glass wool. Recoveries were similar for both calibration levels ranging between the 82% and the 95%. As expected, the lower recoveries corresponded to the musks with lower K_{ow} such as DPMI, and the three nitromusks.

Table 3. Method parameters in Milli-Q water: experimental recovery, repeatability, reproducibility, and method detection and quantification limits expressed in ng L^{-1}.

No.	Musk	Recovery (%, n=3)		Repeatability (%RSD, n=5)		Reproducibility (%RSD, n=5)		MDL	MQL
		5 ng L^{-1}	100 ng L^{-1}	5 ng L^{-1}	100 ng L^{-1}	5 ng L^{-1}	100 ng L^{-1}	(ng L^{-1})	(ng L^{-1})
1	DPMI	85.3	84.7	10.1	3.6	14.8	5.9	0.10	0.30
2	ADBI	93.0	94.1	9.6	4.1	11.6	6.9	0.06	0.20
3	AHMI	94.6	94.3	6.5	4.2	6.1	5.7	0.02	0.10
4	ATII	91.7	90.5	9.5	3.7	12.3	4.8	0.05	0.15
5	HHCB	92.1	93.3	10.3	8.2	12.1	6.8	0.30	1.0
6	AHTN	91.2	92.4	7.9	4.2	8.1	4.7	0.03	0.10
7	MX	85.4	87.3	9.8	3.3	10.1	3.4	0.05	0.15
8	MM	88.4	90.8	4.4	3.2	4.3	3.9	0.06	0.20
9	MK	81.6	81.7	6.3	2.2	6.5	2.3	0.05	0.15

The limits of detection (MDL) were calculated as the concentration corresponding to three times the noise signal of the target ion of each compound except for HHCB which was present in the blanks of the Milli-Q water. For HHCB the MDL was determined as the average of the blank signal of the target ion plus three times the standard deviation of the signal (n=5).

The MDLs ranged from 0.02 ng L^{-1} for AHMI to 0.3 ng L^{-1} for HHCB (see Table 3). The limit of quantification (MQL), which was fixed as the lowest calibration level of each compound, ranged from 0.1 ng L^{-1} for AHMI and AHTN to 1 ng L^{-1} for HHCB. It is worth mentioning that the MDLs and MQLs for HHCB, AHTN and MK obtained in a recent study by SBSE followed by liquid desorption [31] ranged from 12 to 19 ng L^{-1} and from 41 to 62 ng L^{-1}, respectively, which are higher than those found in the present study.

Repeatability and reproducibility between days were also measured at two calibration levels, 5 ng L^{-1} and 100 ng L^{-1} respectively. %RSDs for the tests in the same day ranged from 4.4 and 10.3% for the low calibration level and from 2.2 to 8.2% for the midpoint calibration level. The reproducibility was tested by analysing five replicates of each calibration point on different days and ranged from 4.3 to 14.8% for the 5 ng L^{-1} level to 2.3 to 6.9% for the 100 ng L^{-1} level.

The method was also validated in the real samples. As mentioned before, in order to avoid matrix effects and to not overload the TD-GC-MS system, the influent and effluent samples were diluted with Milli-Q water (5 mL of sample to 100 mL). The RO effluent samples and the river samples were not diluted because of the lower expected concentrations of the musks. Taking into account these precautions, recoveries of the synthetic musks in

the real samples were similar to those obtained in Milli-Q water at low and midpoint calibration levels (5 ng L^{-1} and 100 ng L^{-1}, respectively), therefore no matrix effects were observed and quantification was performed by external calibration spiking the standards in Milli-Q water. Similarly, repeatability and reproducibility presented similar results in the four different samples (% RSD between 2.2 and 10.4 %, n=3).

3.3. Analysis of real water samples

The developed SBSE-GC-MS method was used to determine the presence of nine synthetic musks in four different kind of aqueous matrices (urban WWTP effluent and influent, effluent of a RO treatment plant and river water). Three different samples of each matrix were analysed by triplicate. Figure 2 shows examples of SIM chromatograms from two real samples: the chromatogram of an urban WWTP effluent (diluted in a factor of 1 to 20, Figure 2A) and of a river Ebro sample (Figure 2B).

Table 4 shows the concentration of the synthetic musks detected in the samples. HHCB was the most abundant compound in all the water matrices, with values up to 2069 ng L^{-1} and 1432 ng L^{-1} in the influent and the effluent of urban WWTP, respectively. DPMI, AHMI and AHTN were also detected in all the matrices with values up to 94 ng L^{-1}, 26 ng L^{-1} and 88 ng L^{-1}, respectively. However, ADBI was no detected in the river samples and ATII could only be quantified in some of the influent samples. Regarding the nitromusks, MM was not found in any sample, which agrees with the prohibition of their use in cosmetics in European

Table 4. Concentrations of the synthetic musks in real samples, expressed in ng L^{-1} (n=3).

Musk	Urban WWTP Influent	Urban WWTP Effluent	Effluent RO	River
DPMI	15.7-87.7	29.8-43.3	<MQL-0.67	0.49-1.72
ADBI	3.6-35.4	<MQL-4.56	n.d.-0.24	<MQL
AHMI	<MQL-25.6	<MQL-4.15	<MQL-0.17	n.d.-0.27
ATII	n.d.-8.1	n.d.	n.d.	n.d.
HHCB	476-2069	233-1432	n.d.-1.45	1.40-26.2
AHTN	17.7-78.7	25.4-93.6	n.d.-0.35	0.34-037
MX	22.0-29.1	13.1-126	n.d.-0.3	n.d.-0.55
MM	n.d.	n.d.	n.d.	n.d.
MK	<MQL-20.3	29.2-53.5	n.d.	n.d.-0.80

n.d., values not detected
<MQL, values under the method quantification limit of each sample.

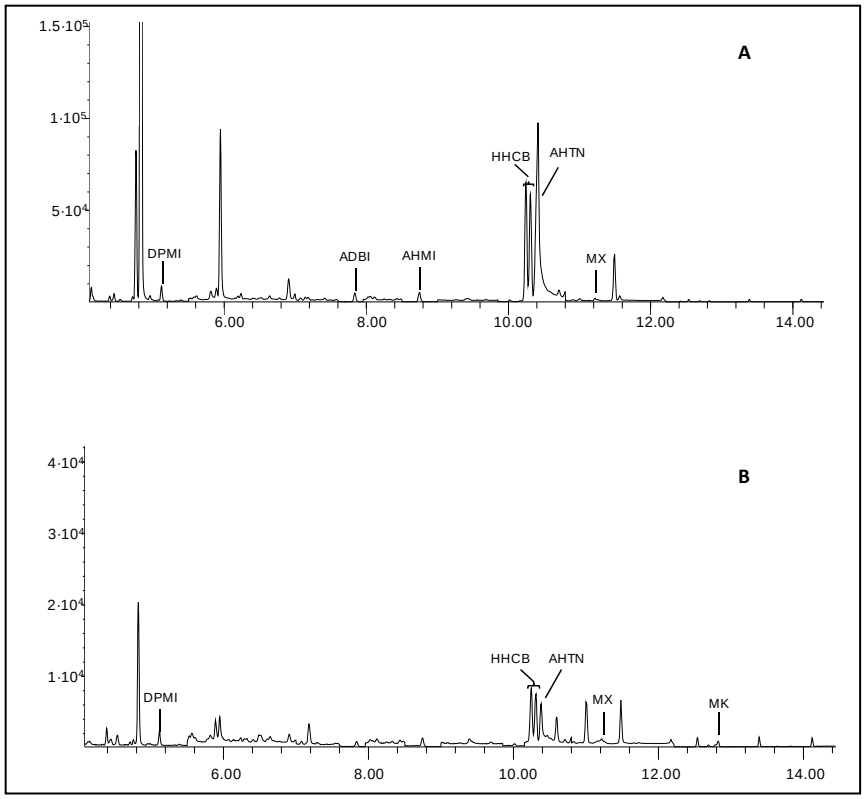


Figure 2. Chromatograms of two real samples: the influent of a urban WWTP diluted in a factor of 1 to 20 (A) and the Ebro river (B).

countries [34]. However, MX and MK were detected in the influents and effluents of the urban WWTP as well as in some river samples with values up to 126 and 53 ng L^{-1}, respectively. This fact demonstrates that, even though use of nitromusks is prohibited in cosmetics, they are still present in other consumer products and therefore they can be found in wastewaters and environmental matrices.

Finally, it is worth mentioning that the low levels of the compounds detected in the analysed effluents of the RO treatment plant (HHCB up to 1.45 ng L^{-1}) indicate that this kind of plants can efficiently remove semi-volatile apolar compounds from complex aqueous matrices.

4. CONCLUSIONS

A method based on SBSE coupled with a conventional TD-GC-MS system was successfully developed for determining 9 synthetic musks in water samples. The developed SBSE method can efficiently trap and desorb these apolar and semivolatile musks, providing limits of quantification at low ng L^{-1} levels. Furthermore, the limited

manipulation of the sample required in this method implies a significant decrease of the risk of external contamination of the samples. The technique was applied in real water matrices, such as wastewater and river water. The most abundant musk was HHCB, with also considerable amounts of AHTN, DPMI and AHMI. Although nitromusks are prohibited in cosmetics, musk moskene and musk ketone were found both in the WWTP and in the river samples.

Acknowledgments

The authors wish to acknowledge the financial support provided to this study by the Spanish Ministry of Science and Innovation through projects CTM-2008-06847-C02-01 and the Department of Innovation, Universities and Enterprises of the Generalitat de Catalunya through project 2009 SGR 223.

REFERENCES

[1] K. Bester, J. Chromatogr. A 1216 (2009) 470.
[2] G.G. Rimkus, Toxicol. Lett. 111 (1999) 37.
[3] H. Brunn, N. Bitsch, J. Amberg-Muller, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part X, vol. 3, Springer-Verlag, Berlin Heidel-berg, 2004, p.259.
[4] T. Luckenbach, D. Epel, Environ. Health Perspect. 113 (2005) A803.
[5] H.P. Hutter, P. Wallner, H. Moshammer, W. Hartl, R. Sattelberger, G. Lorbeer, M. Kundi, Sci. Total Environ. 407 (2009) 4821.
[6] T.A. Ternes, A. Joss, H. Siegrist, Environ. Sci. Technol. 38 (2004) 392A.
[7] S.L. Simonich, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part O, vol. 5, Springer-Verlag, Berlin Heidelberg, 2005, p. 79.
[8] A.M. Peck, K.C. Hornbuckle, Environ. Sci. Technol. 38 (2004) 367.
[9] A.M. Peck, K.C. Hornbuckle, Atmos. Environ. 40 (2006) 6101.
[10] Z.Y. Xie, R. Ebinghaus, C. Temme, O. Heemken, W.G. Ruck, Environ. Sci. Technol. 41 (2007) 5654.
[11] H. Rudel, W. Bohmer, C. Schroter-Kermani, J. Environ. Monit. 8 (2006) 812.
[12] H. Nakata, H. Sasaki, A. Takemura, M. Yoshioka, S. Tanabe, K. Kannan, Environ. Sci. Technol. 41 (2007) 2216.
[13] R. Kallenborn, R. Gatermann, G.G. Rimkus, J. Environ. Monit. 1 (1999) 70N.
[14] S.T. Glassmeyer, E.T. Furlong, D.W. Kolpin, J.D. Cahill, S.D. Zaugg, S.L. Werner, M.T. Meyer, D.D. Kryak, Environ. Sci. Technol. 39 (2005) 5157.
[15] A.M. Peck, Anal. Bioanal. Chem. 386 (2006) 907.

[16] T. Heberer, S. Gramer, H.J. Stan, Acta Hydroch. Hydrob. 27 (1999) 150.
[17] C. Garcia-Jares, M. Llompart, M. Polo, C. Salgado, S. Macias, R. Cela, J. Chromatogr. A 963 (2002) 277.
[18] J. Regueiro, M. Llompart, C. García-Jares, J.C. García-Monteagudo, R. Cela, J. Chromatogr. A 1190 (2008) 27.
[19] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcolumn Sep. 11 (1999) 737.
[20] F.M. Lancas, M.E.C. Queiroz, P. Grossi, I.R.B. Olivares, J. Sep. Sci. 32 (2009) 813.
[21] F. David, P. Sandra, J. Chromatogr. A 1152 (2007) 54.
[22] A. Prieto, O. Basauri, R. Rodil, A. Usobiaga, L.A. Fernandez, N. Etxebarria, O. Zuloaga, J. Chromatogr. A 1217 (2010) 2642.
[23] N. Ramirez, R.M. Marce, F. Borrull, J. Chromatogr. A 1217 (2010) 4430.
[24] R. Gatermann, S. Biselli, H. Huhnerfuss, G.G. Rimkus, S. Franke, M. Hecker, R. Kallenborn, L. Karbe, W.A. Konig, Arch. Environ. Contam. Toxicol. 42 (2002) 447.
[25] W.M. Liu, Y. Hu, J.H. Zhao, Y. Xu, Y.F. Guan, J. Chromatogr. A 1095 (2005) 1.
[26] A.R. Chaves, S.M. Silva, R.H.C. Queiroz, F.M. Lancas, M.E.C. Queiroz, J. Chromatogr. B 850 (2007) 295.
[27] J.B. Quintana, R. Rodil, S. Muniategui-Lorenzo, P. Lopez-Mahia, D. Prada-Rodriguez, J. Chromatogr. A 1174 (2007) 27.
[28] A. Prieto, O. Zuloaga, A. Usobiaga, N. Etxebarria, L.A. Fernandez, J. Chromatogr. A 1174 (2007) 40.
[29] L. Brossa, R.M. Marce, F. Borrull, E. Pocurull, Chromatographia 61 (2005) 61.
[30] M. Bourdat-Deschamps, J.J. Daudin, E. Barriuso, J. Chromatogr. A 1167 (2007) 143.
[31] A.R.M. Silva, J.M.F. Nogueira, Anal. Bioanal. Chem. 396 (2010) 1853.
[32] M. Llompart, C. Garcia-Jares, C. Salgado, M. Polo, R. Cela, J. Chromatogr. A 999 (2003) 185.
[33] E. Wauters, P. Van Caeter, G. Desmet, F. David, C. Devos, P. Sandra, J. Chromatogr. A 1190 (2008) 286.
[34] Council directive 98/62/EEC, Off. J. Eur. Commum. 20 (1998) L253.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.4.2. Simultaneous determination of preservatives and synthetic musks in water samples by stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

SIMULTANEOUS DETERMINATION OF PARABENS AND SYNTHETIC MUSKS IN WATER SAMPLES BY STIR BAR SORPTIVE EXTRACTION AND THERMAL DESORPTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Noelia Ramírez, Francesc Borrull, Rosa Maria Marcé
Department of Analytical Chemistry and Organic Chemistry
Universitat Rovira i Virgili, Marcel·lí Domingo s/n
Sescelades Campus, Tarragona 43007, Spain

Abstract

This study focuses on a method for the simultaneous determination of 14 personal care products - 6 polycyclic musks, 3 nitromusks and 5 parabens – and 1 polycyclic musk degradation product – galaxolidone – in different water matrices. The method is based on stir bar sorptive extraction followed by thermal desorption – gas chromatography – mass spectrometry. Prior to extraction, the parabens were acetylated to improve their affinity for the polydimethylsiloxane phase of the stir bar. The optimised acetylation conditions allowed the parabens to be extracted efficiently without reducing the recovery of the other target compounds. The method showed good linearity, repeatability and reproducibility between days for all compounds and limits of detection at low ng L^{-1} levels (between 0.02 ng L^{-1} and 0.3 ng L^{-1}). The proposed method is also environmentally-friendly, because it does not use organic solvents, and reduces the risk of external pollution, due to the minimal manipulation of the sample required.
The method developed was successfully applied for the analysis of PCPs in different kinds of water matrices: influents and effluents of urban and industrial waste water treatment plants (WWTPs), effluents of a reverse osmosis treatment plant and river waters. The influents of urban WWTP generally showed the highest values for synthetic musk, with concentrations of up to 2219 ng L^{-1} of galaxolide, whereas the highest concentrations of parabens were detected in the industrial WWTP influents (i.e. 23,593 ng L^{-1} of propyl paraben). The most abundant compounds in the river waters were methyl paraben, with values up to 42 ng L^{-1} and galaxolidone, with up to 36 ng L^{-1}.

Keywords**:** Stir bar sorptive extraction (SBSE); Thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS); Personal care products (PCPs); Derivatization; Water samples.

1. INTRODUCTION

Personal care products (PCPs) comprise different groups of compounds that are currently used as additives in cosmetic, household, food and pharmaceutical products, among others. In recent years, several studies have demonstrated the presence of PCPs in environmental matrices, such as water, sediments, biota and air [1-3]. These compounds have been also found in adipose human tissue, breast milk and human blood [4-8] and some are considered endocrine - disrupting chemicals [9,10]. Because of their adverse effects on health and their potential bioaccumulation, PCPs are regarded as emerging organic contaminants [11,12]. The development of accurate methods for simultaneously determining more than one group of these contaminants and their degradation products is consequently of major interest.

Synthetic musk fragrances and paraben preservatives (p - hydroxybenzoic esters) are PCPs with widespread use as additives in the majority of consumer products. Since these compounds enter the waste water due to regular use, the main exposure route into the environment is through waste water effluents. Parabens are relatively polar compounds that can be effectively removed during conventional sewage treatments [13-15]. However, synthetic musks are only partially biodegradable and they are not completely eliminated by waste water treatment plants (WWTPs) [16]. Removal from approximately 50 to more than 90% in WWTPs has been reported for synthetic musks, mainly by means of their sorption onto sludge particles [16,17]. In addition, some degradation products of these PCPs can also be formed during waste water treatment. These derivatives are usually more oxidized and less lipophilic substances, which can be easily found in aquatic environments. The primary metabolite of the polycyclic musk galaxolide, the galaxolidone, has been previously identified in natural waters [1,17] and in fish [18].

Most of the analytical methods developed for determining either synthetic musks or parabens in water are based on solid-phase extraction (SPE) followed by gas or liquid chromatography [1, 19]. Nevertheless, sorptive methods followed by thermal desorption reduce the risk of background contamination, because they avoid the use of organic solvents and require minimal manipulation of the sample. Solid-phase microextraction (SPME) has been successfully used to determine synthetic musks [20-22] and parabens [23,24]. However, few stir bar sorptive extraction (SBSE) methods in combination with thermal desorption for determining these compounds have been published [25-27]. Synthetic musks are apolar compounds, which present a high affinity for the polydimethylsiloxane (PDMS) phase of

the commercial stir bars. Indeed, a recent study has successfully developed a SBSE method coupled with a thermal desorption equipment for determining 9 synthetic musks in water samples [25]. However, parabens are more polar analytes and their low affinity for the PDMS phase implies low recoveries and therefore poor sensitivity [26]. Derivatization is a valuable alternative for the extraction of polar compounds because improves extraction efficiency and peak shape in GC analysis. The *in situ* acetylation of the phenolic group is one of the most frequently used derivatization procedures because of the high derivatization efficiency and the high recovery of the phenol acetate derivatives by the PDMS phase [23, 27-29].

The aim of this study is therefore to develop a method based on SBSE with *in situ* acetylation followed by thermal desorption – gas chromatography – mass spectrometry (TD-GC-MS) for simultaneously determining five parabens, nine synthetic musks and one musk degradation product in water samples. After extraction, the stir bars were placed in empty stainless steel tubes and thermally desorbed in TD equipment. The influence of the acetylation conditions on the SBSE efficiency of the all the target PCPs has been studied in various kinds of waters. The applicability of the method was tested by analysing influent and effluent samples from three industrial and three urban WWTPs, effluent samples from a reverse osmosis plant and three river waters. As far as we know, this is the first time that an SBSE extraction method has been used for the simultaneous determination of these analytes in water samples, and the application of SBSE for the simultaneous determination of water contaminants in a wide range of polarities is therefore demonstrated.

2. EXPERIMENTAL

2.1. Chemical standards

The six polycyclic musks 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (DPMI, cashmeran), 4-acetyl-1,1-dimethyl-6-*tert*-butylindane (ADBI, celestolide), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI, phantolide), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane (ATII, traseolide), 1,3,4,7,8-hexahydro - 4, 6, 6, 7, 8, 8 -hexamethylcyclopenta-(γ)-2-benzopyran (HHCB, galaxolide) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1, 2, 3, 4 - tetrahydronaphthalene (AHTN, tonalide) were supplied by Promochem Iberia (Barcelona, Spain). The nitro musk fragrances 2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene (musk xylene), 1,1,3,3,5-pentamethyl-4,6-dinitroindane (musk moskene) were purchased as 100 mg L^{-1} solutions in acetonitrile from Sigma-Aldrich (Steinheim, Germany) and Riedel de Haën (Seelze, Germany) respectively and 4-aceto-3,5-dimethyl-2,6-dinitro-*tert*-butylbenzene (musk ketone) from Fluka (Buchs,

Switzerland). The 4-hydroxybenzoic acid methyl ester (methyl paraben), 4-hydroxybenzoic acid ethyl ester (ethyl paraben), 4-hydroxybenzoic acid n-propyl ester (propyl paraben) and 4-hydroxybenzoic acid butyl ester (butyl paraben) were purchased from Aldrich and the 4-hydroxybenzoic acid i-propyl ester (i-propyl paraben) was purchased from Alfa Aesar (Karlsruhe, Germany). The degradation product of the galaxolide 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran-1-one (HHCB-lactone, galaxolidone) was kindly provided by IFF (International Flavours and Fragrances, Hilversum, Netherlands). Table 1 includes the formula name of the target compounds and the logarithm of the octanol-water constant (K_{OW}) predicted by the software SRC-KowWIN (Syracuse Research Corp., Syracuse, New York, USA).

The acetylated methyl paraben (methyl 4-acetoxybenzoate, 99% purity) was supplied by Aldrich. The other acetylated parabens, which are unavailable commercially, were prepared by adding 200 µL of acetic anhydride and 5 µL pyridine (from Sigma-Aldrich) to 1 mL of 500 mg L^{-1} standard solution of the parabens in ethyl acetate (GC grade, SDS, Peypin, France) and mixing the result in a vortex for 10 min at ambient temperature [27]. The calculated efficiency of the derivatization was approximately 96%.

The individual standard solutions of the synthetic musks and the lactone were prepared in acetone and the individual standards of parabens and mixtures of all target PCPs were prepared in methanol. These solvents were GC grade with >99.9% purity (from SDS). Helium gas and nitrogen gas with 99.999% purity (Carburos Metálicos, Barcelona, Spain) were used for the thermal desorption and chromatographic analysis. Ultrapure water was obtained using a Purelab ultra purification system (Veolia water, Barcelona, Spain). The acetic anhydride for the paraben derivatization was from Scharlau Chemie (Setmenat, Spain) and the disodium hydrogen phosphate and the sodium carbonate from Panreac (Barcelona, Spain).

2.2. Sample collection

The method's performance was tested in several water types: the influent and effluent of three urban WWTPs; the effluent of a reverse osmosis plant (RO) located after the secondary treatment of one of the urban plants studied; the influent and effluent of three industrial WWTPs (one dedicated to toxic waste disposal, one to the oil recycling industry and one synthesizing additives, emulsions and detergents); and samples from three rivers: the Ebro, the Llobregat and the Ter.

The water samples were collected in amber glass bottles, pre-cleaned overnight with chromic mixture and subsequently rinsed three times with

Table 1. Formula name, retention times (t_R), quantifier and qualifier ions, log K_{OW} and SBSE theoretical recoveries of the target PCPs.

Compound	Formula name	t_R (min)	Quantifier ion	Qualifiers	log K_{ow} [b]	Theor. rec. (%) [c]
Cashmeran (DPMI)	6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone	5.12	191	206 (60), 192 (14)	4.9	94
Methyl paraben (MeP)[a]	4-hydroxybenzoic acid methyl ester	5.76	121	91 (90), 152(80)	2.0	4.5
Ethyl paraben (EtP)[a]	4-hydroxybenzoic acid ethyl ester	6.57	121	166(70), 138 (40)	2.5	13
i-Propyl paraben (i-PrP)[a]	4-hydroxybenzoic acid i-propyl ester	6.85	121	138 (80), 180 (50)	2.9	27
Celestolide (ADBI)	4-acetyl-1,1-dimethyl-6-*tert*-butylindane	7.84	229	244 (45), 173 (20)	6.6	100
Propyl paraben (PrP)[a]	4-hydroxybenzoic acid propyl ester	7.93	138	121 (80), 180 (25)	3.0	31
Phantolide (AHMI)	6-acetyl-1,1,2,3,3,5-hexamethylindane	8.75	229	244 (24), 187 (10)	6.7	100
Butyl paraben (BuP)[a]	4-hydroxybenzoic acid butyl ester	9.48	138	121(50), 194 (15)	3.5	58
Traseolide (ATII)	5-acetyl-1,1,2,6-tetramethyl-3-isopropyl-indane	10.02	215	258 (15), 173 (16)	6.7	100
Galaxolide (HHCB)	1,3,4,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran	10.25	243	213 (15), 258 (10)	5.9	100
Tonalide (AHTN)	7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene	10.38	243	258 (27.5), 159 (20)	5.7	100
Musk Xylene (MX)	2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene	11.22	282	283 (15), 297 (10)	4.8	93
Musk Moskene (MM)	1,1,3,3,5-pentamethyl-4,6-dinitroindan	11.26	263	264 (15), 278 (10)	5.8	99
Musk ketone (MK)	4-aceto-3,5-dimethyl-2,6-dinitro-*tert*-butylbenzene	12.83	279	294 (20), 280 (15)	4.3	91
Galaxolidone (HHCB-lactone)	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(γ)-2-benzopyran-1-one	14.43	257	258 (20), 272 (10)	4.7	96

[a] Retention times, quantifier and qualifier ions of the acetylated derivative.
[b] log k_{ow} values predicted from SRC-KowWin software, except the value for HHCB-lactone (from X. Chen et al. [38]).
[c] Theoretical recoveries calculated for a 100 mL sample and a PDMS stir bar 20 mm long x 0.5 mm film thickness .

ultrapure water and HPLC grade isopropanol. After collection, samples were filtered using a 0.45 µm nylon filter (Whatman, Maidstone, UK), stored at 4 °C and analysed within a week.

2.3. Stir bar sorptive extraction

The extractions were performed with PDMS coated stir bars (20 mm long × 0.5 mm film thickness with ca. 48 µL of phase, from Gerstel (Mülheim an der Ruhr, Germany)). Before each use, the stir bars were conditioned for 3 hours at 300 °C in a flow of 100 mL min^{-1} of pure helium and stored in clean 2 mL vials until use.

The acetylation of parabens was carried out by adding 0.5 g of disodium hydrogen phosphate and 100 µL of acetic anhydride to 100 mL of sample. A clean stir bar was then placed in the vial containing the sample, and immediately capped and stirred at 900 rpm for 4 hours at room temperature. RO effluent and river samples were directly extracted, while the urban and industrial WWTP influent and effluent samples were diluted with ultrapure water to a factor of 1 to 20 before extraction to avoid memory effects in the TD equipment and transfer lines of less volatile compounds [30]. After the extraction, the stir bars were magnetically removed, rinsed with ultrapure water, dried with a lint-free tissue and placed inside a thermally cleaned stainless-steel tube for thermal desorption.

2.4. Thermal desorption GC-MS analysis

Thermal desorption was performed in a Unity Thermal Desorption system combined with an Ultra A autosampler (both from Markes International Limited, Llantrisant, UK). Stir bars were placed in empty stainless steel tubes for thermal desorption (9 cm long × 6.35 mm o.d. × 5 mm i.d., also from Markes). Prior to the analysis, the empty tubes were thermally cleaned at 300 °C for 15 min and then stored in hermetic glass jars under nitrogen atmosphere conditions. The stir bars were purged with helium for 1 min at room temperature before desorption. The stir bar desorption process was performed at 300 °C for 15 minutes using helium carrier gas at 100 mL min^{-1}, in splitless mode and trapping at 0 °C in a Tenax TA trap. The trap was then desorbed at 320 °C for 10 min with a split of 5 mL min^{-1}.

Separation and detection were performed with a 6890N gas chromatograph and 5973 *inert* mass spectrometer (Agilent Technologies. Palo Alto, CA, USA), using a Zebron ZB-50 capillary column (30 m × 0.25 mm × 0.25 µm) provided by Phenomenex (Le Pecq Cedex, France). For the GC-MS analysis, the helium carrier gas flow was set at 2 mL min^{-1}. The oven temperature increased from 100 °C to 170 °C at 30 °C min^{-1}, then to 190 °C at

5 °C min^{-1} and then to 290 °C at 15 °C min^{-1} and was held at this temperature for 4 minutes.

The GC-MS interface was set at 290 °C. The MS-detector acquired in the selective ion monitoring mode (SIM) operated at an electron impact energy of 70 eV. Table 1 shows the retention times and the quantifier and qualifier ions used for the SIM detection.

3. RESULTS AND DISCUSSION

3.1. Method optimisation

3.1.1. Chromatographic conditions

The chromatographic separation of the 14 target PCPs (6 polycyclic musks, 3 nitro musks and the acetylated derivatives of the 5 parabens) and the HHCB-lactone was carried out in a midpolarity phase capillary column (50% diphenyl/50% dimethyl polysiloxane). This kind of coating allows high column flow rates (2 mL min^{-1} in this study) without compromising the resolution, and even leads to the separation of the 4 HHCB diastereoisomers [30].

The acetylated parabens showed much more symmetrical chromatographic peaks and slightly higher retention times than the non-acetylated ones. Under the conditions optimised in this study (see section 2.4), the 15 analytes were resolved in less than 15 min.

3.1.2. Derivatization and stir bar extraction

The SBSE efficiency mainly depends on the amount of the PDMS phase, the volume of the aqueous sample, the sample conditions and the partitioning coefficients of the compounds between the PDMS phase and the aqueous phase that are correlated with the octanol-water distribution coefficients (K_{ow}) [31,32]. A recent study showed that polycyclic musks can almost be quantitatively recovered using stir bars of 20 mm x 0.5 mm with ca. 48 µL of PDMS phase in 100 mL of water samples [25]. However, since PDMS is a non-polar liquid phase, polar analytes with low K_{ow} values have very low recoveries. As can be seen in Table 1, when using stir bars with 48 µL of PDMS phase in 100 mL of aqueous sample, theoretical recoveries of parabens (log K_{ow} between 2.0 and 3.5) range from 4.5% to 58%, whereas recoveries for polycyclic musks (log K_{ow} between 4.3 and 6.7) range from 91% to 100%.The *in situ* derivatization of parabens has consequently been considered in order to improve their recoveries in the PDMS phase.

Acetylation with acetic anhydride in the presence of a base is one of the most frequently used procedures for phenolic compounds, and has been successfully used for the acetylation of parabens [23,27]. Preliminary experiments were performed to check

the suitability of the *in situ* acetylation of parabens and the SBSE extraction of the acetylated derivatives simultaneously with the other target PCPs. These experiments were performed using 100 mL solutions of the target PCPs at a concentration of 100 ng L^{-1} in ultrapure water, with 20 mm x 0.5 mm PDMS stir bars, stirred at 900 rpm for 3 hours at room temperature. The volume of the sample was fixed at 100 mL in order to obtain high sensitivity.

The optimal volume of acetic anhydride was the first parameter studied. Amounts ranging between 50 and 1,000 µL of the acetylating agent were added to the solution in the presence of 2.5 g L^{-1} of sodium carbonate. The highest peak areas for all paraben acetates corresponded to the addition of 100 µL of acetic anhydride. Larger volumes of derivatizing agent provide an acidic medium that is unfavourable for the equilibrium of the acetylation reaction [33]. 100 µL of acetic anhydride were therefore subsequently selected.

The kind of basic salt used in the acetylation process was then selected. Two basic salts, successfully used in previous studies for the acetylation of phenolic compounds [15,34], were tested in additions of 1.0 to 10 g L^{-1}: sodium carbonate and disodium hydrogen phosphate. In general, the responses of the acetylated parabens were higher when using the same amount of Na_2HPO_4 rather than Na_2CO_3, except for ethyl paraben for which the response was slightly higher with Na_2CO_3. Furthermore, the responses of synthetic musks were in general higher with Na_2HPO_4. Regarding the amount of salt, in general the responses of all acetylated parabens increased with the amount of Na_2HPO_4. Since additions of more than 5 g L^{-1} caused a precipitate in the environmental water samples, a concentration of 5 g L^{-1} of Na_2HPO_4 was selected for this study.

Finally, the influence of the temperature was checked. Despite high temperatures leading to an improvement in the acetylation process, a previous study showed that recoveries of synthetic musks decreased as temperatures increased [25].Only mild temperatures (room temperature (ca. 20 °C), 30 °C and 40 °C) were therefore tested. Figure 1 shows the influence of the temperature on the responses of acetylated parabens and three representative musks (DPMI, HHCB and MK), which presented the same behaviour as the other musks and the galaxolidone. The best recoveries were obtained at room temperature, either for the acetylated parabens, the synthetic musks or the galaxolidone, except for the nitro musks MX and MK, for which the recoveries were slightly better at 40 °C. Room temperature was therefore subsequently used for SBSE.

After the acetylation conditions were established, the extraction time was studied. Figure 2 shows the time

profiles for the acetylated parabens and the three representative musks (DPMI, HHCB and MK). In general, the equilibrium was reached after between 4 and 5 hours. An extraction time of 4 hours was consequently selected in order to find the best compromise between sample preparation time and extraction efficiency.

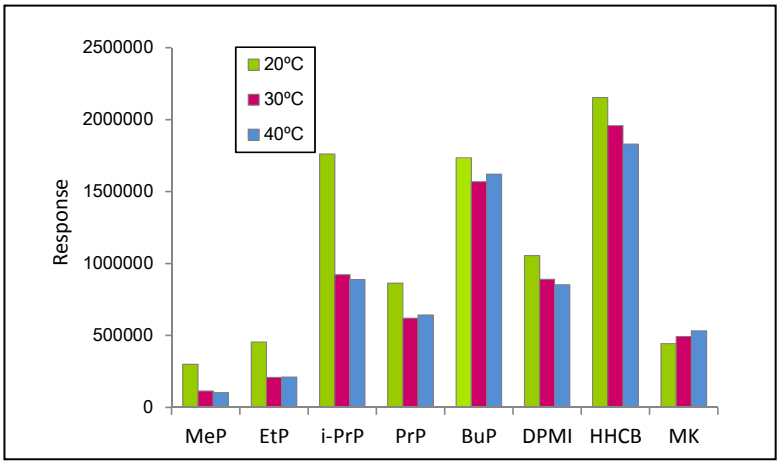


Figure 1. Influence of the temperature in the responses of the acetylated parabens and three representative musks (DPMI, HHCB and MK).

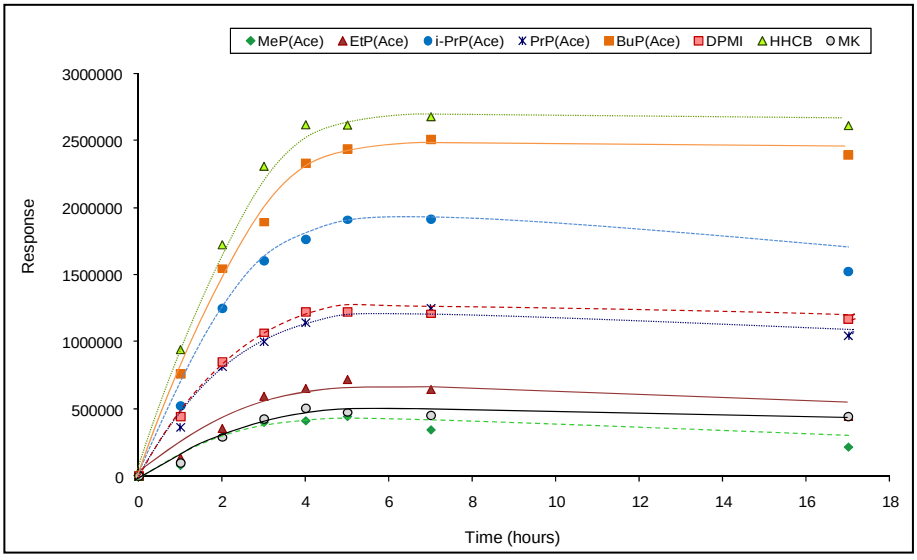


Figure 2. Influence of extraction time in the analytes responses for the acetylated parabens and the three representative musks (DPMI, HHCB and MK).

3.1.3. Stir bar thermal desorption

Regarding the stir bar thermal desorption optimisation, it should be taken into account that the target PCPs are semi-volatile compounds with relatively high boiling points (between 265 and up to ca. 400 °C). A previous study demonstrated that the maximum recommended temperature (300 °C) and flow rate (100 mL min^{-1}) applied for 15 min were necessary to desorb the synthetic musks from the PDMS phase [25]. These conditions were therefore applied in this study to obtain quantitative recoveries of all analytes. A suitable cryogenic trap should be chosen to focus the analytes after their stir bar desorption. A recent study focused on determining 14 PCPs in air [30] showed that Tenax TA is a good trap sorbent which can either retain the compounds or allow their whole desorption. During the desorption process, the Tenax TA cryogenic trap was set at 0 °C for the focusing of the analytes and then desorbed at 320 °C for 10 min, with a helium split flow of 5 mL min^{-1}. Under these desorption conditions, all analytes showed a carry-over of less than 1% at the highest calibration level. The final acetylation, SBSE and TD conditions for the target PCPs are summarised in Table 2.

Table 2. Optimised conditions for the in situ acetylation and SBSE-TD.

Stir bar extraction	
Sample volume	100 mL
Stirring speed	900 rpm
Temperature	room temp.
Time	4 hours
Acetic anhydride	100 µL
Na_2HPO_4	0.5 g
Stir bar thermal desorption	
Temperature	300 °C
Time	15 min
Flow	100 mL min^{-1}
Trap temperature	0 °C
Split	splitless

In order to check the influence of the acetylation in the SBSE process, the signal obtained from the acetylated parabens was compared with the signals of the SBSE of non-acetylated samples. The increase in the chromatographic signal ranged between ca. 2,000-fold higher for the acetylated methyl paraben to 300,000-fold higher for the acetylated butyl paraben compared to the signal for the non-acetylated parabens. Furthermore, the

responses of the synthetic musks and the HHCB-lactone were similar or slightly higher than those obtained under the same conditions without adding the anhydride acetic and the Na_2HPO_4 [25].

3.1.4. Control of blanks

The extensive use of PCPs in a wide range of consumer products means a high risk of background contamination. Despite the SBSE procedure reducing this risk, special precautions were taken throughout the analytical procedure, such as overnight cleaning of the glassware with chromic mixture. Despite these precautions, HHCB signals corresponding to 0.010±0.007 ng (n= 5) were found in blanks of 100 mL of ultrapure water. Moreover, synthetic musks are semi-volatile compounds that can cause memory effects in the TD equipment and transfer lines [30]. To avoid this, the higher calibration level for these compounds was fixed at 20 ng per sample and the influent and effluent WWTP samples were diluted to a factor of 1 to 20 before the extraction. In the case of the acetylated parabens, no memory effects were observed until 150 ng of each paraben per sample.

3.2. Method validation

The linear range of the optimised *in situ* acetylation SBSE-TD-GC-MS method was tested by spiking different amounts of the standards in 100 mL of ultrapure water and in each kind of sample, prepared as described in section 2.3. Linearity was good for all target PCPs in the interval studied (ranging between the limit of quantification of each compound (see Table 3) and 200 ng L^{-1} for the musks and 1500 ng L^{-1} for the acetylated parabens) with coefficient of determination (r^2) values higher than 0.999 for synthetic musks and 0.996 for parabens. Recoveries of the target PCPs were calculated by comparing the peak areas obtained with water spiked at two calibration levels (1 and 100 ng L^{-1}) with the calibration curve obtained by spiking the standards of the musks, the galaxolidone and the acetylated parabens in a tube filled with thermally cleaned deactivated glass wool. As shown in Table 3, the recoveries in ultrapure water were similar for both levels and were higher than 80% for all the target PCPs, except for the acetylated methyl paraben with values ca. 50%. Recoveries in the spiked real waters were similar to those obtained in ultrapure water (i.e. from 49% to 103% in urban WWTP influent diluted in a factor of 1 to 20, and from 50% to 99% in river waters).

Repeatability was checked by analysing five replicates of water spiked with the target PCPs on the same day, at a low and a midpoint calibration level (1 ng L^{-1} and 100 ng L^{-1}). The values in ultrapure water ranged from 4 % RSD for MM to 13 % for the acetylated MeP at the low level, and from 2 % for MK and HHCB-lactone to 10 % for the

Table 3. Method parameters of spiked ultrapure water: experimental recovery (%, n=3), repeatability and reproducibility between days (%RSD, n=5), and method detection limit (MDL) and quantification limit (MQL), expressed in ng L^{-1}.

PCP	Recovery (%, n=3))		Repeatability (%RSD, n=5)		Reproducibility (%RSD, n=5)		MDL (ng L^{-1})	MQL (ng L^{-1})
	1 ng L^{-1}	100 ng L^{-1}	1 ng L^{-1}	100 ng L^{-1}	1 ng L^{-1}	100 ng L^{-1}		
DPMI	85	82	10	4	15	6	0.1	0.3
MeP [a]	47	50	13	10	14	12	0.3	1
EtP [a]	83	82	8	8	9	8	0.17	0.5
i-PrP [a]	86	86	6	6	6	6	0.03	0.1
ADBI	93	91	10	4	12	7	0.08	0.24
PrP [a]	95	91	8	7	8	8	0.2	0.5
AHMI	95	92	7	4	6	6	0.02	0.1
BuP [a]	102	100	3	3	3	3	0.03	0.1
ATII	92	89	10	4	12	5	0.1	0.3
HHCB	92	87	10	8	12	7	0.2	0.5
AHTN	91	88	8	4	8	5	0.03	0.1
MX	85	95	10	3	10	3	0.03	0.1
MM	88	89	4	3	4	4	0.03	0.1
MK	99	100	6	2	6	2	0.03	0.1
HHCB-lactone	95	94	6	2	6	2	0.03	0.08

[a] Method parameters of the acetylated derivative.

acetylated MeP at the midpoint level (see Table 3). Likewise, reproducibility was checked by analysing five replicates in different days. The values for reproducibility between days ranged between 4 % for MM and 15% for DPMI and from 2% for HHCB-lactone to 12% for the acetylated MeP, at the low and midpoint levels respectively.

Repeatability and reproducibility between days in the spiked real waters were similar to those found in ultrapure water and ranged from 5% to 16% (results not shown). In order to evaluate a possible matrix effect, the various real samples were also spiked at two different concentration levels (1 ng L^{-1} and 100 ng L^{-1}). For both levels, the calculated concentrations of the target PCPs were in acceptable agreement with those obtained with ultrapure water, taking into account the repeatability of the method used. Quantification of the samples was therefore performed by external calibration using the calibration curves obtained by spiking the standards in ultrapure water.

The limits of detection (MDL) were calculated as the concentration corresponding to three times the noise

signal of the target ion of each compound, except for HHCB which was present in the blanks of the ultrapure water. For HHCB, the MDL was determined as the average of the blank signal of the target ion plus three times the standard deviation of the signal (n=5). The MDLs ranged from 0.02 ng L^{-1} for AHMI to 0.3 ng L^{-1} for HHCB. The limit of quantification (MQL), which was fixed as the lowest calibration level of each compound, ranged from 0.08 ng L^{-1} for the HHCB-lactone to 0.5 ng L^{-1} for HHCB. These values were also valid for the real waters. Interestingly, the MDLs for the acetylated parabens ranged from 0.03 ng L^{-1} to 0.2 ng L^{-1} and the MQLs from 0.1 ng L^{-1} to 1 ng L^{-1}.

These values are much lower than those found in a previous SBSE study without derivatization (MDLs from 0.015 to 0.02 µg mL^{-1}, [26]) and even lower than those published with derivatization (MDLs from 0.64 ng L^{-1} to 1.86 ng L^{-1} [27]).

3.3. Analysis of water samples

The SBSE-TD-GC-MS method with the derivatization of parabens was used to determine the presence of the 14 PCPs and the HHCB-lactone in the different kinds of aqueous matrices (influent and effluent of urban WWTP, influent and effluent of industrial WWTP, effluent of a RO treatment plant and river water). In order to obtain more representtative values, three different samples of each matrix were selected for the study and were analysed in triplicate. Fig. 3 shows the SIM chromatogram of an urban WWTP effluent (diluted in a factor of 1 to 20, Fig. 3A) and for river water (Fig. 3B) indicating the target PCPs found in these samples.

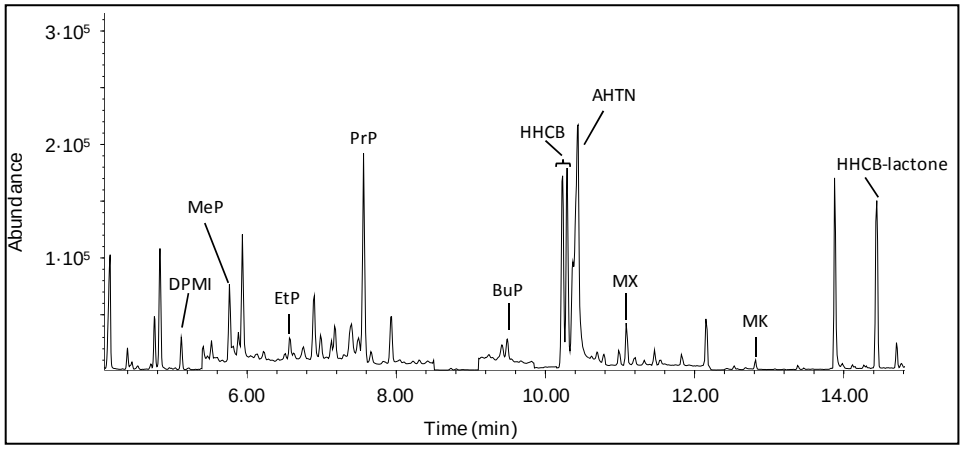


Figure 3A. Chromatogram of the effluent of an urban WWTP diluted to a factor of 1 to 20. The peaks of the found acetylated parabens, synthetic musks and HHCB-lactone are indicated.

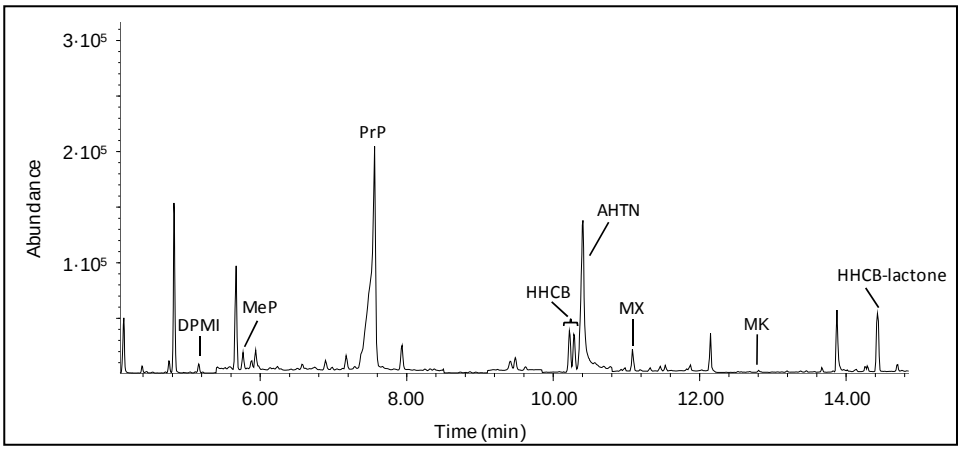


Figure 3B. Chromatogram of one river water. The peaks of the found acetylated parabens, synthetic musks and HHCB-lactone are indicated.

Table 4 summarises the concentrations of the target PCPs detected in each kind of water. As expected, the influents of the WWTPs showed the highest values. For the industrial WWTPs the highest concentrations were found in the disposal of toxic waste, followed by the additive, emulsion and detergent industry (individual results not shown). Because of its activity, the oil recycling industry presented low values. The effluents from the RO plant located after the secondary treatment of one of the urban WWTP showed the lowest PCP higher in industrial WWTPs (up to 1232 ng L^{-1} in the influents and 137 ng L^{-1} in the effluents).The values of AHTN and MX were also considerable (up to 264 ng L^{-1} and 84 ng L^{-1} in urban WWTPs effluents, respectively). MM was not detected in any sample, which was consistent with the prohibition of their use in cosmetics in European countries [35]. The musk values concentrations. These low concentrations indicate that RO plants can efficiently remove semi-volatile apolar compounds from aqueous matrices. As for river waters, the Ebro river generally showed the lowest PCP values, followed by the Ter and Llobregat rivers.

As regards the individual concentrations of PCPs, HHCB was the most abundant polycyclic musk in urban WWTPs and river waters, with values up to 2219 ng L^{-1} and 954 ng L^{-1} in the influent and the effluent of urban WWTPs, respectively, while DPMI was obtained in this study were similar to those found in previous studies [21, 36].

The degradation product HHCB-lactone was detected in all the samples, except in the effluents of the RO WWTP, in concentrations ranging between 10 ng L^{-1} in river water and 690 ng L^{-1} in influent of urban WWTP. It has been reported that HHCB-lactone can be

Table 4. Concentrations of the target PCPs found in the water samples, expressed in ng L^{-1}.

Compound	Urban WWTP			Industrial WWTP		River
	Influent	Effluent	Effluent RO	Influent	Effluent	
DPMI	n.d.-112	n.d.-82	n.d.-0.3	n.d.-1232	n.d.-137	n.d.-3.0
MeP	n.d.-696	n.d.-5.9	n.d.	n.d.-14243	n.d.-328	n.d.-42
EtP	n.d.-48	n.d.	n.d.	n.d.-5927	n.d.-5.9	n.d.-1.1
i-PrP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ADBI	n.d.-32	n.d.-25	n.d.-1.3	1.79-26	n.d.-12	n.d.
PrP	n.d.-5.3	n.d.	n.d.	n.d.-23593	n.d.-15	n.d.-2.5
AHMI	n.d.-31	n.d.-11	n.d.-1.0	n.d.-13	n.d.	n.d.
BuP	20.1-52	n.d.-56	n.d.	n.d.-681	n.d.-42	n.d.
ATII	n.d.-27	n.d.	n.d.	n.d.-10	n.d.	n.d.
HHCB	360-2219	288-954	<MQL-1.0	n.d.-57	n.d.-64	3.1-16
AHTN	19-264	25-28	0.2-0.3	14-21	5.7-20	0.9-2.0
MX	45-232	40-96	0.3-1.1	n.d.-20	n.d.	0.6-0.9
MM	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MK	n.d.-84	n.d.-20	n.d.	n.d.-19	n.d.	3.6-7.2
HHCB-lactone	142-690	120-532	n.d.	n.d.-153	n.d.-143	10-36

n.d., values under the method detection limit of each kind of sample.
<MQL, values under the method quantification limit of each kind of sample.

produced in waste water biological treatments [3, 17, 37]. However, in this study there was no clear evidence of this, because the HHCB-lactone/HHCB ratios calculated were similar in influents and effluents of urban WWTPs, but higher in effluents than in influents of industrial WWTPs. Furthermore, in the river samples the concentrations of HHCB-lactone were from 2 to 3.5-fold higher than the corresponding HHCB values. These results are consistent with those found in a previous study, which determined the transformations of HHCB in HHCB-lactone in the Ruhr river in Germany [17].

Finally, the presence of parabens was especially important in the influent of the disposal of toxic waste industry. In general, the most abundant parabens were PrP and MeP with values of up to 23593 ng L^{-1} and 14243 ng L^{-1} in influents and effluents of the industry mentioned above, respectively. The large quantities of these parabens in the water samples can be explained by the synergic preservative effect obtained when the two compounds are used together [1]. The removal rates of parabens found in this study were higher than 90 % in both the urban and industrial WWTPs, which is consistent with those found in previous studies [13, 14, 19].

4. CONCLUSIONS

An SBSE method followed by TD-GC-MS has been successfully developed for the simultaneous determination of 14 PCPs - 6 polycyclic musks, 3 nitromusks

and 5 parabens - and 1 polycyclic musk degradation product in water samples. The acetylation of the parabens prior to SBSE increased the affinity of these polar compounds for the PDMS phase without decreasing the recoveries of the other target PCPs. To our knowledge, this method provides the lowest limits of detection for the determination of parabens in water matrices. Furthermore, the minimal manipulation of the sample required minimises the risk of background contamination, which is one of the main drawbacks when determining PCPs.

The proposed method was successfully applied for the analysis of WWTP waters and river waters. The most abundant polycyclic musk was HHCB and the most abundant parabens were methyl and propyl paraben. The presence of the degradation product HHCB-lactone was also important, especially in urban WWTPs.

This study has therefore demonstrated the applicability of SBSE for the simultaneous determination of water contaminants in a wide range of polarities.

Acknowledgments

The authors wish to acknowledge the financial support provided to this study by the Spanish Ministry of Science and Innovation through the project CTM-2008-06847-C02-01 and the Department of Innovation, Universities and Enterprises of the Generalitat de Catalunya through project 2009 SGR 223.

REFERENCES

[1] A.M. Peck, Anal. Bioanal. Chem., 386 (2006) 907.

[2] V. Matamoros, E. Jover, J.M. Bayona, Anal. Bioanal. Chem., 393 (2009) 847.

[3] K. Bester, J. Chromatogr. A, 1216 (2009) 470.

[4] P.D. Darbre, P.W. Harvey, Journal of Applied Toxicology, 28 (2008) 561.

[5] P.D. Darbre, A. Aljarrah, W.R. Miller, N.G. Coldham, M.J. Sauer, G.S. Pope, Journal of Applied Toxicology, 24 (2004) 5.

[6] H. Brunn, N. Bitsch, J. Amberg-Muller, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part X, vol.3, Springer-Verlag, Berlin, 2004, p. 259.

[7] T. Luckenbach, D. Epel, Environ. Health Perspect., 113 (2005) A803.

[8] H.P. Hutter, P. Wallner, H. Moshammer, W. Hartl, R. Sattelberger, G. Lorbeer, M. Kundi, Sci. Total Environ., 407 (2009) 4821.

[9] E.J. Routledge, J. Parker, J. Odum, J. Ashby, J.P. Sumpter, Toxicology and Applied Pharmacology, 153 (1998) 12.

[10] N. Bitsch, C. Dudas, W. Korner, K. Failing, S. Biselli, G. Rimkus, H. Brunn, Arch. Environ. Contam. Toxicol., 43 (2002) 257.

[11] C. García-Jares, J. Regueiro, R. Barro, T. Dagnac, M. Llompart, J. Chromatogr. A, 1216 (2009) 567.
[12] S.D. Richardson, Anal. Chem., 79 (2007) 4295.
[13] I. González-Mariño, J.B. Quintana, I. Rodríguez, R. Cela, Rapid Commun. Mass Spectrom., 23 (2009) 1756.
[14] H.B. Lee, T.E. Peart, M.L. Svoboda, J. Chromatogr. A, 1094 (2005) 122.
[15] J. Regueiro, M. Llompart, E. Psillakis, J.C. García-Monteagudo, C. García-Jares, Talanta, 79 (2009) 1387.
[16] S.L. Simonich, in: G. Rimkus (Ed.), The Handbook of Environmental Chemistry, Part O, vol.5, Springer-Verlag, Berlin, 2005, p. 79.
[17] K. Bester, J. Environ. Monit., 7 (2005) 43.
[18] R. Kallenborn, R. Gatermann, T. Nygard, J. Knutzen, M. Schlabach, Fresenius Environmental Bulletin, 10 (2001) 832.
[19] M. Pedrouzo, F. Borrull, R.M. Marcé, E. Pocurull, J. Chromatogr. A, 1216 (2009) 6994.
[20] T. Heberer, S. Gramer, H.J. Stan, Acta Hydrochimica Et Hydrobiologica, 27 (1999) 150.
[21] J. Regueiro, M. Llompart, C. García-Jares, J.C. García-Monteagudo, R. Cela, J. Chromatogr. A, 1190 (2008) 27.
[22] C. García-Jares, M. Llompart, M. Polo, C. Salgado, S. Macías, R. Cela, J. Chromatogr. A, 963 (2002) 277.
[23] J. Regueiro, E. Becerril, C. García-Jares, M. Llompart, J. Chromatogr. A, 1216 (2009) 4693.
[24] P. Canosa, I. Rodríguez, E. Rubí, M.H. Bollaín, R. Cela, J. Chromatogr. A, 1124 (2006) 3.
[25] N. Ramírez, R.M. Marcé, F. Borrull, J. Chromatogr. A, 1218 (2011) 156.
[26] N. Ochiai, K. Sasamoto, M. Takino, S. Yamashita, S. Daishima, A.C. Heiden, A. Hoffmann, Anal. Bioanal. Chem., 373 (2002) 56.
[27] A. Casas Ferreira, M. Möder, M. Fernández Laespada, Anal. Bioanal. Chem., 399 (2011) 945.
[28] A. Prieto, O. Basauri, R. Rodil, A. Usobiaga, L.A. Fernández, N. Etxebarria, O. Zuloaga, J. Chromatogr. A, 1217 (2010) 2642.
[29] N. Ramírez, R.M. Marcé, F. Borrull, J. Chromatogr. A (2011) DOI: 10.1016/j.chrima.2011.05.098.
[30] N. Ramírez, R.M. Marcé, F. Borrull, J. Chromatogr. A, 1217 (2010) 4430.
[31] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcolumn Sep., 11 (1999) 737.
[32] F. David, P. Sandra, J. Chromatogr. A, 1152 (2007) 54.
[33] N. Itoh, H. Tao, T. Ibusuki, Anal. Chim. Acta, 535 (2005) 243.
[34] M. Llompart, M. Lourido, P. Landín, C. García-Jares, R. Cela, J. Chromatogr. A, 963 (2002) 137.
[35] Council Directive 98/62/EEC. Off. J. European Commun. L253 (1998) 20.

[36] D.H. Chen, X.Y. Zeng, Y.Q. Sheng, X.H. Bi, H.Y. Gui, G.Y. Sheng, J.M. Fu, Chemosphere, 66 (2007) 252.

[37] Y. Horii, J.L. Reiner, B.G. Loganathan, K.S. Kumar, K. Sajwan, K. Kannan, Chemosphere, 68 (2007) 2011.

[38] X.J. Chen, U. Pauly, S. Rehfus, K. Bester, Chemosphere, 76 (2009) 1094.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

The results presented in this section demonstrate that SBSE followed by TD-GC-MS determination is a reliable alternative to more conventional analytical methods for determining PCPs of different polarities in water samples.

As previously discussed, because of the ubiquitous presence of PCPs in the environment, one of the main challenges of their determination is avoiding the risk of background contamination. The developed SBSE-TD-GC-MS methods minimise the risk of external contamination because stir bars are thermally desorbed directly after the SBSE process. Nevertheless, further precautions were taken as seen in the studies, such as the overnight cleaning of the glassware using a chromic mixture and the subsequent accurate rinse off with ultrapure water and isopropanol of HPLC grade. Despite these precautions, galaxolide signals were found in the blanks (0.010±0.007 ng) and were taken into account when calculating the LODs. Moreover, since Markes^{TM} TD equipment was used in both methods for the stir bar desorption, memory effects could be observed in the equipment interfaces during the TD of semi-volatile compounds (see section 3.3.2, and Figure 1.18 in the introduction). For both methods developed here, the maximum calibration levels were fixed to 20 ng for synthetic musks and galaxolidone and 150 ng for parabens to avoid memory effects. Furthermore, because of the high concentrations of PCPs expected in WWTP influent and effluents, these samples were diluted to a factor of 1 to 20 prior to SBSE. The dilution of these concentrated samples also avoided possible matrix effects found in similar methods [1]. The samples from rivers and from the effluent of the reverse osmosis plant presented low concentrations of the target PCPs and, therefore, were directly extracted without dilution.

In order to enhance sensitivity in both studies, the sample volume was fixed to 100 mL and the stir bar size to 20 mm length × 0.5 mm film thickness with approximately 48 µL of PDMS phase. These conditions theoretically provide recoveries for the synthetic musks and the galaxolidone higher than 90%. The stirring rate was also fixed at a medium level (900 rpm) so that stir bar lifetimes were not reduced. In addition, other SBSE parameters were optimised. In the study that focus on the determination of synthetic musks, generally, best SBSE efficiencies for the target musks were obtained from 4 hours of extraction time at neutral pH and room temperature, without the addition of a salt or organic modifier. For the TD conditions of the stir bar desorption, the maximum recommended desorption temperature (300 °C) and the maximum helium flow (100 mL min^{-1}) applied for 15 minutes were necessary to obtain the quantitative recovery of the analytes. The kind of sorbent for the cryogenic trap and the trap desorption conditions were optimised for the determination of PCPs in air, as mentioned in section 3.3, and were applied for the target compounds of these studies. The chromatographic conditions were also previously optimised, as seen in section 3.3.

The method developed showed recoveries higher than 82%, RSD lower than 15% and LODs ranging from 0.02 to 0.3 ng L^{-1}. These are lower than those obtained by SBSE followed by LD [2] and among the lowest LODs found in the recent literature for these musks [3-5].

For the simultaneous determination of the parabens and synthetic musks, not only were the optimal acetylation conditions of parabens studied, but also their influence on the extraction of the non-derivatized PCPs (synthetic musks and galaxolidone). The results of this study showed that under the optimised conditions (acetylation with 100 µL of acetic anhydride and 5 g L^{-1} of Na_2HPO_4 and 4 h of SBSE extraction), the chromatographic signals of the parabens were 2000 to 300,000 times higher than the signals from the non-acetylated ones. Furthermore, no decreases in the affinity of the synthetic musks were observed under the acetylation conditions. Recoveries were higher than 82% for the parabens, except for the methyl parabens, whose recovery was ca. 50%. This enhancement in the SBSE recoveries provides LODs lower than 0.3 ng L^{-1} for the target parabens. As mentioned in the paper, these are - to our knowledge - the lowest LODs for parabens with SBSE methods found in the literature [1,6]. This study also demonstrated that the recoveries of synthetic musks were not significantly affected by the presence of the derivatizing agents, so SBSE can be used for the simultaneous determination of organic contaminants with a wide range of polarities.

In a similar way to the air samples mentioned before, the most abundant synthetic musk in the samples was galaxolide, which was to be expected because of its high use in household products. They were also considerable amounts of tonalide and musk xylene in urban WWTPs, and of cashmeran in industrial WWTPs. Accordingly with the results found in air matrices (see section 3.3), musk moskene was not detected in any of the water samples. This concurs with the prohibition of its use in cosmetics in Europe [7]. The degradation product galaxolidone was found in most of the water samples. Although galaxolidone is reported to be produced during conventional waste water treatments, there was no clear evidence of this in our study and further investigation is needed. The highest levels of parabens found in industrial WWTPs were n-propyl and methyl paraben. These higher values concur with the synergistic antimicrobial effect when both parabens are used together. Regarding the efficiencies of the urban and industrial WWTPs in our study, removal efficiencies of the polar parabens are higher than those observed for the apolar musks, which concurs with previous reported literature [8,9]. However, the low levels of PCPs obtained after the RO treatment could indicate the high removal efficiency of these waste water treatments. Finally, the target PCPs were also found in the river waters with values up to 16 ng L^{-1} for galaxolide and 36 ng L^{-1} for galaxolidone. The concentrations of this degradation product of ca. 20 ng L^{-1} in river waters have previously been reported [10]. The presence of the target PCPs in

the river waters emphasises the need for further investigation into waste water treatments and their ability to efficiently remove these compounds and so reduce the main pathway of PCPs into the environment.

References

[1] A. Casas Ferreira, M. Möder, M. Fernández Laespada, Anal. Bioanal. Chem. 399 (2011) 945.

[2] A.R.M. Silva, J.M.F. Nogueira, Anal. Bioanal. Chem. 396 (2010) 1853.

[3] J. Regueiro, M. Llompart, C. García-Jares, J.C. García-Monteagudo, R. Cela, J. Chromatogr. A 1190 (2008) 27.

[4] Y. Lv, T. Yuan, J.Y. Hu, W.H. Wang, Anal. Sci. 25 (2009) 1125.

[5] M.J. Gómez, S. Herrera, D. Solé, E. García-Calvo, A.R. Fernández-Alba, Anal. Chem. 83 (2011) 2638.

[6] N. Ochiai, K. Sasamoto, M. Takino, S. Yamashita, S. Daishima, A.C. Heiden, A. Hoffmann, Anal. Bioanal. Chem. 373 (2002) 56.

[7] Council directive 98/62/EEC, Off. J. Eur. Commun. L253 (1998) 20.

[8] K. Bester, Chemosphere 57 (2004) 863.

[9] I. González-Mariño, J.B. Quintana, I. Rodríguez, R. Cela, Rapid Commun. Mass Spectrom. 23 (2009) 1756.

[10] K. Bester, J. Environ. Monit. 7 (2005) 43.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

3.5. Emerging organic contaminants in house dust

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

In the previous sections, the ubiquitous presence of VOCs, PAHs and EOCs, such as PCPs, in outdoor and indoor air, particulate matter and water samples has been demonstrated. As mentioned in the introduction, the atmosphere is considered the main long-range transport medium for some contaminants and settled indoor dust acts as a sink and repository of semi-volatile contaminants. Therefore, the determination of organic contaminants bound to indoor dust is an issue of growing interest because of human health concerns. Numerous persistent organic pollutants have already been found in indoor dust, such as PAH [1] brominated diphenyl ethers [2], phthalates [3], perfluorinated sulphonamides [4] and dioxins [5], among others. Therefore, the determination of the contaminants in settled indoor dust is considered an indication of indoor pollution and is currently an important source of information when drawing up human exposure assessments [6,7]. This exposure to indoor dust is especially relevant for children because their daily ingestion of dust is estimated to be 100 mg [8].

Because of the relevance of the characterisation of the organic contaminants present in indoor dust, several studies have focused on the development of analytical methods for determining contaminants in dust. Because of the complexity of house dust, which is an heterogeneous matrix composed of a wide range of inorganic and organic materials, exhaustive sample preparation techniques are required for the sensitive and selective determination of the target organic contaminants. Most of the methods found in the literature are based on microwave assisted extraction (MAE) [9] and pressurised liquid extraction (PLE) [10]. PLE is rapid and efficient and reduces the consumption of organic solvents in comparison with more classic extraction methods. Moreover PLE has some advantages over MAE extraction, such as the fact that the extracts are already filtered after the PLE process. Therefore, the two methods presented in this section are based on PLE. After PLE, a clean-up step is usually needed prior to GC-MS analysis in order to eliminate co-extraction chemicals that can interfere in the analysis. The addition of a clean-up step is time-consuming and increases the risk of background contamination and losses of the target analytes. To overcome this, the two PLE methods presented here develop different strategies to enhance the selectivity of house dust extraction.

The studies presented in this section focus on the determination of different organic contaminants in settled dust. Following the research line started in our previous studies, the first article of this section is focused on the determination of parabens, which are considered endocrine-disrupting chemicals (EDCs) because of their known endocrine activity [11]. As mentioned in the introduction, parabens are preservatives used in a wide range of consumer products, such as pharmaceuticals, cosmetics and food, and previous studies have demonstrated their presence in indoor dust [12-14].

Although most PLE methods use organic solvents, some applications using water as a solvent can be found in recent literature [15]. Pressurised water extraction (PHWE) is an environmentally-friendly method that avoids the use of organic solvents. Since polarity of water decreases at high temperature and pressure, PHWE can efficiently extract organic contaminants in a wide range of polarities from solid samples [16,17]. PHWE has been applied for the extraction of a wide range of organic contaminants, such as amines or PAHs among others [15], from solid matrices, such as sludge and soils. However, to our knowledge, the study presented here is the first application of PHWE for the extraction of parabens and the first time it has been applied to indoor dust samples. After PHWE, the analytes should be extracted from the water. Because of the success obtained in the determination of parabens from aqueous samples by derivatization and SBSE, we were encouraged to apply SBSE after PHWE. Therefore, this study is focused on the development of a PHWE method for determining parabens in house dust followed by the in situ derivatization and SBSE and the direct TD-GC-MS analysis. The influence on the extraction efficiency of the main parameters (extraction time, temperature, number of cycles) has been studied using design of experiment strategies.

In the second study presented here, we have focused on the determination of organic nitrogen contaminants related to tobacco smoke, which is one of the most important sources of indoor pollution. As mentioned in the introduction, nicotine is the most abundant organic compound emitted from tobacco. Nicotine can be oxidised and form tobacco-specific nitrosamines (TSNAs) which are considered to be one of the most carcinogenic chemicals formed during the burning of tobacco [18]. Furthermore, the formation of some volatile genotoxic and carcinogenic N-nitrosamines has also been related to second hand smoke [19,20]. Although these compounds have been determined in tobacco smoke [21], as far as we know, the study presented here represents the first time that they have been determined in house dust.

In this study, a different clean-up strategy based on in-cell clean-up PLE was developed for the selective determination of 9 volatile N-nitrosamines, nicotine and 5 TSNAs in smoking and non-smoking house dust. To that end, the performance of 4 different active sorbents (alumina, C_{18}, Florisil and silica) and 4 different organic solvents (acetone, dichloromethane, ethyl acetate and methanol) was tested. Once these parameters were fixed, the PLE conditions were optimised using a multifactorial design of experiments. The PLE optimisation was performed using a GC-MS system. For the determination and quantification of the analytes in the samples, comprehensive GC (GC×GC) followed by nitrogen chemiluminiscence detection (NCD) was used. GC×GC allows higher peak resolution and separation power than one dimensional GC and the NCD detector, specific for organic nitrogen compounds, has demonstrated high

sensitivity for N-nitrosamines [22]. Therefore, these both techniques are very suitable for the determination of organic nitrogen contaminants from complex samples, such as indoor dust.

In both studies, the optimised methods were applied for the determination of the target compounds in different house dust samples. A paper with the results obtained from the first study has been accepted for publication in *Journal of Chromatography A*. A paper with the results of the second study have been submitted for publication to *Environmental Science & Technology*. The second study was developed in collaboration with the Analytical, Environmental and Atmospheric Chemistry Group of the Department of Chemistry of the University of York.

References

[1] R.M. Maertens, X.F. Yang, J.P. Zhu, R.W. Gagne, G.R. Douglas, P.A. White, Environ. Sci. Technol. 42 (2008) 1747.
[2] B.H. Wilford, M. Shoeib, T. Harner, J.P. Zhu, K.C. Jones, Environ. Sci. Technol. 39 (2005) 7027.
[3] S. Langer, C.J. Weschler, A. Fischer, G. Beko, J. Toftum, G. Clausen, Atmos. Environ. 44 (2010) 2294.
[4] M. Shoeib, T. Harner, B.H. Wilford, K.C. Jones, J.P. Zhu, Environ. Sci. Technol. 39 (2005) 6599.
[5] Y. Kang, K.C. Cheung, Z.W. Cai, M.H. Wong, Ecotox. Environ. Safe. 74 (2011) 947.
[6] R.M. Maertens, J. Bailey, P.A. White, Mutat. Res.-Rev. Mutat. Res. 567 (2004) 401.
[7] W. Butte, B. Heinzow, Rev. Environ. Contam. T. 175 (2002) 1.
[8] W.R. Ott, A.C. Steinemann, L.A. Wallace, Exposure Analysis, Taylor & Francis, Boca Raton, 2007.
[9] J. Regueiro, M. Llompart, C. García-Jares, R. Cela, J. Chromatogr. A 1174 (2007) 112.
[10] I. Carpinteiro, B. Abuín, I. Rodríguez, M. Ramil, R. Cela, J. Chromatogr. A 1217 (2010) 3729.
[11] P.D. Darbre, P.W. Harvey, J. Appl. Toxicol. 28 (2008) 561.
[12] R.A. Rudel, D.E. Camann, J.D. Spengler, L.R. Korn, J.G. Brody, Environ. Sci. Technol. 37 (2003) 4543.
[13] R.A. Rudel, R.E. Dodson, L.J. Perovich, R. Morello-Frosch, D.E. Camann, M.M. Zuniga, A.Y. Yau, A.C. Just, J.G. Brody, Environ. Sci. Technol. 44 (2010) 6583.
[14] P. Canosa, D. Pérez-Palacios, A. Garrido-López, M.T. Tena, I. Rodríguez, E. Rubí, R. Cela, J. Chromatogr. A 1161 (2007) 105.
[15] C.C. Teo, S.N. Tan, J.W.H. Yong, C.S. Hew, E.S. Ong, J. Chromatogr. A 1217 (2010) 2484.
[16] M. García-López, I. Rodríguez, R. Cela, J. Chromatogr. A 1216 (2009) 6986.
[17] A. Llop, F. Borrull, E. Pocurull, Anal. Chim. Acta 665 (2010) 231.

[18] S.S. Hecht, D. Hoffmann, Carcinogenesis 9 (1988) 875.
[19] K.R.R. Mahanama, J.M. Daisey, Environ. Sci. Technol. 30 (1996) 1477.
[20] H. Klus, H. Begutter, G. Scherer, A.R. Tricker, F. Adlkofer, Indoor Built. Environ. 1 (1992) 348.
[21] M. Sleiman, R.L. Maddalena, L.A. Gundel, H. Destaillats, 1216 (2009) 7899.
[22] M.Z. Özel, J.F. Hamilton, A.C. Lewis, Environ. Sci. Technol. 45 (2011) 1497.

3.5.1. Determination of parabens in house dust by pressurised hot water extraction followed by stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

DETERMINATION OF PARABENS IN HOUSE DUST BY PRESSURISED HOT WATER EXTRACTION FOLLOWED BY STIR BAR SORPTIVE EXTRACTION AND THERMAL DESORPTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Noelia Ramírez, Rosa Maria Marcé, Francesc Borrull
Department of Analytical Chemistry and Organic Chemistry
Universitat Rovira i Virgili, Marcel·lí Domingo s/n
Sescelades Campus, Tarragona 43007, Spain

Abstract

This study describes the development of a new method for determining p-hydroxybenzoic esters (parabens) in house dust. This optimised method was based on the pressurised hot water extraction (PHWE) of house dust, followed by the acetylation of the extracted parabens, stir bar sorptive extraction (SBSE) with a polydimethylsiloxane stir bar, and finally analysis using thermal desorption – gas chromatography – mass spectrometry (TD-GC-MS). The combination of SBSE after PHWE allows the analytes to be preconcentrated and extracted from the aqueous extract in a single step with minimal manipulation of the sample. Furthermore the in situ acetylation of parabens prior to SBSE improved their extraction efficiency and their GC-MS signal. The method showed recoveries of between 40 and 80%, good linearity, repeatability and reproducibility (< 10% RSD, at 100 ng g^{-1}, n=5), low limits of detection (from 1.0 ng g^{-1} for propyl paraben to 2.1 ng g^{-1} for methyl paraben) and quantification (from 3.3 ng g^{-1} for propyl paraben to 8.5 ng g^{-1} for methyl paraben).
The proposed method was applied to the analysis of house dust samples. All the target parabens were found in the samples. Methyl and propyl parabens were the most abundant, with concentrations up to 2440 ng g^{-1} and 910 ng g^{-1}, respectively. The high levels of parabens found in the samples confirm the importance of determining organic contaminants in indoor environments

Keywords**:** Pressurised hot water extraction (PHWE); Stir bar sorptive extraction (SBSE); Thermal desorption (TD); Gas chromatography-mass spectrometry (GC-MS); p-hydroxybenzoic esters (parabens); House dust

1. INTRODUCTION

Numerous studies have demonstrated that indoor air (both gas and particle phases) contains a wide spectrum of organic pollutants in high concentrations [1,2]. Furthermore, contaminants bound to indoor dust are more persistent than those bound to outdoor airborne particles because they are better protected from biotic and abiotic degradation and accumulate over time. Consequently, contaminants bound to indoor dust

have a higher exposure potential [3] and this exposure is of particular importance regarding younger children, because of the ways they behave and because they tend to spend longer times in indoor environments. Indeed the main exposure route to toxic pollutants for children is the ingestion of dust: the average infant's daily ingestion of dust is estimated to be 100 mg per day, more than twice that of adults [1].

House dust is a heterogeneous complex matrix, composed of inorganic and organic materials such as skin tissues, hair fibres, mites and particulate matter emanating from carpets and furniture. Several studies have demonstrated the occurrence of a large number of toxic pollutants in house dust including metals such as lead, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates, and other persistent pollutants [4-7]. Recently, some studies have also detected the presence of personal care products (PCPs) in house dust, such as p-hydroxybenzoic esters (parabens) [8-10] and synthetic musk fragrances [11, 12]. Parabens are the most common preservatives and antimicrobial agents used in personal care, pharmaceutical and food products. These compounds are considered endocrine disrupting chemicals (EDCs), because of their endocrine activity [13,14], and have been detected in human tissues, including breast tumours [15,16]. However, there is little information about their absorption into the human body through the skin or the respiratory system. Therefore, developing reliable methods for determining parabens in house dust should be a major concern.

Because of the complexity of house dust, the selective determination of a specific group of organic pollutants usually involves a multi-step process that generally consists of an extraction procedure followed by clean-up and preconcentration steps prior to the GC analysis. Most of the extraction methods used for house dust employ organic solvents to extract the analytes either by Soxhlet extraction [8,17,18], ultrasound-assisted extraction [19, 20], pressurised liquid extraction (PLE) [9, 11,21,22] or microwave assisted solvent extraction (MASE) [12,23]. Pressurised hot water extraction (PHWE), which is an environmentally friendly method that reduces the usage of organic solvents, might be a good alternative to more conventional extraction methods. Since the polarity of water decreases at high temperatures under pressure, PHWE can selectively extract a wide range of medium to low polarity analytes [24]. PHWE has been successfully applied to the extraction of a wide range of organic pollutants such as amines, aromatic polycyclic hydrocarbons (PAHs) and pesticides among others from different solid matrices [25-28]. However, as far as we know, this process has not yet been used for the extraction of organic pollutants from house dust.

After the PHWE, the aqueous extract requires a preconcentration and further extraction step, which can be done through liquid-liquid extraction (LLE) [29], solid-phase extraction (SPE) [25], solid-phase micro extraction (SPME) [27,30,31] or stir bar sorptive extraction (SBSE) [26], etc. SBSE is a powerful and sensitive solventless technique which can extract and preconcentrate the analytes from the PHWE extract in one step. However, given that parabens are quite polar compounds with a low affinity with the polydimethylsiloxane (PDMS) phase of commercial stir bars, a derivatization step such as the acetylation of the phenolic group with acetic anhydride in basic medium should be carried out prior to the extraction to enhance recoveries [32].

Therefore, the aim of this study is to develop a method for determining parabens in house dust that uses PHWE followed by the in situ acetylation of parabens with SBSE extraction and thermal desorption – gas chromatography – mass spectrometry (TD-GC-MS) analysis. To the best of our knowledge, this study represents the first time that PHWE extraction is applied to both the extraction of organic pollutants from house dust and the extraction of parabens from a solid matrix. The method described here is environmentally friendly because it uses water as the extraction solvent. This eliminates the risk of external contamination because only minimal manipulation of the sample is required. The method is also more sensitive in that it analyzes all of the extracted parabens. The method was tested to see if it could determine five parabens in several house dust samples.

2.1. EXPERIMENTAL

2.1. Chemical standards

The target parabens 4-hydroxybenzoic acid methyl ester (methyl paraben), 4-hydroxybenzoic acid ethyl ester (ethyl paraben), 4-hydroxybenzoic acid n-propyl ester (propyl paraben), and 4-hydroxybenzoic acid butyl ester (butyl paraben) were supplied by Aldrich (Steinheim, Germany) and the 4-hydroxybenzoic acid i-propyl ester (i-propyl paraben) was purchased from Alfa Aesar (Karlsruhe, Germany).

The acetylated methyl paraben (methyl 4-acetoxybenzoate, 99% purity) was supplied by Aldrich. The remaining acetylated parabens, unavailable commercially, were prepared by adding 200 μL of acetic anhydride and 5 μL pyridine to 1 mL of 500 mg L^{-1} standard solution of the parabens in ethyl acetate and mixing this in a vortex for 10 min at ambient temperature [32]. The calculated efficiency of the derivatization was ca. 96%.

The individual standard solutions of parabens and the mixtures were prepared in methanol (GC grade with >99.9% purity, SDS, Peypin, France). Other solvents used in the optimisation of the method (acetone and acetonitrile) were also GC grade from SDS. Helium gas and nitrogen gas with

99.999% purity (Carburos Metálicos, Barcelona, Spain) were used for the thermal desorption and chromatographic analysis. Ultrapure water was obtained using a Purelab ultrapurification system (Veolia water, Barcelona, Spain). Sigma-Aldrich supplied Hyflo Super Cel diatomaceous earth for filling the extraction cells of the pressurised liquid extraction equipment. The acetic anhydride for the paraben derivatization was from Scharlau Chemie (Setmenat, Spain) and the disodium hydrogen phosphate from Panreac (Barcelona, Spain).

2.2. Sample collection and preparation

House dust was collected from conventional vacuum cleaners that were in regular use in private homes. The dust was then sieved with a stainless steel sieve and a fraction under 100 µm was stored in amber glass vials and kept at 4 °C until analysis.

The method was optimized and validated with spiked samples of pooled house dust. Spiked samples were prepared by adding different volumes of the standard solution of the target parabens to acetone, always making sure that enough solution was added to cover the entire sample. The mixture was accurately homogenised and kept in a cupboard funnel at room temperature until the solvent had completely evaporated and then aged for at least one week. It was then stored in amber glass vials at 4 °C before being extracted.

2.3. Pressurised Hot Water Extraction and Stir Bar Sorptive Extraction

PHWE was performed using an ASE 200 Accelerated Solvent Extraction system (Dionex, Sunnyvale, CA, USA) in 11 mL stainless steel extraction cells. Under the optimised conditions, 100 mg of sieved house dust were dispersed in a mortar with 1 g of diatomaceous earth. Next, the extraction cells were filled with two cellulose filters placed at the bottom of the cell, followed by 1 g of diatomaceous earth, the dispersed sample, and then more diatomaceous earth until the cell was full. Extraction began with a preheating step of 5 min, followed by a 5 min static period at 80 °C and a pressure of 1500 psi. The extraction process was performed in 4 cycles with a flush volume of 100% and a purge time of 120 s. Diatomaceous earth was previously conditioned at 400 °C in a muffle for 6 hours and then kept in a desiccator.

Prior to the SBSE process, the aqueous extracts from the PHWE (ca. 25-35 mL) were filtered under vacuum using 45 µm nylon filters (Whatman, Maidstone, UK), increased to 100 mL with ultrapure water and placed into vials. Next, 0.5 g of Na_2HPO_4 and 1000 µL of acetic anhydride were added for the in situ acetylation of the parabens. A clean stir

bar was then placed in the vial containing the sample and the vial was immediately capped and stirred at 900 rpm for 4 hours at room temperature. After extraction, the stir bars were magnetically removed, rinsed with ultrapure water, dried with a lint-free tissue and placed inside a thermally cleaned stainless-steel tube for the thermal desorption.

SBSE extraction of the target parabens was carried out with PDMS coated stir bars (20 mm length × 0.5 mm film thickness with ca. 48 µL of PDMS phase, from Gerstel (Mülheim an der Ruhr, Germany)). Before each use, the stir bars were thermally cleaned at 300 °C for 3 hours in pure helium flow of 100 mL min^{-1} and stored in clean 2 mL vials until their use.

PHWE and SBSE processes were optimised using house dust samples spiked at a final concentration of 1000 ng g^{-1} of each paraben. In order to assess possible contamination, procedural blanks were also made by filling the cells only with diatomaceous earth. No signal of the target parabens was found in these blanks.

2.4. TD–GC–MS analysis

Thermal desorption of the stir bars was performed in a Unity Thermal Desorption system combined with an Ultra A autosampler (both from Markes International Limited, Llantrisant, UK). Stir bars were placed in empty stainless-steel tubes for thermal desorption (9 cm length × 6.35 mm o.d. × 5 mm i.d., also from Markes). Prior to the analysis, the empty tubes were thermally cleaned at 300 °C for 15 min and then stored in a hermetic glass jar under nitrogen atmosphere. The optimized stir bar thermal desorption conditions were: pre-purge for 1 min at room temperature, stir bar desorption at 300 °C for 15 minutes using helium carrier gas at 100 mL min^{-1} in splitless mode, trapping at 0 °C in a Tenax TA trap and finally trap desorption at 320 °C for 10 min with a split of 5 mL min^{-1}.

Separation and detection were performed in a 6890N gas chromatograph and 5973 *inert* mass spectrometer (Agilent Technologies. Palo Alto, CA, USA) using a Zebron ZB-50 capillary column (30 m × 0.25 mm × 0.25 µm) provided by Phenomenex (Le Pecq Cedex, France). For the GC-MS analysis, the helium carrier gas flow was set at 2 mL min^{-1}. The oven temperature program began at 100 °C, was then increased to 150 °C at 30 °C min^{-1}, then to 190 °C at 5 °C min^{-1} and finally to 290 °C at 15 °C min^{-1}. The GC–MS interface was set at 290 °C. The MS-detector acquired in the selective ion monitoring mode (SIM) operated at an electron impact energy of 70 eV. Table 1 shows the retention times and the quantifier and qualifier ions used for the SIM detection of the acetylated derivatives of the parabens.

Table 1. Target parabens and the retention times (t_R), quantifier and qualifier ions (with their percent abundances in brackets) of the acetylated derivatives.

Compound	t_R (min)	Quantifier ion	Qualifier ions
Methyl paraben (MeP)	5.76	121	91 (90), 152(80)
Ethyl paraben (EtP)	6.57	121	166(70), 138 (40)
i-Propyl paraben (i-PrP)	6.74	121	138 (80), 180 (50)
Propyl paraben (PrP)	7.93	138	121 (80), 180 (25)
Butyl paraben (BuP)	9.48	138	121(50), 194 (15)

3. RESULTS AND DISCUSSION

3.1. Method optimisation

3.1.1. TD–GC–MS

Acetylated parabens are less polar than the non-acetylated parabens. As a result, the derivatives present much more symmetrical chromatographic peaks because the acetylation of the phenolic groups prevents the hydroxyl group from interacting with the GC capillary column. The acetylated parabens also showed higher retention times than the non-derivatizated parabens, and their mass spectra were similar to the parabens and their mass spectra were similar to the mass spectra of those non-derivatized parabens with increased molecular ion [33]. For the GC separation, a midpolarity phase capillary column was used (50% diphenyl/50% dimethyl polysiloxane) that separated the acetylated parabens in less than 10 min.

Regarding the TD process, the acetylated derivatives of parabens are semivolatile compounds with relatively high boiling points (between 249 and 300 °C). Therefore, high desorption temperatures and flow should be applied to the PDMS stir bars for the quantitative desorption of the analytes. This study tested different desorption temperatures (from 250 to 300 °C), times (from 5 to 20 min) and flows (from 50 to 100 mL min^{-1}). Higher temperatures can degrade the PDMS phase and higher flows can prevent the analytes from being retained in the cryogenic trap. Carry-over of the acetylated parabens was under 1% when the maximal temperature (300 °C) and flow (100 mL min^{-1}) were applied for 15 min. Longer times did not improve the extraction efficiencies. The acetylated parabens were then trapped in a Tenax TA cryogenic trap set at 0 °C during stir bar desorption and then desorbed at 320 °C for 10 min with a split flow of 5 mL min^{-1}.

3.1.2. PHWE and SBSE

Parabens are quite polar compounds with relatively low octanol–water partition coefficients (log K_{ow} between 2.0 for methyl paraben and 3.5 for

butyl paraben). Theoretical recoveries range from 4.5% to 58% for these compounds when calculated for PDMS stir bars with 48 µL of phase and 100 mL of sample volume. Consequently, it was decided to test to see if the acetylation of parabens with acetic anhydride in the presence of a basic salt prior to the SBSE extraction would improve their recoveries in the PDMS phase. When optimizing the PHWE process, the initial acetylation and SBSE conditions were set as follows: 0.5 g of Na_2HPO_4 and 100 µL of acetic anhydride extracted with a PDMS stir bar (20 mm x 0.5 mm) stirred at 900 rpm and at room temperature for 3 hours. Because of their high viscosity and turbidity, the extracts were filtered under vacuum with 45 µm nylon filters and diluted to 100 mL with ultrapure water prior to the SBSE process in order to prevent interferences during the extraction. Spiked house dust samples at a concentration of 1000 ng g^{-1} were used for the optimisation phase.

Initial PHWE experiments were carried out in order to determine the optimal amount of house dust and the extraction solvent. The first experiments were conducted with 1 g of house dust extracted with ultrapure water in mild conditions (1 cycle, 80 °C, 1500 psi for 5 min). However, the extracts obtained were dark brown with high viscosity and a thick foam on the surface and were very difficult to filter. One explanation for this may be that, as mentioned in the introduction, skin tissues are a common component of house dust. PHWE could, therefore, extract the fatty acids bound to these tissues, which have very low solubility in cold water, thus increasing the viscosity of the extracts. Extractions were then performed using a smaller quantity of sample: 800 mg, 500 mg, 200 mg and 100 mg. Finally, an amount of 100 mg was chosen for the study because the viscosity and turbidity of the extracts decreased at smaller quantities. Smaller quantities of house dust would compromise the sensitivity of the method.

Adding certain organic modifiers to the water may improve the extraction efficiencies of analytes [24]. Therefore, the addition of organic solvents was tested to see if it had any influence. This was done by adding volumes of 10, 25 and 50% methanol, acetone and acetonitrile. The total volume of these solvents in the SBSE samples (once the extracts were diluted to 100 mL with ultrapure water) ranged between 1.5-10 % (taking into account that ca.15-20 mL of extract were obtained in 1 cycle of PHWE). In general, responses decreased as more organic solvent was added, except for i-propyl paraben whose responses increased as more acetonitrile was added. Decreases in the paraben responses after the addition of larger amounts of organic modifiers can be explained by the negative effect of these solvents on the SBSE step (either because the efficiency of the in situ acetylation of the parabens decreases or because the affinity of the compounds with the

PDMS phase decreases). The i-propyl paraben may behave differently because the organic modifier added during the PHWE step had a positive effect on it which was higher than the negative effect that the organic modifier had on the i-propyl paraben during the subsequent SBSE step.

By way of an example, Figure 1 shows how the type and amount of organic solvent influence the responses of acetylated i-propyl paraben (Figure 1A) and acetylated butyl paraben (Figure 1B).

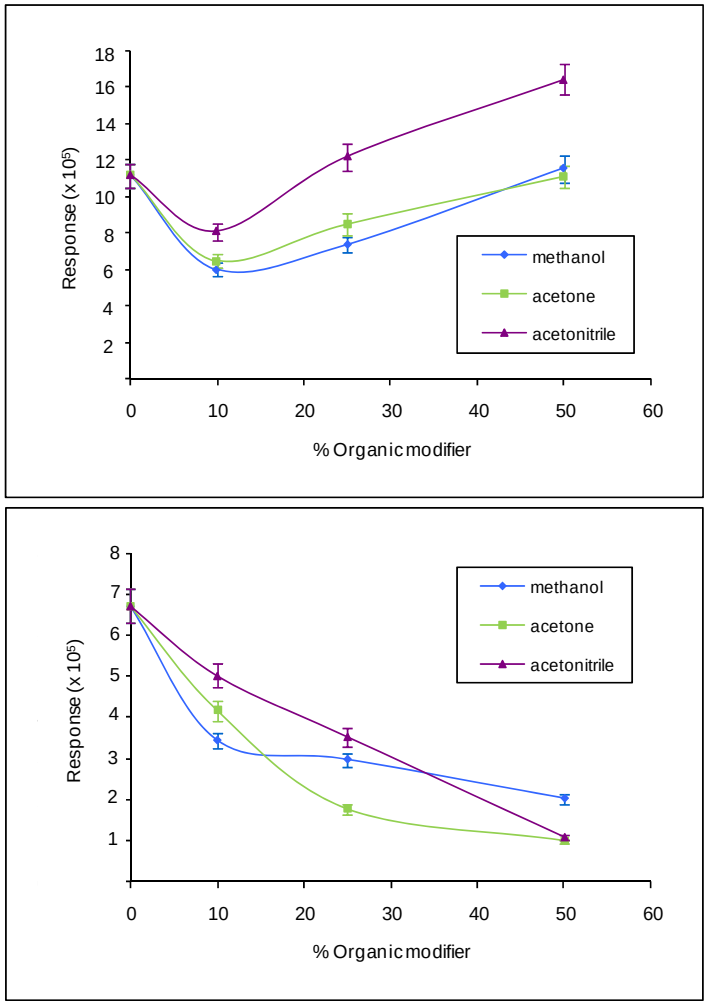


Figure 1. Influence of the type and amount of organic modifier in the PHWE responses for the acetylated i-propyl paraben (A) and the acetylated butyl paraben (B). (PHWE conditions: 80 °C, 1500 psi, 5 min, 1 cycle, 100% flush volume and 120 s purge).

In the light of these results, ultrapure water without any organic modifier was selected as the extraction solvent.

The influence of extraction temperature, time and number of cycles was evaluated using a multifactorial design 3^2 2^1 composed of 18 experiments. Table 2 summarizes the factors and levels selected for the design. The factor levels were selected on the basis of previous PLE papers that investigated organic solvents that determined parabens from dust [9] and from sewage sludge [34]. Statistical analysis was carried out with Statgraphics-Plus 5.1 (Magnugistic, Rockville, MD, USA). In all experiments, pressure was set at 1500 psi (enough to maintain water in a liquid state in this range of temperatures), flush volume at 100% and purge time at 120 s (until the extraction cell content was completely dry).

Table 2. Factors and levels selected for the 3^2 2^1 design.

Factors	Lower	Intermediate	Upper
Temperature (°C)	80	100	120
Time (min)	5	10	15
Cycles	2	-	3

Figure 2 shows the calculated standardised effects of the three factor and the two-factor interactions for the acetylated methyl paraben. The standardised effect is obtained by dividing the estimated effect by its standard error. The vertical line indicates the statistically significant bound at the 95% confidence level.

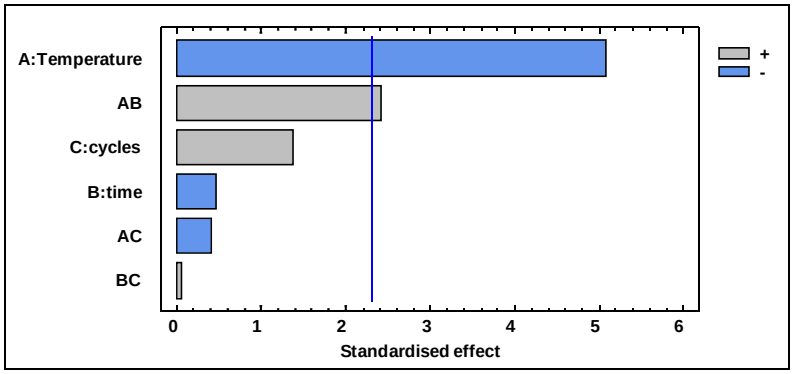


Figure 2. Standardized Pareto chart of the mean effects and two-factor interactions for the factorial design of acetylated methyl paraben.

Figure 3 compares the response surface of the extraction temperature with the extraction time for 2 extraction cycles for the same paraben.

Extraction temperature had the largest effect on the extraction efficiency, with lower temperatures being more favourable than higher temperatures. One possible explanation may be that extract viscosity increased with higher temperatures. High viscosity may decrease the efficiency of the derivatization reaction and the affinity of the acetylated parabens for the PDMS phase. The extraction time temperature (120 °C) and highest extraction time (15 min). Consequently, an extraction temperature of 80 °C and an extraction time of 5 min were set as a compromise between the results. In order to enhance the responses, depended on the temperature. The increase in time from 5 to 15 min decreased the response at low temperatures, whilst at high temperatures the effect was the opposite. This temperature - time interaction (AB) was responsible for the non-statistical significance of the effect of time (Figure 2). The number of cycles had the lowest effect on the response.

Results were similar for all acetylated parabens, except for the acetylated butyl paraben (the least polar of the target compounds) for which higher responses were obtained at the highest different numbers of cycles (from 2 to 5) were tested in these conditions. For the acetylated i-propyl paraben and butyl paraben the best responses were obtained at 4 cycles of extraction.

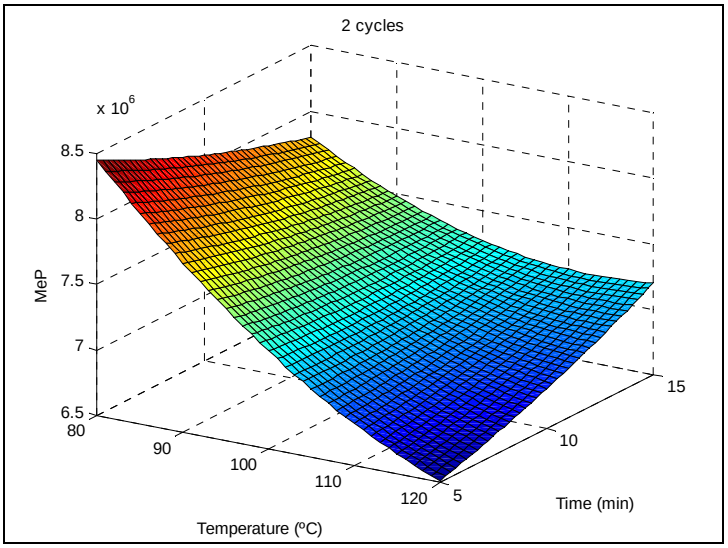


Figure 3. Acetylated methyl paraben response surface for the extraction temperature against the extraction time (2 cycles).

For the acetylated derivatives of methyl, ethyl and propyl paraben, the responses were less affected by the number of cycles and only a slight increase was detected between 3 and 4 cycles. Therefore, 4 cycles were selected as the optimum number.

Once the PHWE parameters were established, the amount of the derivatizing agents for the in situ acetylation of parabens prior to the SBSE was optimised. The amount of basic salt was fixed at 0.5 g because higher amounts gave rise to a precipitate in the extracts. The amount of acetic anhydride was optimised by adding different amounts of this reactive (from 100 µL to 5 mL) to the extracts. The highest responses for all parabens were obtained with 1 mL of acetic anhydride (results not shown). Larger volumes of this reactive provided an acidic medium that was unfavourable for the equilibrium of the acetylation reaction. A similar tendency has been observed in other studies [32, 35]. Therefore, a volume of 1 mL of acetic anhydride was used. Under these acetylation conditions no signal of the non-acetylated parabens was detected in the chromatograms, therefore it was assumed that the derivatization of the parabens was complete.

Finally, different SBSE times were studied. Results showed that the equilibrium was reached between 3 and 5 hours. Consequently, a 4 h extraction time was selected as a compromise between sample preparation time and extraction efficiency. Table 3 shows the optimised parameters for the PHWE and SBSE processes.

Table 3. Optimised conditions for the PHWE and the in situ acetylation-SBSE of parabens in house dust.

Pressurised hot water extraction	
Amount of sample	100 mg
Solvent	Water
Cell volume	11 mL
No. of cycles	4
Static time	5 min
Temperature	80 °C
Pressure	1500 psi
Flush volume	100 %
Purge time	120 s
Stir bar sorptive extraction	
Sample volume	100 mL
Stirring speed	900 rpm
Temperature	Room temp.
Time	4 hours
Acetic anhydride	1000 µL
Na_2HPO_4	0.5 g

3.2. Method validation

Table 4 shows the main method parameters of the acetylated parabens for the optimised PHWE followed by in situ derivatization and SBSE-TD-GC-MS. Calibration was performed by spiking 100 mg of house dust sample with different amounts of the standards, these amounts ranging from the LOD of each paraben (see Table 4) to 1500 ng g^{-1}. Linearity was good with the coefficient of determination (r^2) values above 0.996 for all the target parabens.

To calculate recoveries of the whole method, the peak areas obtained at two calibration levels (100 and 1000 ng g^{-1}) were compared with a calibration curve obtained by spiking the same amount of the standards of the acetylated parabens (see section 2.1.) in a tube filled with thermally cleaned deactivated glass wool. As Table 4 shows, recoveries were similar for both levels and ranged from 40% for the acetylated methyl paraben to 80% for the acetylated propyl paraben. The low recovery for the acetylated methyl paraben can be explained by its low affinity with the PDMS phase of the stir bar [32].

Repeatability and reproducibility between days were also checked at two calibration levels (100 and 1000 ng g^{-1}). Repeatability values, expressed as %RSD, ranged between 1.9% for the acetylated methyl and propyl paraben and 8.1% for the i-propyl paraben. Reproducibility between days ranged from 2.3% for the acetylated propyl paraben to 9.5% for the acetylated i-propyl paraben.

Table 4. Main method parameters for the acetylated parabens at a midpoint (100 ng g^{-1}) and a high (1000 ng g^{-1}) calibration level: recovery, repeatability and reproducibility between days, and the detection and quantification of the method.

Acetylated paraben	Recovery (%)		Repeatability (%RSD, n=5)		Reproducibility (%RSD, n=5)		LOD (ng g^{-1})	LOQ (ng g^{-1})
	100 ng g^{-1}	1000 ng g^{-1}	100 ng g^{-1}	1000 ng g^{-1}	100 ng g^{-1}	1000 ng g^{-1}		
MeP	43	40	2.3	1.9	2.6	2.4	2.1	8.5
EtP	59	57	3.1	2.8	3.3	3.4	1.9	6.0
i-PrP	54	52	7.9	8.1	8.5	9.4	1.3	3.8
PrP	78	80	1.9	1.8	2.6	2.3	1.0	3.3
BuP	60	61	4.9	4.8	5.4	5.2	1.5	4.2

The limits of detection (LOD) were determined as three times the standard deviation of the target ion's signal in the non-spiked house dust samples (n=5). The LODs ranged from 1 ng g^{-1} for propyl paraben to 2.1 ng g^{-1} for methyl paraben (see Table 4). The limit of quantification (LOQ), which was fixed as the lowest calibration level of each compound, ranged from 3.3 ng g^{-1} for

propyl paraben to 8.5 ng g^{-1} for methyl paraben. It is worth mentioning that these limits are comparable with the limits obtained in previous methods which used organic solvents instead of water for the pressurised extraction of parabens in indoor dust [9, 10].

3.3. Analysis of house dust samples

The PHWE-SBSE-TD-GC-MS method described above with in situ acetylation of parabens was used to determine the presence of the target parabens in different house dust samples. Each sample was analysed in triplicate. Figure 4 shows the SIM chromatogram of a non-spiked house dust sample with the peaks corresponding to the acetylated parabens indicated.

Table 5 shows the concentration of the target parabens found in the house dust samples. The most abundant parabens were methyl paraben (178-2440 ng g^{-1}) and propyl paraben (112-910 ng g^{-1}), which is consistent with the fact that they are the most commonly used parabens due to the antimicrobial synergic effect produced when using the two parabens together [36].

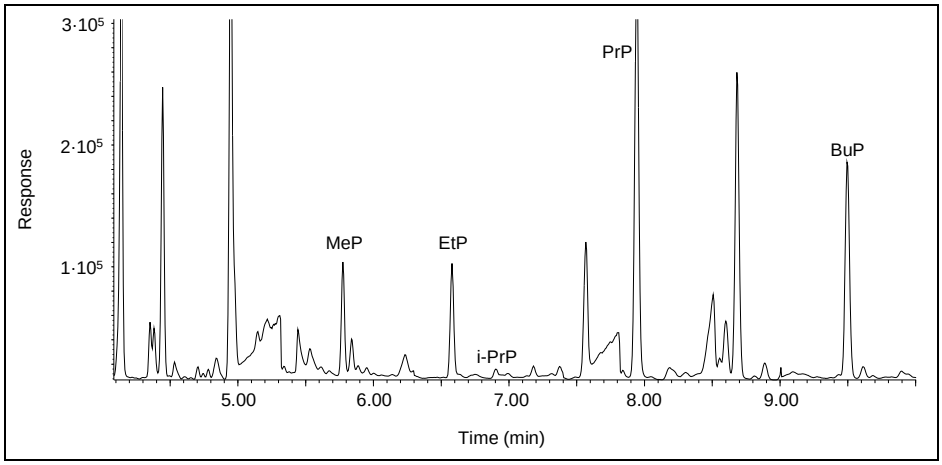


Figure 4. Chromatogram of a house dust sample, indicating peaks of the acetylated parabens.

Ethyl paraben values ranged from 56 to 977 ng g^{-1}, butyl paraben from 95 to 285 ng g^{-1} and i-propyl paraben, which was the least abundant, from values below the limit of quantification to 45 ng g^{-1}. The values of parabens found in this study are similar to those found previously in other private houses [9, 10]. This fact can demonstrate the accumulation of parabens in dust particles and, therefore, the importance of determining these compounds in house dust.

Table 5. Average, maximal and minimal concentrations of the target parabens found in the house dust samples, expressed in ng g^{-1} (6 different samples, n=3).

Paraben	MeP	EtP	i-PrP	PrP	BuP
Average	912	276	33	425	212
Max.	2440	977	45	910	285
Min.	178	56	<LOQ	112	95

<LOQ, value under the limit of quantification

4. CONCLUSIONS

This study successfully developed a method for determining parabens in house dust The optimised method was based on the PHWE of house dust, followed by the acetylation of the extracted parabens, SBSE with a PDMS stir bar, and analysis by means of TD-GC-MS. The method avoids the risk of background contamination because it requires minimal manipulation of the sample. Furthermore, the acetylation of the parabens prior to SBSE increased the affinity of these compounds with the PDMS and improved their chromatographic signal. The method showed good linearity, repeatability, reproducibility and limits of detection and quantification at low ng g^{-1} levels.

The proposed method was used to analyze house dust samples. All the target parabens were found in the samples, with methyl and propyl parabens being the most abundant. The high values of these PCPs found in the samples confirm the importance of determining organic contaminants in indoor environments.

Acknowledgments

The authors wish to acknowledge the financial support provided to this study by the Spanish Ministry of Science and Innovation through project CTM-2008-06847-C02-01 and the Department of Innovation, Universities and Enterprise of the Catalan Government through project 2009 SGR 223.

REFERENCES

[1] W.R. Ott, A.C. Steinemann, L.A. Wallace, Exposure analysis. Taylor & Francis, Boca Raton, Florida, 2006.

[2] USEPA, EPA Indoor Air Quality Implementation Plan. EPA/600/8-87/031, 1987.

[3] J.W. Roberts, W.T. Budd, J. Chuang, R.G. Lewis, Chemical Contaminants in House Dust: Occurrences and Sources [Govt Reports Announcements & Index (GRA&I)]. Atmospheric Research and Exposure Assessment Lab: Research Triangle Park, NC, 1993.

[4] H.M. Hwang, E.K. Park, T.M. Young, B.D. Hammock, Sci. Total Environ., 404 (2008) 26.

[5] Z.Y. Xie, R. Ebinghaus, Anal. Chim. Acta, 610 (2008) 156.
[6] C.J. Weschler, W.W. Nazaroff, Atmos. Environ., 42 (2008) 9018.
[7] C. García-Jares, J. Regueiro, R. Barro, T. Dagnac, M. Llompart, J. Chromatogr. A, 1216 (2009) 567.
[8] R.A. Rudel, D.E. Camann, J.D. Spengler, L.R. Korn, J.G. Brody, Environ. Sci. Technol., 37 (2003) 4543.
[9] P. Canosa, D. Pérez-Palacios, A. Garrido-López, M.T. Tena, I. Rodríguez, E. Rubí, R. Cela, J. Chromatogr. A, 1161 (2007) 105.
[10] P. Canosa, I. Rodríguez, E. Rubí, R. Cela, Anal. Chem., 79 (2007) 1675.
[11] H. Fromme, T. Lahrz, M. Piloty, H. Gebhart, A. Oddoy, H. Ruden, Indoor Air, 14 (2004) 188.
[12] J. Regueiro, M. Llompart, C. García-Jares, R. Cela, J. Chromatogr. A, 1174 (2007) 112.
[13] E.J. Routledge, J. Parker, J. Odum, J. Ashby, J.P. Sumpter, Toxicol. Appl.Pharmacol., 153 (1998) 12.
[14] P.D. Darbre, P.W. Harvey, J. Appl. Toxicol., 28 (2008) 561.
[15] P.D. Darbre, A. Aljarrah, W.R. Miller, N.G. Coldham, M.J. Sauer, G.S. Pope, J. Appl. Toxicol., 24 (2004) 5.
[16] M.G. Soni, G.A. Burdock, S.L. Taylor, N.A. Greenberg, Food Chem. Toxicol., 39 (2001) 513.
[17] B.H. Wilford, M. Shoeib, T. Harner, J.P. Zhu, K.C. Jones, Environ. Sci. Technol., 39 (2005) 7027.
[18] M. Shoeib, T. Harner, B.H. Wilford, K.C. Jones, J.P. Zhu, Environ. Sci. Technol., 39 (2005) 6599.
[19] H. Fromme, A. Mattulat, T. Lahrz, H. Ruden, Chemosphere, 58 (2005) 1377.
[20] A. Sjodin, H. Carlsson, K. Thuresson, S. Sjolin, A. Bergman, C. Ostman, Environ. Sci. Technol., 35 (2001) 448.
[21] I. Carpinteiro, B. Abuín, I. Rodríguez, M. Ramil, R. Cela, J. Chromatogr. A, 1217 (2010) 3729.
[22] M.P. Martínez, J.D. Carrillo, M.T. Tena, Anal. Bioanal. Chem., 397 (2010) 257.
[23] J. Regueiro, M. Llompart, C. García-Jares, R. Cela, Anal. Bioanal. Chem., 388 (2007) 1095.
[24] C.C. Teo, S.N. Tan, J.W.H. Yong, C.S. Hew, E.S. Ong, J. Chromatogr. A, 1217 (2010) 2484.
[25] M. García-López, I. Rodríguez, R. Cela, J. Chromatogr. A, 1216 (2009) 6986.
[26] R. Rodil, P. Popp, J. Chromatogr. A, 1124 (2006) 82.
[27] A. Llop, F. Borrull, E. Pocurull, Anal. Chim. Acta, 665 (2010) 231.
[28] M.R. Burkhardt, S.D. Zaugg, T.L. Burbank, M.C. Olson, J.L. Iverson, Anal. Chim. Acta, 549 (2005) 104.
[29] P. Richter, B. Sepúlveda, R. Oliva, K. Calderón, R. Seguel, J. Chromatogr. A, 994 (2003) 169.
[30] E. Concha-Grana, V. Fernández-González, G. Grueiro-Noche, S. Muniategui-Lorenzo, P. López-Mahía, E. Fernández-Fernández, D.

Prada-Rodríguez, Chemosphere, 79 (2010) 698.

[31] V. Fernández-González, E. Concha-Grana, S. Muniategui-Lorenzo, P. López-Mahía, D. Prada-Rodríguez, J. Chromatogr. A, 1196 (2008) 65.

[32] A. Casas Ferreira, M. Möder, M. Fernández Laespada, Anal. Bioanal. Chem., 399 (2011) 945.

[33] T.R. Croley, B.C. Lynn, Rapid Commun. Mass Spectrom., 12 (1998) 171.

[34] A. Nieto, F. Borrull, R.M. Marce, E. Pocurull, J. Chromatogr. A, 1216 (2009) 5619.

[35] M. Bourdat-Deschamps, J.J. Daudin, E. Barriuso, J. Chromatogr. A, 1167 (2007) 143.

[36] A.M. Peck, Anal. Bioanal. Chem., 386 (2006) 907.

3.5.2. Determination of nicotine and N-nitrosamines in house dust by pressurized liquid extraction and two dimensional gas chromatography-nitrogen chimiluminiscence detection

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

DETERMINATION OF NICOTINE AND N-NITROSAMINES IN HOUSE DUST BY PRESSURIZED LIQUID EXTRACTION AND COMPREHENSIVE GAS CHROMATOGRAPHY – NITROGEN CHEMILUMINISCENCE DETECTION

Noelia Ramírez[1], Mustafa Z. Özel[2], Jacqueline F. Hamilton[2], Rosa M. Marcé[1], Francesc Borrull[1], Alastair C. Lewis[3]

[1] Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, Sescelades Campus, Tarragona 43007, Spain

[2] The University of York, Department of Chemistry, Heslington, York YO10 5DD, UK

[3] National Centre for Atmospheric Science, The University of York, Department of Chemistry, Heslington, York YO10 5DD, UK

Abstract

A novel, highly selective method for the determination of nicotine, N-nitrosamines and tobacco-specific nitrosamines (TSNAs) in indoor dust samples is presented in this study. Samples were extracted by in-cell clean-up pressurized liquid extraction (PLE) that allows high extraction efficiency with moderate consumption of organic solvents. The extracts were analysed by comprehensive gas chromatography and detected with a nitrogen chemiluminiscence detector (GC×GC-NCD) that provided enhanced selectivity and sensitivity for organic nitrogen containing compounds. Method validation showed good linearity, repeatability and reproducibility (%RSD < 8%). Recovery was higher than 80% for most target compounds and limits of detection lower than 16 ng g^{-1}.

The method was used for the determination of the nitrosamine target compounds in house dust samples from both smoking and non-smoking households. All the analytes were found in the samples, nicotine being the most abundant compound in smokers' dust and one of the most abundant in non-smokers' dust. To our knowledge this is the first time that volatile N-nitrosamines and TSNAs have been determined in indoor dust samples. The results demonstrate the presence of these highly carcinogenic compounds in house dust, with inherent human exposure through inhalation and/or involuntary ingestion of house dust.

Keywords: Nicotine; Tobacco-specific nitrosamines (TSNAs); House dust; Comprehensive gas chromatography (GC×GC); Nitrogen chemiluminiscence detector (NCD); Pressurized liquid extraction (PLE).

1. INTRODUCTION

House dust has been identified as a major source of environmental contaminants including pesticides, polycyclic aromatic hydrocarbons (PAHs), phthalates, several metals, and other chemicals of human health concern[1, 2]. Since contaminants bound to indoor dust are more persistent than those outdoors, indoor dust has been recognised as a significant source of human exposure for an increasing number of pollutants. For instance, the ingestion of house dust has been estimated to be the major route of exposure to some persistent pollutants for children[3]. Furthermore, recently, it has been demonstrated that indoor dust may be the main route of exposure to polybrominated diphenyl ethers for both adults and children[4]. House dust is therefore a key pollutant vector and one which demands further examination for the presence of other contaminants of human health concern.

One of the most important sources of indoor pollution is tobacco smoke. Nicotine is the most abundant organic compound emitted during smoking[5]. It reacts during the burning of tobacco to form tobacco-specific nitrosamines (TSNAs). TSNAs are amongst the most abundant carcinogenic compounds identified in tobacco smoke[6] and they have been related to acute leukemia[7] and lung cancer[8]. Of all TSNAs identified, N'-nitrosonornicotine (NNN) and 4-(methylnitrosoamino)-1-(3-pyridyl)-1-butanone (NNK) are the most prevalent carcinogens in tobacco products and are classified as carcinogenic for humans (Group 1 IARC)[9]. Another interesting TSNA is 4-(methylnitrosoamino) - 1 - (3-pyridyl)-1-butanol (NNAL), which is the main metabolite of NNK and has the same dangers[10]. Moreover, more volatile N-nitrosamines, with genotoxic and carcinogenic properties can be formed in the atmosphere because of the presence of nitrogen-containing species originating during combustion processes[11]. Some studies have also detected the presence of volatile N-nitrosamines, such as N-nitroso-dimethylamine and N-nitrosopyrroli-dyne, in environmental tobacco smoke[12, 13].

Nicotine deposits almost entirely on indoor surfaces and persists for long time [14, 15]. This deposited nicotine can also form TSNAs by reaction with atmospheric species present in indoor environments, such as ozone, nitrous acid and nitrogen oxides. Given the high levels of nicotine typically found in environments contaminated with tobacco and the low volatility of TSNAs, these contaminants can persist for weeks to months in these indoor environments[5]. Furthermore, several experiments have suggested that airborne NNK concentrations in sidestream cigarette smoke can increase by 50% to 200% per hour during the first 6 h after cigarettes are extinguished[16]. Whereas direct inhalation of second hand smoke (SHS)

is an exposure pathway of concern, non smokers, especially children, are at risk through contact with surfaces and dust contaminated with residual smoke gases and particles[17] (the so called third hand smoke (THS))[18]. Several studies have detected nicotine in indoor dust and surfaces[17, 19]. However, to our knowledge, there is no information about the presence of TSNAs and volatile N-nitrosamines in indoor dust.

The complexity of dust composition and high adsorption capacity of dust particles requires the use of exhaustive extraction techniques. Furthermore, the extracts obtained from dust samples are complex with a large number of co-extracted interferences. Pressurized liquid extraction (PLE) is an efficient extraction method which can address this problem and, therefore, has been successfully applied for the extraction of organic pollutants in house dust, such as benzotriazole light stabilisers[20], brominated diphenyl ethers[21] and polycyclic aromatic hydrocarbons[22]. Furthermore, the option of integrating an in-cell clean-up active sorbent into the PLE process, has considerably reduced the time and steps needed for sample treatment prior to the analysis[23].

Several techniques have been used for the analytical determination of nicotine and N-nitrosamines, the most common of which is gas chromatography (GC). GC has been coupled with different detectors such as, mass spectrometry (MS)[19], especially ion trap MS[24, 25]; thermal energy analysis (TEA), which is the more widely used method for TSNA determination[26]; and nitrogen specific detectors, e.g. the nitrogen-phosphorous[27] or nitrogen chemiluminiscence detector (NCD)[28]. Comprehensive gas chromatography (GC×GC), which has an increased separation power and much better sensitivity and peak resolution than one dimensional GC, has been used for the determination of organic contaminants in complex matrices[29]. Moreover, the combination of an element specific detector can provide more resolution of the target analytes with enhanced sensitivity. In this sense, a GC×GC-NCD has recently been used for determining organic nitrogen compounds (ON) in aerosol samples, showing higher selectivity and sensitivity than mass spectrometry detectors[30].

Hence, the aim of this study is the development of a selective analytical method for the determination of nicotine and N-nitrosamines (9 volatile N-nitrosamines and 5 TSNAs) in indoor dust based on in-cell clean-up PLE, followed by GC×GC-NCD determination. Parameters affecting the efficiency and selectivity of the analytical method are discussed. Dust samples collected from non-smoking and smoking households were analysed with the proposed method. To our knowledge, this study represents the first time that the occurrence of N-nitrosamines, including TSNAs, in house dust has been reported.

2. EXPERIMENTAL

2.1. Chemical standards

The standards of the target compounds involved a mixture of 9 nitrosamines at 2000 mg L^{-1} in methanol [EPA 8270/Appendix IX Nitrosamines Mix, from Sigma-Aldrich, (Steinheim, Germany) including N-nitroso-dimethylamine (NDMA), N-nitroso-methylethylamine (NMEA), N-nitroso-diethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA), N-nitroso-morpholine (NMor), N-nitrosopyrro-lidine (NPyr), N-nitrosopiperidine (NPip), N-nitrosodi - n - butylamine (NDBA) and N-nitrosodiphenylamine (NDPhA) and an the individual standard of nicotine, also from Sigma-Aldrich. TSNAs of the N'-nitrosonornicotine (NNN), N'-nitrosoanatabine (NAT), N'-nitrosoanabasine (NAB), 4-(methyl-nitrosoamino)-1-(3-pyridyl)-1-butanone (NNK) and 4-(methylnitrosoamino)-1-(3-pyridyl)-1-butanol (NNAL) from Fluka (Buchs, Switzerland). The standards had a minimal purity of 97% except for NNAL, of which the purity was ≥92%. Figure 1 shows the chemical structure of the target compounds.

The standard solutions of the target compounds were prepared in methanol and the diluted mixtures in ethyl acetate (GC grade with >99.9% purity, SDS, Peypin, France). Other solvents used in the optimisation of the method (acetone and dichloromethane) were also GC grade from SDS. Hyflo Super Cel diatomaceous earth for filling the extraction cells of the pressurized liquid extraction equipment was supplied by Sigma-Aldrich, C_{18} (Bond Elute LRC, 10 CC) was from Varian (Harbor city, CA, USA), Silica (230-400 mesh) and Alumina (70-230 mesh) were provided by Merck (Darmstadt, Germany) and Florisil (60-100 mesh) by Fluka. The sorbents were first conditioned at 400ºC for 6 hours and then stored in closed vials, at room temperature, before their use. Helium gas of purity 99.999% was used for the chromatographic analysis.

2.2. Sample collection and preparation

House dust was collected from non-smoking and smoking private homes, using conventional vacuum cleaners in regular use in the households between July and December 2010. The collected dust was next sieved with a stainless steel sieve and the fraction under 100 µm was stored in amber glass vials and kept at 4 °C until analysis.

Method optimisation and validation was carried out using spiked samples of house dust. Spiked samples were prepared by adding different volumes of standard solution of the target compounds in ethyl acetate, adding enough volume of solvent to cover the entire sample. The mixture was accurately homogenised and kept in a cupboard funnel at room temperature until the solvent had completely evaporated and then aged for at least one week. It was then stored in amber glass vials at 4 °C before being extracted.

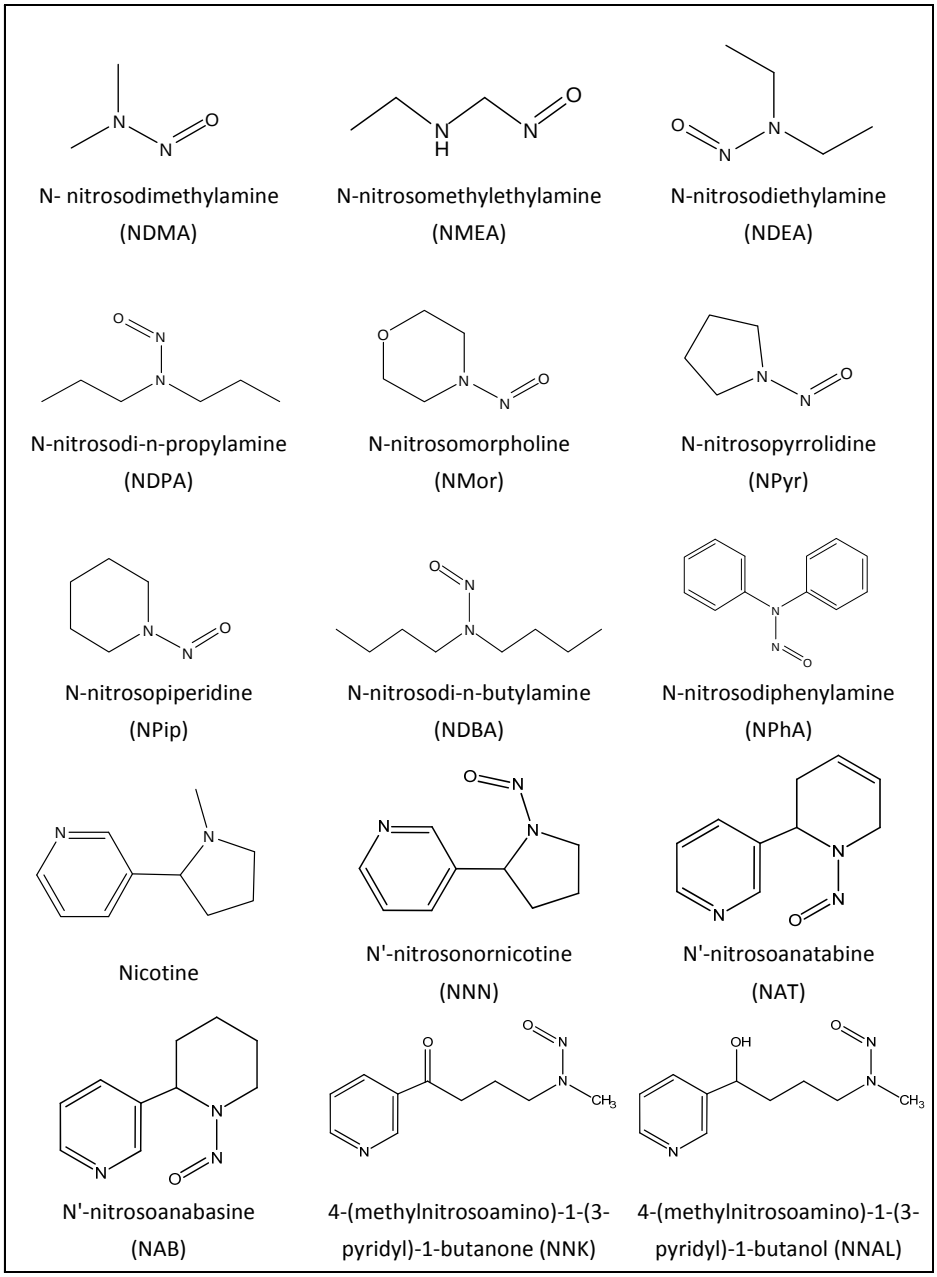


Figure 1. Chemical structures of the target N-nitrosamines, nicotine and tobacco-specific nitrosamines.

2.3. Pressurized liquid extraction

Extractions were performed using an ASE 200 Accelerated Solvent Extraction system (Dionex, Sunnyvale, CA, USA) in 11 mL stainless steel extraction cells. Ethyl acetate was used as the extraction solvent. Under the optimized conditions, 0.5 g of sieved house dust were mixed and dispersed in a mortar with 1 g of silica. Next, the extraction cells were filled with two cellulose filters placed at the bottom of the cell, followed by 1 g of diatomaceous earth, the dispersed sample, and then more diatomaceous earth until the cell was full. The extraction was carried out at 100 °C, with the cells pressurized at 1500 psi, using 3 consecutive static cycles of 10 min each. The flush volume was 100% and the purge time 100 s. The extracts were then filtered with a 0.45 µm nylon syringe filter, evaporated to a volume of ca. 0.5 mL, and made up to 1 mL with ethyl acetate. The PLE process was optimized using house dust samples spiked at a final concentration of 20 µg g^{-1} of each target compound. In order to assess possible contamination, procedural blanks were also performed by filling the cells with only 1 g of silica and diatomaceous earth. No signal of the target compounds was found in these blanks.

2.4. Chromatographic analysis

In this study, two chromatographic systems were used to analyse the extracts. For the optimisation of PLE conditions, a one dimensional GC-MS system was used. The GC-MS equipment was a 6890N GC and 5973 *inert* MS from Agilent Technologies (Palo Alto, CA, USA), equipped with a Zebron ZB-50 capillary column (30 m × 0.25 mm × 0.25 µm) provided by Phenomenex (Le Pecq Cedex, France). For the GC-MS analysis, the inlet was set at 200ºC and injections (1 µL of extracts) were performed in pulsed splitless mode at a pressure of 30 psi for 2 min. The helium carrier gas flow was set at 1 mL min^{-1}. The oven temperature program began at 40 °C for 2 min, was then increased to 100 °C at 15 °C min^{-1}, and next to 250 °C at 20 °C min^{-1} and kept at that temperature for 3 min. The GC–MS interface was set at 280 °C. The MS-detector was in the selective ion monitoring mode (SIM) operating at an electron impact energy of 70 eV.

Once the PLE conditions were optimized, the method validation and the quantification of the samples were done in a GC×GC–NCD system that consisted of a 7890 gas chromatograph and an 255 Nitrogen Chemi-luminiscence Detector, both from Agilent. The GC was equipped with a secondary oven to fit the second column, and a modulator between first and second GC columns based on a Leco (Cheshire, UK) liquid nitrogen two stage cold jet system. The modulator and the secondary oven operated at +15 °C above the GC oven temperature and the modulation period was 5 s. The

first column was a non-polar BPX5 (30 m × 0.32 mm i.d. × 0.25 µm film thickness) and the second column a BPX50 (1.5 m × 0.10 mm i.d. × 0.10 µm film thickness) both from SGE Analytical Science (VIC, Australia).

Extracts (1 µL) were injected into the GC×GC-NCD using a Gerstel automated liquid injector (Gerstel, Mulheim an der Ruhr, Germany). Injections were performed in pulsed splitless mode at a temperature of 210 °C and a pressure of 30 psi for 2 min. The initial temperature of the first dimension column was 55°C for 1 minute and the subsequent temperature program was a heating rate of 5 °C min^{-1} until 255 °C was reached and held isothermally for a further 1 minute. The initial temperature of the second dimension column was 70 °C for 1 minute and a 5°C min^{-1} heating rate was used until 270 °C was reached and held isothermally for further 1 min. Helium was used as a carrier gas at a constant flow of 1 mL min^{-1}. Pyrolysis of the analytes in the NCD was carried out at 900 °C under a hydrogen flow rate of 4 mL min^{-1} and an oxygen flow rate of 10 mL min^{-1}. Data from the NCD was collected at 50 Hz over the entire course of the analysis.

3. RESULTS AND DISCUSSION

3.1. Chromatographic optimization

In this study, two chromatographic systems were used. First, the extracts obtained in the PLE optimisation were analysed using a one dimension GC-MS because of its high simplicity. Furthermore, the detection in a MS provided the unequivocal identification of the analytes in the complex extracts. The use of a midpolarity phase capillary column (a 50% diphenyl/50% dimethyl polysiloxane) allows the separation of NMor and NPyr that usually coelute when using more apolar GC columns. However, low sensitivity can be achieved with the GC-MS system and, therefore, GCxGC-NCD was selected for the method validation and the analysis of the house dust samples. The inlet temperature was set at 210 °C in both chromatographic methods because TSNAs degraded in the injector at higher temperatures.

The main parameters to optimize for NCD are pyrolysis temperature and hydrogen and oxygen flow rates. As seen in Figure 1 nitrosamines are characterized by a N-NO bond, which is the weakest in the molecule and therefore can be selectively broken under moderate conditions. Previous studies demonstrated that the higher responses of the most volatile N-nitrosamines were obtained at an oxygen rate of 5 mL min^{-1} and a pyrolysis temperature of 450 °C, without the use of hydrogen[31]. However, higher oxygen flow rates and pyrolysis temperatures (10 mL min^{-1} and 900°C) with a hydrogen flow rate of 4 mL min^{-1} provided better responses for other organic nitrogen compounds (ON)[30]. In this study, the NCD parameters were optimized injecting 5

replicates of a standard solution of 10 μg L^{-1} of the 15 ON in ethyl acetate. The highest responses for all target ON compounds were obtained at a pyrolysis temperature of 900°C using hydrogen and oxygen at flow rates of 4 mL min^{-1} and 10 mL min^{-1}, respectively. A potentially important advantage of using NCD as a detector is that it produced an equimolar response to organic nitrogen compounds. ON compounds responded with equal nitrogen responses confirming the response of the detector to be independent of the molecular structure or other functionality[30, 32]. However, in this study, two of the target compounds did not shown equimolarity, nicotine and NNAL, possibly because of degradation reactions occurred during pyrolysis of this compounds. Therefore, standard calibration curves were used to quantify the samples.

3.2. PLE optimization

Initial PLE experiments were carried out in order to determine the optimal extraction solvent. Taking into account the solubility of the target compounds, four solvents were tested as extraction solvents: dichloromethane, ethyl acetate, methanol and acetone. For these experiments, 0.5 g of pooled house dust spiked at 20 μg g^{-1} mixed with 1 g of diatomaceous earth were extracted at 80°C and 1500 psi in one single cycle of 5 min. In all the experiments, the flush volume and purge time were fixed at 100% and 100 s, respectively. Extracts were filtered with a 0.45 μm nylon syringe filter, evaporated to a volume of ca. 0.5 mL, and adjusted to 1 mL with the extraction solvent and analysed by GC-MS. Figure 2 shows the extraction efficiencies for the four solvents for nine representative compounds. The responses in Figure 2 were normalized with respect to the responses obtained with ethyl acetate. It was found that the higher the polarity of the extraction solvent, the more complex the visual appearance of the corresponding extracts. In this sense, methanol extracts were cloudy and difficult to filter. As seen in Figure 2, in general the best results were obtained when using ethyl acetate, therefore, it was used as extraction solvent thereafter.

As commented in the introduction, house dust is a complex matrix, which contains a large range of organic contaminants[1]. In order to enhance selectivity and eliminate interferences from the extracts, four sorbents were tested as in cell clean-up sorbents: C_{18}, silica, alumina and florisil. Fractions of 0.5 g of pooled house dust spiked at 20 μg g^{-1} where mixed and dispersed in a mortar with 1 g of the above sorbents. For these experiments the PLE conditions were the same than those described above for the solvent optimization (1 single cycle of 5 min at 80°C and 1500 psi) using ethyl acetate as extraction solvent. The chromatograms obtained by GC-MS with each sorbent were compared with

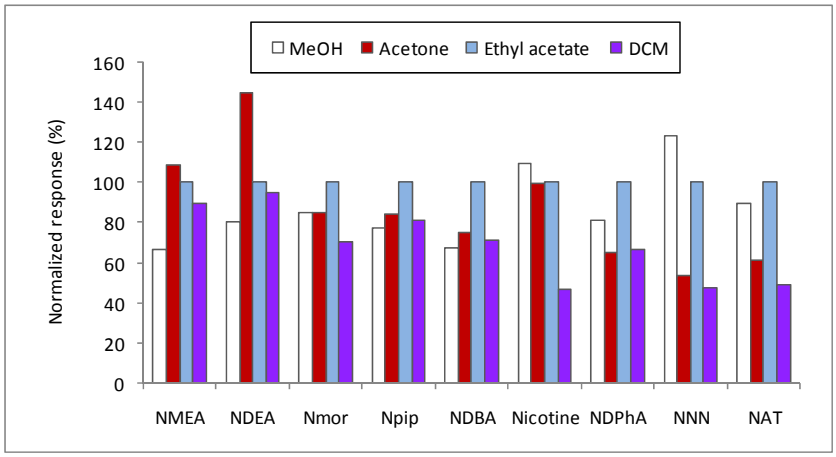


Figure 2. Influence of the solvent on the efficiency of the extraction process. (See text for PLE extraction conditions).

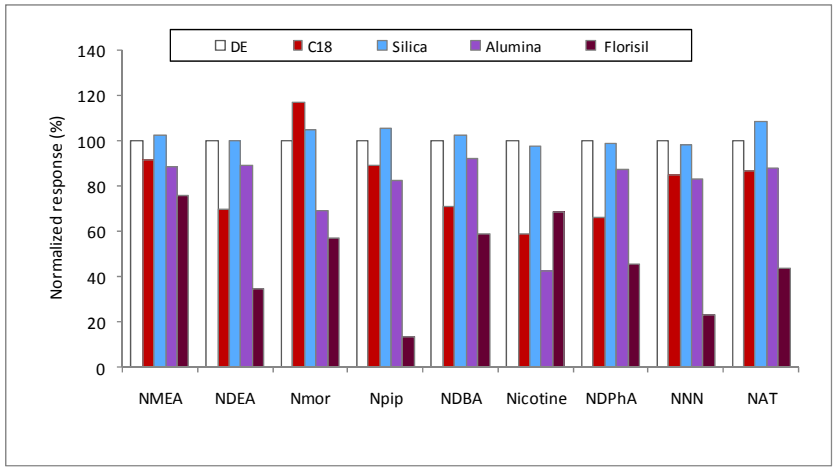


Figure 3. Influence of the kind of clean-up sorbent on the efficiency of the extraction process. Extractions were performed in 1 cycle at 80 ºC, 1500 psi, 5 min, 100% flush volume and 100 s of purge time.

those obtained with diatomaceous earth (DE), which is a non-retentive inert sorbent. Figure 3 shows the normalized response obtained with the different clean-up sorbents for nine representative target compounds with respect to the DE extracts (without clean-up). As seen in the figure, the least retentive sorbent for the target compounds was silica, the responses obtained for the target compounds with 1 g of this sorbent being similar to those obtained with DE. The signal of some compounds was higher with silica than with DE because the elimination of interferences made the peaks of the target compounds better to quantify. Florisil was in general the most

retentive sorbent. Regarding the reduction of co-extracting interferences, C_{18} did not lead to any significant reduction of them in comparison with diatomaceous earth; however cleaner extracts and less complex GC-MS chromatograms were achieved with silica, florisil and alumina. In light of these results, silica was chosen as the clean-up sorbent for the next experiments. Next the optimal amount of silica to be used was tested from 0.5 to 2.0 g. Amounts higher than 1 g led to a slight decrease in the responses. Therefore, 1 g of silica was fixed for the in-cell clean-up.

The effects of extraction temperature, time and number of cycles on the efficiency of the extraction were simultaneously evaluated using a multifactorial design $3^2 2^1$ of 18 experiments. Table 1 summarises the factors and levels selected for the design. The factor levels were selected based on previous house dust studies[20, 23, 33]. Statistical analysis was carried out with Statgraphics-Plus 5.1 (Magnugistic, Rockville, MD, USA). In all experiments,

Table 1. Factors and levels selected for the $3^2 2^1$ design.

Factors	Lower	Intermediate	Upper
Temperature (°C)	80	100	120
Time (min)	5	10	15
Cycles	1	-	3

the pressure was set at 1500 psi (enough to maintain ethyl acetate in a liquid state in this range of temperatures), flush volume at 100% and purge time at 100 s (until the extraction cell content was completely dry). As an example of the results, Figure 4 shows the fitted response surface for NDPA at 3 cycles. Similar response surfaces were obtained for most of the target compounds. In general, time increases the chromatographic responses up to 10 min, except for NDMA whose responses were higher using longer extraction times. Regarding the effect of temperature, in general, responses were greater at higher temperatures. However, for most compounds at 10 min of extraction responses at 120°C were similar of slightly lower than those obtained at 100°C. Furthermore, the chromatograms of the dust extracts at 120°C showed more co-extraction interferences, which made the quantification of the target compounds difficult. Therefore, 10 min of extraction time and a temperature of 100°C were selected as a compromise between the results. Finally, since the number of cycles of 10 min each had a slightly positive effect for most compounds, three cycles were selected thereafter. The optimized conditions for the PLE extraction are summarized in Table 2.

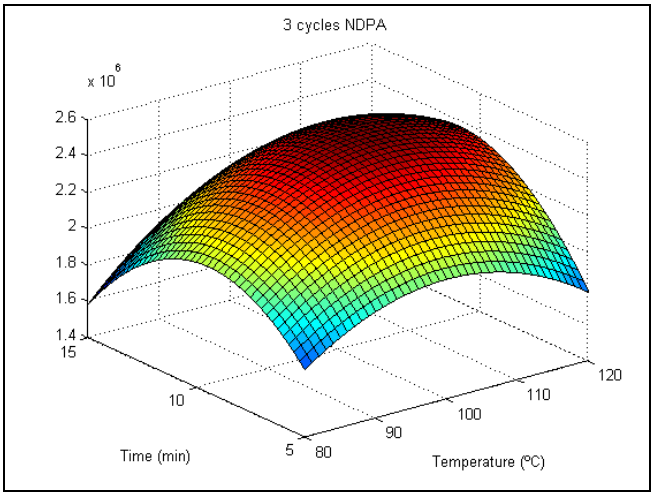


Figure 4. NDBA response surface for the extraction temperature against the extraction time for 3 cycles.

Table 2. Optimized conditons for the pressurized liquid extraction of the nitrosamines in house dust.

Pressurized liquid extraction	
Amount of sample	0.5 g
Solvent	Ethyl acetate
Cell volume	11 mL
No. of cycles	3
Static time	10 min
Temperature	100 °C
Pressure	1500 psi
Flush volume	100 %
Purge time	100 s

3.3. Method validation

Once PLE parametres were optimized, the method was validated using GC×GC-NCD determination. First the main instrumental parameters of the GC×GC-NCD system were evaluated, which are summarized in Table 3. The instrumental limits of detection (LODs) and limits of quantification (LOQs) were calculated based on the standard deviation at low concentrations (10 pg of each target compound). LODs were calculated according to EPA protocol 40 CFR 136[34] multiplying the Student t-value (n=10, 95% confidence level) per the standard deviation of 10 replicates and LOQs as ten times the standard

deviation. The combination of comprehensive GC with the NCD detection demonstrated a high sensitivity allowing limits of detection (LODs) and limits of quantification (LOQs) at low pg levels, ranging from 1.7 to 7.3 pg and from 7.2 to 31.5 pg, respectively. Linearity was good for all the target compounds with correlation coefficient values (r^2) between 0.9915-0.9994 for the linearity ranges shown in Table 3. Instrumental repeatability was under 5% for a low calibration level (50 pg, n=5).

The whole method (in-cell clean-up PLE GC×GC-NCD) parameters were evaluated with spiked samples of house dust at a low and a high calibration level (1 and 50 μg g^{-1}, respectively). Repeatability and reproducibility between days were below 8% RSD for all the target compounds (n=5). To calculate recoveries, the peak areas obtained by spiking the pooled house dust at the two calibration levels were compared with a calibration curve obtained by direct injection of the standards. As shown in Table 4 recoveries were similar for both levels and were higher than 80% for the majority of the target compounds. The most volatile N-nitrosamines, such as NDMA, NMEA and NDEA showed lower recoveries probably because were partially lost during the evaporation process.

Table 3. Main instrumental parameters for the GCxGC-NCD system: first and secon dimension retention times (t_R), limit of detection and limit of quantification and linear range expressed in pg.

Compound	1st t_R (s)	2nd t_R (s)	LOD (pg)	LOQ (pg)	Linear range (pg)
NDMA	470	1.46	1.7	7.2	7-25000
NMEA	565	1.54	1.7	7.4	7-40000
NDEA	670	1.58	1.7	7.3	7-15000
NDPA	970	1.62	1.2	5.3	5-40000
NPYR	995	1.94	1.7	7.5	7-25000
NMOR	995	1.94	1.6	6.9	7-25000
NPIP	1070	1.88	1.5	6.3	6-30000
NDBA	1300	1.64	1.9	8.3	8-40000
Nicotine	1460	1.8	7.3	31.5	32-20000
NDPhA	1880	2.16	3.0	13.1	13-25000
NNN	2075	2.58	4.3	18.8	19-25000
NAT	2135	2.60	3.0	12.8	13-20000
NAB	2160	2.56	2.8	12.1	12-25000
NNK	2295	2.82	4.2	18.2	18-25000
NNAL	2400	3.08	7.1	30.8	31-15000

Table 4. Method parametres: recoveries of pooled spiked house dust sampes spiked at 1 μg g^{-1} and 50 μg g^{-1}, method detection limit (MDL) and method quantification limit (MQL), expressed in ng g^{-1}.

Compound	Recovery		LOD (ng g^{-1})	LOQ (ng g^{-1})
	1 μg g^{-1}	50 μg g^{-1}		
NDMA	56	53	5.8	25.3
NMEA	76	75	4.5	19.5
NDEA	82	79	4.1	17.7
NDPA	97	93	2.5	10.9
NPYR	98	102	4.0	17.4
NMOR	86	82	3.3	14.1
NPIP	81	80	3.6	15.5
NDBA	85	81	4.5	19.4
Nicotine	92	88	15.8	68.5
NDPhA	101	97	6.0	25.9
NNN	99	101	8.7	37.5
NAT	98	99	6.0	25.9
NAB	98	101	5.6	24.4
NNK	106	103	8.4	36.4
NNAL	101	98	14.2	61.6

Since recovery values were similar for both calibration levels, no matrix effects were observed and quantification was performed by external calibration. Method detection limits (MDLs) ranged between 2.5 ng g^{-1} for NDPA and 15.8 ng g^{-1} for nicotine and method quantification limits (MQLs) were from 11 ng g^{-1} to 68 ng g^{-1} for the same compounds. A previously reported MDL of nicotine in house dust[19] using a GC and nitrogen-phosphorus detection was similar (20 ng g^{-1}).

3.4. Analysis of house dust samples

The optimized in-cell clean-up PLE GC×GC-NCD method was applied for the determination of nicotine and the target N-nitrosamines in house dust samples from smoking and non-smoking homes (four samples of each). As an example, Figure 5 shows the separation of ON compounds using GC×GC-NCD from one of the non-smoking samples. Over 60 ON compounds including Nicotine, N-nitrosamines and TSNAs were seen. The chromatogram is presented as a contour plot with the retention times on columns 1 (indicating decreasing volatility) and 2 (indicating increasing polarity) on the X and Y-axes, respectively. Peak identification is based primarily on retention times of standard compounds. Each spot on the chromatogram represents an individual

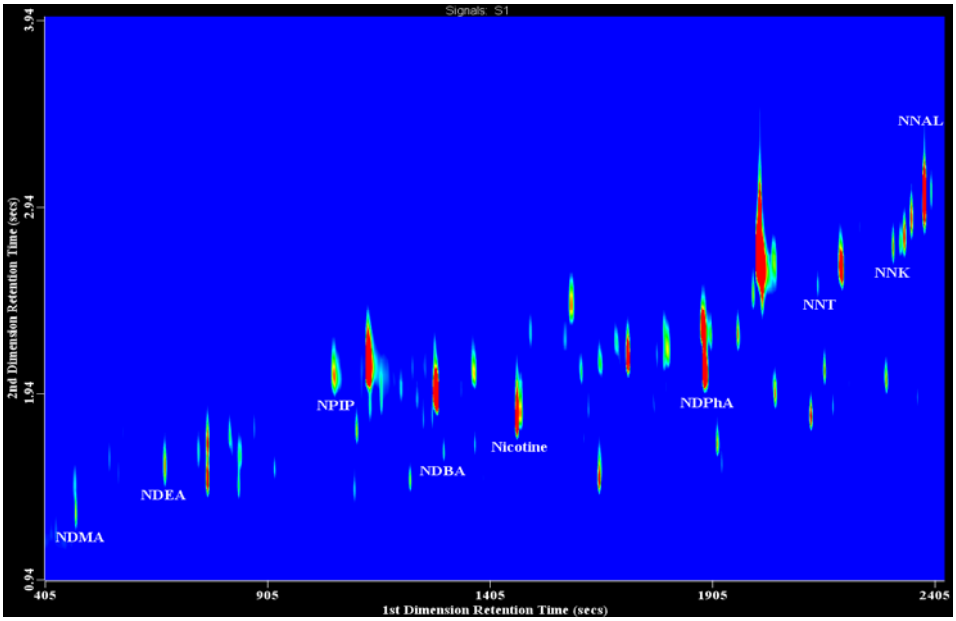


Figure 5. GC×GC-NCD chromatogram of non-smokers' household dust. The peaks of the indentified target compounds are indicated.

ON compound. The signals corresponding to the target compounds were found in this sample. As it can be seen, despite the complexity of the extracts, very simplified chromatograms were obtained using the optimized method.

A summary of the average, maximal and minimal concentrations found in the non-smoking and smoking households' dust samples is presented in Table 5. NPyr and NMor were quantified together because of their similar retention times. As expected, total concentrations of these ONs were in general higher in smokers' samples than in those of non-smokers', the average total concentrations being approximately 3-fold higher in smokers' house dust.

In some of the samples, all the target compounds were detected. The most abundant ON in non-smoking samples was NDPhA with values up to 4.15 μg g^{-1}. Other abundant N-nitrosamines in these samples were NMEA (up to 2.89 μg g^{-1}) and NDEA (up to 2.81 μg g^{-1}). Nicotine was also one of the most abundant ONs in non-smokers' dust with concentrations ranging from 1 μg g^{-1} to 2.83 μg g^{-1}. It was however the most abundant compound in smokers' dust samples with concentrations from 1.27 μg g^{-1} to 21.6 μg g^{-1} (more than 7-fold higher than in non smokers' dust). Nicotine concentrations found here were lower than those found in house dust samples in Baltimore (USA), that showed median nicotine concentrations of 11.7 μg g^{-1} in non-smoking

Table 5. Average, maximal and minimal concentrations of the target compounds found in the samples, expressed in μg g^{-1}.

Compound	Non-smoking			Smoking		
	Average	Max	Min	Average	Max	Min
NDMA	0.45	1.11	0.10	0.29	0.79	0.48
NMEA	0.77	2.89	0.05	0.35	0.63	0.17
NDEA	0.92	2.81	0.23	0.32	0.90	0.03
NDPA	0.26	0.48	0.14	0.67	1.85	0.08
NMor/NPyr	0.11	0.15	n.d.	0.25	0.39	n.d.
NPip	0.67	0.85	n.d.	0.54	0.99	n.d.
NDBA	0.11	0.13	n.d.	1.22	1.98	n.d.
Nicotine	1.91	2.83	0.95	14.7	21.6	1.27
NDPhA	2.08	4.15	1.00	4.46	13.7	0.12
NNN	0.12	0.23	<MQL	0.31	0.46	n.d.
NAT	0.35	0.42	n.d.	3.28	6.54	n.d.
NAB	0.25	0.39	n.d.	0.67	0.93	n.d.
NNK	0.55	0.68	0.42	0.89	2.29	0.24
NNAL	2.02	3.68	n.d.	n.d.	n.d.	n.d.
Total	9.60	12.3	3.53	26.3	38.9	3.12

n.d., values under the method detection limit
<MQL, values uder the method quantification limit

homes and 43.4 μg g^{-1} in smoking homes[19]. Regarding TSNAs, the most abundant were NAT and NNK with values of up to 6.54 μg g^{-1} and 2.29 μg g^{-1}, respectively in smokers' dust. However, NNAL was only detected in 3 non-smoking samples (in concentrations up to 3.68 μg g^{-1}) but was not detected in any of the smoking samples. As commented in the introduction, NNAL is the main degradation product of NNK, however NNAL concentrations did not show correlation with NNK concentrations in these house dust samples. The presence of nicotine and TSNAs in non-smokers' dust, may demonstrate the influence of outdoor pollution in indoor environments. In addition, smoking visitors could have visited these non-smokers' houses and contributed to their house dust with their dead skin, fabric fibres and hairs. Nevertheless, further investigation and determination of these TSNAs in more house dust samples is needed.

As commented before, previous studies have only determined nicotine in house dust[17, 19], but none of the N-nitrosamines selected in this study have been previously reported in this matrix. This study has demonstrated the presence of these highly carcinogenic target ON compounds (nicotine, N-nitrosamines and TSNAs) in both non-smoking and smoking household dust

and therefore there is inherent human exposure to these compounds through inhalation and/or ingestion of house dust. It should be noted that PLE is an effective extraction method and that the overall results show that GC×GC-NCD was an efficient technique for the analysis of volatile nicotine, N-nitrosamines and TSNAs from house dust.

Acknowledgments

The authors wish to acknowledge the financial support provided to this study by the Spanish Ministry of Science and Innovation through project CTM-2008-06847-C02-01 and the Department of Innovation, Universities and Companies of the Generalitat de Catalunya through project 2009 SGR 223.

REFERENCES

(1) Butte, W.; Heinzow, B., Pollutants in house dust as indicators of indoor contamination. *Rev. Environ. Contam. T.* **2002,** *175*, 1-46.

(2) Barro, R.; Regueiro, J.; Llompart, M.; García-Jares, C., Analysis of industrial contaminants in indoor air: Part 1. Volatile organic compounds, carbonyl compounds, polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *J. Chromatogr. A* **2009,** *1216*, (3), 540-566.

(3) Ott, W. R., Steinemann, A. C., Wallace, L. A., Eds. *Exposure Analysis*; Taylor & Francis: Boca Raton, FL., 2007.

(4) Lorber, M., Exposure of Americans to polybrominated diphenyl ethers. *J. Expos. Sci. Environ. Epidemiol.* **2008,** *18*, (1), 2-19.

(5) Sleiman, M.; Gundel, L. A.; Pankow, J. F.; Jacob, P.; Singer, B. C.; Destaillats, H., Formation of carcinogens indoors by surface-mediated reactions of nicotine with nitrous acid, leading to potential thirdhand smoke hazards. *Proc. Natl. Acad. Sci. U. S. A.* **2010,** *107*, (15), 6576-6581.

(6) Hecht, S. S.; Hoffmann, D., Tobacco-specific nitrosamines, an important group of carcinogens in tobacco and tobacco-smoke. *Carcinogenesis* **1988,** *9*, (6), 875-884.

(7) Thomas, X.; Chelghoum, Y., Cigarette smoking and acute leukemia. *Leuk. Lymphoma* **2004,** *45*, (6), 1103-1109.

(8) Hecht, S. S., Tobacco smoke carcinogens and lung cancer. *J. Natl. Cancer Inst.* **1999,** *91*, (14), 1194-1210.

(9) *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 89: Smokeless Tobacco and Some Tobacco-specific N-Nitrosamines;* World Health Organization Interantional Agency for Research on Cancer: Lyon, 2007; http://monographs.iarc.fr/ENG / recentpub / mono89.pdf.

(10) Hecht, S. S., Progress and challenges in selected areas of tobacco carcinogenesis. *Chem. Res. Toxicol.* **2008,** *21*, (1), 160-171.

(11) *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 17: Some N-nitroso Compounds;* World Health Organization Interantional Agency for Research on Cancer: Lyon, 1998; http://monographs.iarc.fr/ENG/Monographs/vol17/ volume17.pdf.

(12) Mahanama, K. R. R.; Daisey, J. M., Volatile N-nitrosamines in environmental tobacco smoke: Sampling, analysis, emission factors, and indoor air exposures. *Environ. Sci. Technol.* **1996,** *30*, (5), 1477-1484.

(13) Klus, H.; Begutter, H.; Scherer, G.; Tricker, A. R.; Adlkofer, F., Tobacco-Specific and Volatile N-Nitrosamines in Environmental Tobacco Smoke of Offices. *Indoor Built. Environ.* **1992,** *1*, (6), 348-350.

(14) Singer, B. C.; Revzan, K. L.; Hotchi, T.; Hodgson, A. T.; Brown, N. J., Sorption of organic gases in a furnished room. *Atmos. Environ.* **2004,** *38*, (16), 2483-2494.

(15) Singer, B. C.; Hodgson, A. T.; Nazaroff, W. W., Gas-phase organics in environmental tobacco smoke: 2. Exposure-relevant emission factors and indirect exposures from habitual smoking. *Atmos. Environ.* **2003,** *37*, (39-40), 5551-5561.

(16) Schick, S. F.; Glantz, S., Concentrations of the carcinogen 4- (methyinitrosamino)1-(3-pyridyl)-1-butanone in sidestrearn cigarette smoke increase after release into indoor air: Results from unpublished tobacco industry research. *Cancer Epidemiol. Biomarkers Prev.* **2007,** *16*, (8), 1547-1553.

(17) Matt, G. E.; Quintana, P. J. E.; Hovell, M. F.; Bernert, J. T.; Song, S.; Novianti, N.; Juarez, T.; Floro, J.; Gehrman, C.; Garcia, M.; Larson, S., Households contaminated by environmental tobacco smoke: sources of infant exposures. *Tob. Control* **2004,** *13*, (1), 29-37.

(18) Winickoff, J. P.; Friebely, J.; Tanski, S. E.; Sherrod, C.; Matt, G. E.; Hovell, M. F.; McMillen, R. C., Beliefs About the Health Effects of "Thirdhand" Smoke and Home Smoking Bans. *Pediatrics* **2009,** *123*, (1), E74-E79.

(19) Kim, S.; Aung, T.; Berkeley, E.; Diette, G. B.; Breysse, P. N., Measurement of nicotine in household dust. *Environ. Res.* **2008,** *108*, (3), 289-293. (20) Carpinteiro, I.; Abuin, B.; Rodriguez, I.; Ramil, M.; Cela, R., Pressurized solvent extraction followed by gas chromatography tandem mass spectrometry for the determination of benzotriazole light stabilizers in indoor dust. *J.*

Chromatogr. A **2010,** *1217*, (24), 3729-3735.

(21) Martínez, M. P.; Carrillo, J. D.; Tena, M. T., Determination of brominated diphenyl ethers (from mono- to hexa- congeners) in indoor dust by pressurised liquid extraction with in-cell clean-up and gas chromatography-mass spectrometry. *Anal. Bioanal. Chem.* **2010,** *397*, (1), 257-267.

(22) Maertens, R. M.; Yang, X. F.; Zhu, J. P.; Gagne, R. W.; Douglas, G. R.; White, P. A., Mutagenic and carcinogenic hazards of settled house dust I: Polycyclic aromatic hydrocarbon content and excess lifetime cancer risk from preschool exposure. *Environ. Sci. Technol.* **2008,** *42*, (5), 1747-1753.

(23) Canosa, P.; Pérez-Palacios, D.; Garrido-López, A.; Tena, M. T.; Rodríguez, I.; Rubí, E.; Cela, R., Pressurized liquid extraction with in-cell clean-up followed by gas chromatography-tandem mass spectrometry for the selective determination of parabens and triclosan in indoor dust. *J. Chromatogr. A* **2007,** *1161*, (1-2), 105-112.

(24) Llop, A.; Borrull, F.; Pocurull, E., Fully automated determination of N-nitrosamines in environmental waters by headspace solid-phase microextraction followed by GCMS- MS. *J. Sep. Sci.* **2010,** *33*, (23-24), 3692-3700.

(25) Zhou, J.; Bai, R.; Zhu, Y. F., Determination of four tobacco-specific nitrosamines in mainstream cigarette smoke by gas chromatography/ion trap mass spectrometry. *Rapid Commun. Mass Sp.* **2007,** *21*, (24), 4086-4092.

(26) Shah, K. A.; Karnes, H. T., A review of the analysis of tobacco-specific nitrosamines in biological matrices. *Crit. Rev. Toxicol.* **2010,** *40*, (4), 305-327.

(27) Jurado-Sánchez, B.; Ballesteros, E.; Gallego, M., Evaluation of stationary phases and gas chromatographic detectors for determination of amines in water. *J. Sep. Sci.* **2010,** *33*, (21), 3365-3373.

(28) Grebel, J. E.; Suffet, I. H. M., Nitrogen-phosphorus detection and nitrogen chemiluminescence detection of volatile nitrosamines in water matrices: Optimization and performance comparison. *J. Chromatogr. A* **2007,** *1175*, (1), 141-144.

(29) Adahchour, M.; Beens, J.; Brinkman, U. A. T., Recent developments in the application of comprehensive two-dimensional gas chromatography. *J. Chromatogr. A* **2008,** *1186*, (1-2), 67-108.

(30) Özel, M. Z.; Hamilton, J. F.; Lewis, A. C., New Sensitive and Quantitative Analysis Method for Organic Nitrogen Compounds in Urban Aerosol Samples. *Environ. Sci. Technol.* **2011,** *45*, (4), 1497-1505.

(31) Özel, M. Z.; Gogus, F.; Yagci, S.; Hamilton, J. F.; Lewis, A. C., Determination of volatile nitrosamines in various meat products using comprehensive gas chromatography-nitrogen chemiluminescence detection. *Food Chem. Toxicol.* **2010,** *48*, (11), 3268-3273.

(32) Jones, B. M.; Daughton, C. G., Chemi-luminescence vs kjeldahl determination of nitrogen in oil-shale retort waters and organonitrogen compounds. *Anal. Chem.* **1985,** *57*, (12), 2320-2325.

(33) Ramírez, N.; Marcé, R. M.; Borrull, F., Determination of parabens in house dust by pressurised hot water extraction followed by stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry. *J. Chromatogr. A* **2011;** DOI 10.1016/j.chroma. 2011.05.098.

(34) Analytical Detection Limit Guidance & Laboratory Guide for Determining Method Detection Limits; PUBL-TS-056-96; United States Environmental Protection Agency, Department of Natural Resources Laboratory Certification Program: Wisconsin,1996; http://www.dnr.state.wi.us/org/es/science/lc/outreach/-publications/lod%20guidance%20document.pdf.

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

We have demonstrated that the methods presented in this section, based on PLE, are extremely effective at determining organic contaminants in house dust. Taking into account the different characteristics of the target compounds of each study and the subsequent determination methods, different PLE strategies were developed: PHWE followed by SBSE and GC-MS for the determination of parabens, and sorbent in-cell clean-up PLE using an organic solvent for the determination of nicotine and N-nitrosamines. For both methods, the main PLE parameters were optimised including extraction solvent, the amount of house dust, the temperature, the time of extraction and the number of cycles of extraction.

For the determination of parabens, the addition of an organic modifier to the water was tested first. Although the presence of an organic solvent in the extraction mixture can help the PLE of organic contaminants, it had a negative effect for most of the target parabens, possibly because of a decrease in the acetylation and subsequent SBSE of the extracts. The amount of house dust extracted was a critical parameter to optimise in this study. Since house dust is a complex mixture, high amounts of dust provided high viscous extracts and were difficult to handle. Similarly, high temperatures also lead to viscous extracts. Therefore, the best recoveries were obtained using only 100 mg of house dust with a moderate temperature of extraction (80 °C). Once PLE parameters were fixed, SBSE conditions were also optimised. It should be mentioned that in this study, 1 mL of anhydride acetic showed the highest recoveries of the target parabens. This volume was 10 times higher than the one used in the study for the SBSE determination of parabens described in section 3.4, because higher concentrations of parabens and other phenolic compounds are present in house dust than in water samples.

The PHWE, SBSE and TD-GC-MS method presents several advantages compared to other analytical methods. First, it is environmentally-friendly because water is used as the extraction solvent. Furthermore, the use of SBSE followed by TD for the extraction of the parabens from the stir bar requires minimal manipulation of the sample and, therefore, the risk of external contamination is minimised. As an example of the reduced risk of external contamination, it should be pointed out that no signal of the target parabens was found in the procedural blanks. Recoveries for the target parabens were good for most target parabens, except for methyl paraben. The low yield obtained for methyl paraben can be explained by the low affinity of the acetylated derivative of this paraben for the stir bar PDMS phase. This was also observed in the study of the previous section. Nevertheless, LODs of this method ranged between 1.0 and 2.1 ng g^{-1}, which are similar to the lowest limits of previous studies reported in the literature [1], all of which used organic solvents for the extraction instead of water.

A different PLE strategy - in-cell clean-up PLE - was developed for the determination of N-nitrosamines and nicotine in house dust. In this study, GC-MS was used to optimise PLE parameters. Among the solvents tested, ethyl acetate showed the best extraction efficiencies overall. Regarding the amount of extracted house dust, 500 mg was used in this study to enhance the sensitivity of the method, because dust extracts obtained with ethyl acetate were less viscous and easy to handle than those found in the parabens study which were extracted with water. For the selection of the clean-up sorbent, the performance of C_{18}, silica, alumina and florisil was tested. Silica was shown to be the least retentive for the target nitrosamines. Silica also showed the best clean-up efficiency in previous in-cell clean-up PLE methods for the extraction of the target analytes from house dust samples [1,2].

The GC-MS system presented low sensitivity for the studied compounds, especially for TSNAs that presented LODs at the mg g^{-1} with these determination techniques. In order to further enhance selectivity and sensitivity, GC×GC followed by NCD detection was used to validate the method and quantify the samples. As seen in the paper, the in-cell clean-up PLE followed by GC×GC-NCD determination provided clear chromatograms in which the target compounds were easy to quantify. The high selectivity of the GC×GC and the use of a specific nitrogen detector provided very low instrumental LODs, ranging from 1.7 pg to 7.3 pg. LODs of the whole method ranged from 5.8 ng g^{-1} to 15.8 ng g^{-1}. The method developed also showed good linearity and repeatability. Moreover, quantitative recoveries were obtained, except for the most volatile N-nitrosamines (N-nitrosodimethylamine (NDMA) and N-nitrosomethylethylamine (NMEA)) which was probably due to their evaporation during the concentration step. The integration of the extraction and clean-up in one single step in the developed method provided extracts ready to analyse after the concentration to a lower volume.

Regarding the occurrence of organic contaminants, all of the target contaminants were found in some of the house dust samples selected for these studies. The highest concentrations of parabens found in house dust corresponded to methyl and propyl paraben, with average values of 912 ng g^{-1} and 425 ng g^{-1}, respectively. This was also the case with the results found in water samples (see section 3.4). Isopropyl paraben was the least-detected paraben. The concentrations of parabens found in the samples matched those found in previous studies [1,4].

On the other hand, nicotine and most of the target N-nitrosamines were found in both non-smoking and smoking house dust samples. However, the total average concentration of the target compounds in smoking house dust was nearly 3 times higher than those reported in non-smoking homes. Moreover, nicotine values were up

to 2.8 μg g^{-1} in non-smoking home dust samples and up to 21.6 μg g^{-1} in dust samples taken from smoking homes.

The presence of nicotine and TSNAs in both kinds of samples demonstrates the influence of outdoor pollution in indoor environments. Organic contaminants can reach indoor environments for instance by their diffusion on the air, or by their deposition on clothes and shoes. Another important conclusion is that it has been confirmed the harmful effect of tobacco smoke, even in non-smoking environments. As mentioned in the introduction, some of the nitrosamines studied here are considered carcinogenic to humans [5,6]. Considering the time people spend indoors and the estimated ingestion and inhalation of dust, exposure to volatile N-nitrosamines and TNSAs from house dust is not negligible and risk assessment research concerning this exposure should be done in the future.

References

[1] P. Canosa, D. Pérez-Palacios, A. Garrido-López, M.T. Tena, I. Rodríguez, E. Rubí, R. Cela, J. Chromatogr. A 1161 (2007) 105.
[2] I. Carpinteiro, B. Abuin, I. Rodriguez, M. Ramil, R. Cela, J. Chromatogr. A 1217 (2010) 3729.
[3] J.F. Hamilton, J. Chromatogr. Sci. 48 (2010) 274.
[4] P. Canosa, I. Rodríguez, E. Rubí, R. Cela, Anal. Chem. 79 (2007) 1675.
[5] IARC monographs volume 89. Available on: http://monographs.iarc.fr/ENG/Monographs/vol89/mono89-7E.pdf (accessed 27.04.2011).
[6] IARC monographs volume 17. Available on: http://monographs.iarc.fr/ENG/Monographs/vol17/volume17.pdf (accessed 27.04.2011).

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

4. CONCLUSIONS

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

The major conclusions that can be drawn from the studies presented in this Doctoral Thesis can be summarised as follows:

1. The methods developed in this Doctoral Thesis to determine volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), personal care products (PCPs) and N-nitrosamines showed limits of quantification low enough for their determination in air, particulate matter, settled dust, waste waters, and surface waters.

2. The enrichment into solid sorbents followed by thermal desorption (TD) is a useful technique for the determination of volatile organic compounds and semi-volatile PCPs (synthetic musks, insect repellents and parabens) in indoor and outdoor air, and it provides high recoveries. Compared with high-volume sampling techniques, TD is faster, requires lower preconcentration volumes and avoids the use of organic solvents. Furthermore, the risk of background contamination is minimised since the sorbent tubes are directly analysed after sampling.

3. When comparing the performance of TD and liquid desorption (LD) methods for the determination of VOCs in ambient air, the TD method showed, in general, better repeatability, recovery and LODs using lower sample volumes of air, whereas the LD showed cleaner blanks. In some cases, performance with real samples showed differences in the concentrations of the VOCs, with those determined by TD being generally higher.

4. Pressurised liquid extraction (PLE) is a suitable technique for the extraction of semi-volatile compounds from solid samples, such as airborne particulate matter and house dust. The use of water as an extraction solvent in combination with subsequent SBSE provided good LODs of parabens and avoided the use of organic solvents. It is demonstrated that the use of in-cell clean-up PLE strategies is useful for the reduction of matrix interferences.

5. Stir bar sorptive extraction (SBSE) using polydimethylsiloxane (PDMS) as a sorbent was found to be effective for the extraction of PCPs, such as musks and parabens, from water samples. The in-situ acetylation of the more polar analytes is presented as a good alternative for the extraction of parabens which show low affinity for the PDMS phase.

6. Comprehensive gas chromatography coupled with nitrogen chemiluminiscence detection (GC×GC-NCD) demonstrated a high selectivity and sensitivity for determining nicotine and N-nitrosamines.

7. Air emissions from an industrial waste water treatment plant (WWTP) showed high concentrations of some hazardous VOCs. Acrylonitrile and styrene were the most abundant and the concentrations of chloroform, 1,4-dioxane, ethylbenzene, 1,2,3-trimethylbenzene and 1,4-diethylbenzene were also high. These results indicate that VOC emissions from industrial WWTPs should be considered as an important source of hazardous air contaminants.

8. The high concentrations of PCPs found in air, dust and water samples reflect the widespread use of these compounds. Galaxolide and tonalide were the synthetic musks most found and methylparaben and propylparaben were the parabens most found in the different environmental matrices.

9. PCP concentrations found in effluents of urban and industrial WWTPs confirm that conventional biological waste water treatments do not remove the most polar PCPs efficiently. Higher removal efficiencies were found after reverse osmosis treatment. The presence of PCPs in river waters was also confirmed.

10. The presence of high concentrations of organic contaminants in house dust confirms the inherent human exposure to these pollutants through inhalation and/or ingestion of house dust. Furthermore, the presence of nicotine and tobacco-specific nitrosamines in non-smoking house dust samples demonstrates the influence of outdoor pollution in indoor environments.

11. Cancer risk assessment by inhalation of PAHs and VOCs around the most important chemical site in southern Europe was evaluated for the first time. Although none of these contaminants showed high individual cancer risk values, the overall estimated risk for both kinds of contaminants was higher than the WHO and USEPA recommended values, and therefore, should not be underestimated.

12. Risk assessment results of PAHs indicated that the contribution of gas phase PAHs to the cancer risk was not negligible. Furthermore, other VOCs besides benzene have also contributed to cancer risk. These results should be taken into account in future regulatory approaches.

Annex I. List of abbreviations

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

AcP	Acenaphthene
AcPy	Acenaphthylene
ADBI	Celestolide
AHTN	Tonalide
AHMI	Phantolide
Ant	Anthracene
APCI	Atmospheric pressure chemical ionization
APPI	Atmospheric pressure ionization
ATII	Traseolide
ATSDR	Agency for Toxic Substances and Disease Registry
BaA	Benzo[a]anthracene
BaP	Benzo[a]pyrene
BbF	Benzo[b]fluoranthene
BeP	Benzo[e]pyrene
BFRs	Brominated flame retardants
BghiP	Benzo[g,h,i]perylene
BkF	Benzo[k]fluoranthene
BSTFA	N,O-bis(trimethylsylil)trifluoroacetamide
BTEX	Benzene, toluene, ethylbenzene and xylenes
CAR	Carboxen
CE	Capillary electrophoresis
CFME	Continuous flow microextraction
Chr	Chrysene
CI	Chemical ionization
CIS	Cooled injection system
CNTs	Carbon nanotubes
DahA	Dibenzo[a,h]anthracene
DBPs	Disinfection by-products
DCM	Dichloromethane
DEET	*N,N*-diethyl-*m*-toluamide
DLLME	Dispersive liquid-liquid microextraction
DOAS	Differential optical absorption spectroscopy analyser
DPMI	Cashmeran
DS-MS	Direct air sampling mass spectrometry
DVB	Divinyl benzene
EDC	Electron capture detector
EDCs	Endocrine disrupting compounds
EI	Electron impact
EN	European Normative
EOCs	Emerging organic contaminants
ESI	Electrospray ionization

EU	European Union
FID	Flame ionization detector
Flu	Fluorene
FluT	Fluoranthene
FTIR	Fourier-transform infrared spectrometry
GC	Gas chromatography
GC×GC	Comprehensive two-dimensional gas chromatography
GGFs	Glass fibre filters
HFLPME	Hollow-fibre liquid-phase microextraction
HHCB	Galaxolide
HHSE	Headspace sorptive extraction
HILIC	Hydrophilic interaction chromatography
HS	Head space
IARC	International Agency for Research on Cancer
Ind	Indeno[1,2,3-c,d]pyrene
IRIS	Integrated Registration Information System
IT	Ion trap
LC	Liquid chromatography
LCR	Lifetime cancer risk
LD	Liquid desorption
LLE	Liquid-liquid extraction
LOD	Limit of detection
LOQ	Limit of quantification
LPCI	Low pressure chemical ionization
LPGC	Low pressure gas chromatography
LPME	Liquid-phase microextraction
LVI	Large volume injection
MAE	Microwave assisted extraction
MeP	Methyl paraben
MEPs	Microextraction in packed syringe
MIPs	Molecularly-imprinted polymers
MISPE	Molecularly-imprinted polymer solid-phase extraction
MS	Mass spectrometry
MSPD	Matrix solid-phase dispersion
MWCNTs	Multi-walled carbon nanotubes
NAB	N'-nitrosoanabasine
NAT	N'-nitrosoanatabine
NCD	Nitrogen chimiluminiscence detector
NCI	Negative chemical ionization
NDBA	N-nitrosodi-n-butylamine
NDEA	N-nitrosomethylethylamine

NDMA	N-dimethylamine
NDPA	N-nitrosodi-n-propylamine
NIOSH	National Institute for Occupational Safety and Health
NMEA	N-nitrosomethylethylamine
NMor	N-nitrosomorpholine
NNAL	4-(methylnitrosoamino)-1-(3-pyridyl)-1-butanol
NNK	4-(methylnitrosoamino)-1-(3-pyridyl)-1-butanone
NNN	N'-nitrosonornicotine
NOCs	N-nitroso compounds
NDPhA	N-nitrosodiphenylamine
NPD	Nitrogen-phosphorous detector
NPip	N-nitrosopiperidine
NPyr	N-nitrosopyrrolidine
NTDs	Needle trap devices
OC	On-column
OSF	Organic solvent film
OSHA	Occupational Safety and Health Administration
PA	Phenanthrene
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCPs	Personal care pproducts
PDMS	Polydimethylsiloxane
PLE	Pressurised liquid extraction
$PM_{2.5}$	Particulate matter ≤2.5 µm
PM_{10}	Particulate matter ≤10 µm
POPs	Persistent organic pollutants
PPy	Polypyrrole polymers
PTR-MS	Proton transfer reaction mass spectrometry
PTV	Programmed temperature-vaporizer
PUF	Polyurethane foam
Pyr	Pyrene
Q	Quadrupole
QFFs	Quartz fibre filters
QqQ	Triple quadrupole
Q-TOF	Quadrupole- time-of-flight
Qtrap	Quadrupole-ion trap
RfC	Reference Concentration
RO	Reverse osmosis
SBSE	Stir bar sorptive extraction
SDME	Single-drop microextraction
SFE	Supercritical fluid extraction

SHS	Second hand smoke
SIM	Selected ion monitoring
SOA	Secondary organic aerosol
SPE	Solid-phase extraction
SPDE	Solid-phase dynamic extraction
SPME	Solid-phase microextraction
SVOCs	Semi-volatile organic compounds
SWCNTs	Single-walled carbon nanotubes
TD	Thermal desorption
TDU	Thermal desorption unity
TEFs	Toxic Equivalence Factors
THS	Third hand smoke
TOF	Time-of-fligh
TSNAs	Tobacco-specific nitrosamines
TSP	Total suspended particles
UHPLC	Ultra-high performance liquid chromatography
UR	Unit risk
US	Ultrasound
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VOCs	Volatile organic compounds
WHO	World Health Organization
WWTP	Waste water treatment plant

Annex II. Publications

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011

List of publications derived from this Doctoral Thesis:

- Determination of volatile organic compounds in industrial wastewater plant air emissions by multi-sorbent adsorption and thermal desorption-gas chromatography-mass spectrometry. *Int. J. Environ. Anal. Chem.* (DOI: 10.1080/03067310903584073), (section 3.1.1).

- Comparative study of solvent extraction and thermal desorption methods for determining a wide range of volatile organic compounds in ambient air. *Talanta* 82(2010)719-727, (section 3.1.2).

- Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites *Environ. Health Perspect.* (DOI: 10.1289/ehp.1002855), (section 3.2.1).

- Chronic risk assessment of exposure to volatile organic compounds in the atmosphere near industrial sites. *Environ. Int.* (submitted), (section 3.2.2).

- Development of a thermal desorption-gas chromatography-mass spectrometry method for determining personal care products in air *J. Chromatogr. A*, 1217(2010)4430-4438, (section 3.3.1).

- Development of a stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry method for determining synthetic musks in water samples. *J. Chromatogr. A*, 1218(2011)156-161, (section 3.4.1.).

- Simultaneous determination of preservatives and synthetic musks in water samples by stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry. *Talanta* (submitted), (section 3.4.2.).

- Determination of parabens in house dust by pressurised hot water extraction followed by stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry. *J. Chromatogr. A,* DOI: 10.1016/j.chroma.2011.05.098, (section 3.5.1).

- Determination of nicotine and N-nitrosamines in house dust by pressurised liquid extraction and two dimensional gas chromatography – nitrogen chemiluminescence detection. *Environ. Sci. Technol.* (submitted), (section 3.5.2).

UNIVERSITAT ROVIRA I VIRGILI
ORGANIC CONTAMINANTS IN ENVIRONMENTAL ATMOSPHERES AND WATERS
Noelia Ramírez González
DL: T. 1454-2011