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Potentiometric flow injection system for the determination of polyethoxylate nonionic surfactants using tubular ion-selective electrodes

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Abstract

A flow injection system for the determination of polyethoxylated nonionic surfactants is described. Potentiometric detection based on tubular flow-through ion-selective electrodes (ISEs) sensitive to this type of surfactants was used. As ion-exchanger, the plasticised PVC membrane incorporates the ion pair between the adduct of a nonionic surfactant with barium and tetraphenylborate. Two different membrane compositions were studied. They differed in the nonionic surfactant used in the ion-exchanger preparation: either nonylphenoxypolyethoxylate with 5 (Ig5) or 12 (Ig12) ethylene oxide units were used. Experimental results showed that the use of Ig5 membrane with a barium salt adjusting solution allowed lower detection limits, while Ig12 ISE with potassium salt solution presented enhanced sensitivity. Both FI systems were evaluated employing three different polyethoxylate standards, which could be determined down to ca. 10^{-5} M. Precision was 3% R.S.D. for $n = 50$ using repetitive injections of a 3×10^{-4} M Ig12 standard. Preliminary tests of an on-line preconcentration flow system employing the developed sensing devices are also shown.

Keywords: Flow injection system; Flow-through tubular ion-selective electrode; Nonionic surfactants; Alkylphenol polyethoxylates

1. Introduction

Surfactants are a relevant class of organic compounds, which are widely employed, and so expelled to natural water reservoirs. Although anionic surfactants are still the most produced, the use of nonionic surfactants (NIS), mainly alkylethoxylates, increased, due to their applicability in domestic and industrial fields [1].

The analysis of NIS in the environment is important not only because they are toxic, but also for their biodegradation metabolites that are more persistent than their parent compounds [2]. Lately, these compounds are receiving attention due to their suspected oestrogenic effects and their classification as endocrine disruptors [3].

Much effort is being placed on NIS determination at low levels in environmental samples [4]. Both *group methods* (which provide global measurements) and more *selective methods* are available for the analysis of these kind of surfactants [5]. An accepted global method for their control in most aqueous systems is the cobalt thiocyanate active substances (CTAS) method [6]. This spectrophotometric method has drawbacks

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such as low sample processing capability, complexity and low specificity, although sample sublation and ion-exchange ameliorate the last one.

Overall, chromatographic approaches are preferred because they allow an improved selectivity and individual NIS speciation [7]. However, increasing environmental concerns have fostered the development of automated analytical systems for environmental monitoring with added features for in situ, real time and remote operation. The use of chemical sensors as detectors integrated in automated flow-systems has proved to achieve simple, robust and automatic analysers for environmental monitoring [8].

On the other hand, ion-selective electrodes (ISEs) sensitive to NIS have already been reported [9,10]. They were plasticised poly(vinyl)chloride (PVC) membrane sensors, whose recognition element was a tetraphenylborate salt of the complex between the barium ion and an NIS polyethoxylate. To explain their response, Okada [11] suggested that polyethoxylates in solution interact with the metal cation (per example, barium) at the water/membrane interface, forming complexes. He points out that slopes of 50–70 or 30 mV per decade could be observed depending on the cation charge. Khmel'nitskaya and Kolokolov [12] applied these kind of sensors as indicator electrodes in the titration of NIS with tetraphenylborate solutions in the presence of barium salts. In a recent work, we optimised and characterised all-solid-state sensors based on these membranes to obtain stable, reproducible and long lived devices [13]. Additionally, an NIS electrode has recently been introduced commercially and applied for NIS titrations [14].

Flow injection analysis (FIA) has been applied to a large variety of analytes, but few publications concerning the analysis of NIS can be found. Most of them are based on chemiluminiscence [15], fluorimetry [16] or spectrophotometric detection [17–20]. Masadome et al. [21,22] reported a FI system for NIS, using potentiometric detection. The used sensors were a special type of ISE, which do not contain an electroactive agent, where their response is solely due to the plasticised membrane [23].

In this paper, a FI system is proposed for the global determination of NIS of the polyethoxylate type with potentiometric detection using especially designed, tubular flow-through, all-solid-state sensors. Preliminary tests with an on-line preconcentration flow system will be also presented. This system is designed to improve the detection limits, with the aim of a possible application for the unattended monitoring of NIS at trace levels.

2. Experimental

2.1. Apparatus

The FI system used for the determination of nonionic surfactants is depicted in Fig. 1. A two-channel flow system, used to adjust the ionic strength of the sample and a four-channel peristaltic pump (Gilson Minipuls 2) equipped with PVC pump tubing (Elkay, Boston, MA) were used. The sample was manually injected with a laboratory-made multifunctional rotary valve [24]. All used tubing had a 0.7 mm i.d. (Tecator, Hoganas, Sweden).

Potentiometric measurements were taken with an optoisolated potentiometric ISE Amplifier (MBT Environmental, Barcelona, Spain), which allows the simultaneous use of four indicator electrodes. The reference device was a double junction Ag/AgCl electrode (Orion 900200). The solution employed in the salt bridge was the same used as the adjusting solution. Adaptors for the reference electrode and the grounding electrode were described earlier [25].

The system was computer-controlled, using a 40 MHz AT-386 computer with an A/D and I/O card (Advantech PC Lab 812 PG, Taiwan), and especially developed software using QuickBASIC [26].

2.2. Reagents and solutions

The nonionic surfactants used as reference materials were standard-grade polyethoxylates. The hydrophobic chains were a nonylphenoxide, Igepal CO-720 (Ig12) (Aldrich, USA), an octylphenoxide, Triton X-100 (Fluka, Switzerland) and a lauryl alcohol polyethoxylate (LAP) (Kao Soaps, Barcelona, Spain) with 12, 9 and 9 ethylene oxide units, respectively. The standard solutions were prepared daily by diluting a 1×10^{-2} M stock solution. Stock solutions were prepared every month by weighing directly the corresponding salt and they were stored at 5°C to prevent degradation. To prepare the LAP stock solution, a 75% (v/v) ethanol solution was needed to dissolve the solid.

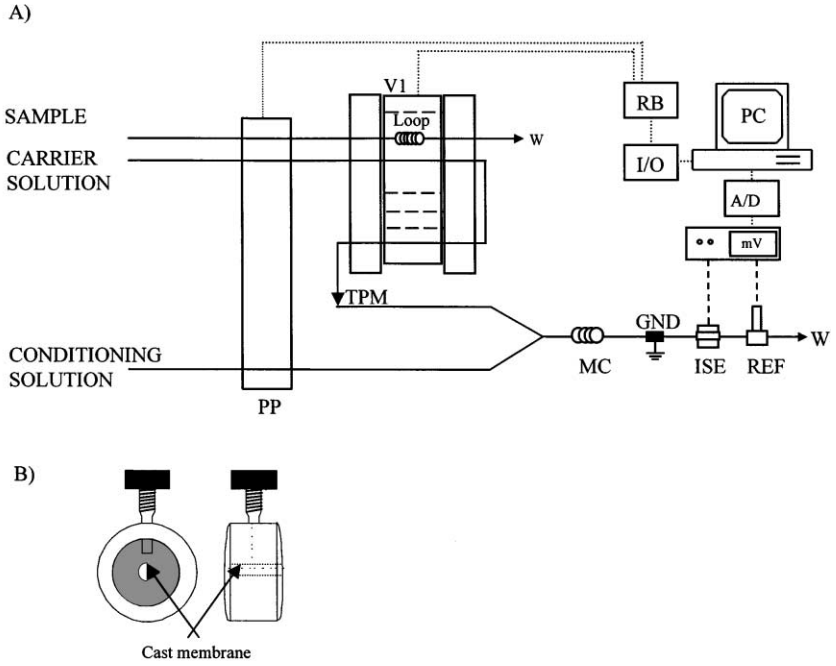

Fig. 1. (A) Manifold used for the direct determination of NIS. PP, peristaltic pump; V1, multifunctional rotary valve with a defined injection volume (loop); TPM, to potentiometric measurements; W, waste; MC, mixing coil; GND, grounding electrode; ISE, surfactant electrode; REF, reference electrode; PC, personal computer; A/D, data acquisition card; I/O, digital control card; RB, relay board; (···) communication lines. Carrier solution: distilled water. (B) Detail of the flow-through tubular electrode.

Reagents used for the preparation of the electrode membranes and the working solutions were of analytical reagent grade. Doubly distilled water was used throughout except the carrier solution, which was distilled water.

2.3. Preparation of flow-through tubular ISEs

The indicator electrode was an all-solid-state, tubular, flow-through electrode (see Fig. 1). It has a poly(vinyl)chloride (PVC) matrix membrane selective to nonionic surfactants, which was cast in the inner wall exposed to the flow. This membrane was prepared following procedures previously developed in our laboratories [27]. The plasticised membrane employed a tetraphenylborate salt of the complex formed between the barium ion and a polyethoxylate NIS, being the latter the electroactive recognition element responsible for the selectivity. Two different membranes were tested, which differed in the nature of the barium complex used. Both were nonylphenoxypolyethoxylates, whose differences were in the number of ethylene oxide units, 5 (Ig5/ISE) or 12 (Ig12/ISE).

The PVC matrix membranes were prepared by dissolving 7.0 wt.% of the barium-ethoxylate complex, 30.0 wt.% of PVC (Fluka) and 63.0 wt.% of *o*-nitrophenyloctyl ether (Fluka) as the plasticiser, in tetrahidrofuran (5 ml in correspondence to 100.0 mg of PVC). The ISEs were conditioned for 12 h. in a 1×10^{-3} M Ig12 solution, previously to its first use.

3. Results and discussion

3.1. Optimisation of the FI system

3.1.1. Injected volume and flow rate

The performance of the developed ISEs, such as response characteristics, selectivity and pH dependence, has been previously described for a conventional potentiometric design [13].

However, when working in a flow system, the hydrodynamic parameters (tube lengths and flow rates) and the composition of the adjusting solution have to be optimised to achieve the maximum sensitivity of the system and to maximise the sample throughput. Two electrode units of each membrane (Ig5 and Ig12) were used for this optimisation.

First, the injection volume was studied, using 0.01 M potassium sulphate as an ionic strength adjusting solution. It was verified that an increase of the injected volume of the sample produced an increment of the measured signal until it reached a steady value for injected volumes greater than 300 μl. This corresponded to peak heights of 43 and 53 mV for the Ig5 and Ig12 membranes, respectively. Nevertheless, 200 μl were taken as the optimum value, in order to reduce the return-to-baseline time.

The flow rate influences the response of the ISEs and the return-to-baseline time. The high response time of this type of membranes has already been described [28]. Therefore, the flow rate influence on the electrode response should be evaluated. This was made by varying the total flow from 0.9 to 4.5 ml min^{-1}, but we did not notice significative variations in the peak heights. Apart from this, an increase of the flow rate within the above-described range causes a reduction of 8–2 min in the return-to-baseline time (taken at the 90% recovery). Perhaps, flow rates lower than 0.9 ml min^{-1} could allow higher responses, but working with so low flow rates could reduce dramatically the sample throughput. As a compromise between both opposed effects, the flow rate was kept constant at 2.5 ml min^{-1} in all-subsequent experiments, which can be considered usual for these systems.

3.1.2. Adjusting solution and ionic strength

The composition of the adjusting solution is another variable of significance. A certain saline level is required to buffer the ionic strength (I) of the samples and to define an appropriate conductivity of the carrier solution flowing through the potentiometric detector. The saline composition also influences the response rate, the wash-out time of the ISEs, and their performance characteristics. Specially, it can affect the upper limit of linear response (ULLR), because of the dependence of the surfactant critical micelle concentration (CMC) on the ionic media used [26]. Several different common salts were assayed for the adjusting solution. First, potassium sulphate, potassium chloride and barium chloride were compared to study the anion or the cation influence on the response of the membranes. These specific monovalent and bivalent ions were chosen because of their previously observed effect on the sensitivity of the sensor [13].

Table 1 displays the performance characteristics of the ISEs obtained in the different assayed media. The calibration curves were built plotting the peak height (H) versus the logarithm of NIS concentration (ranging from 1×10^{-6} to 1×10^{-3} M). Higher concentrations were not used because of the CMC limit. The sensitivity (s) of the electrodes was obtained by linear regression in the linear response range. The detection limit (DL) was estimated from a nonlinear curve fit of all the experimental data [29].

From the table, we can observe that the nature of the anion used does not show any influence. Different response patterns can be observed if we compare results when the cationic component of the adjusting solution salt is varied. For instance, with the

Table 1
Calibration parameters obtained with both membranes using different adjusting solutions with the same ionic strength ($I = 0.1$ M)[a]

ISE	Adjusting solution	s[b] (mV per decade)	r^2	n	Linear range (M)	Detection limit (M)
Ig5	K_2SO_4	32.56 (±5)	0.997	4	2×10^{-4}–1×10^{-3}	2.0×10^{-4}
	KCl	33.87 (±7)	0.997	4	3×10^{-4}–1×10^{-3}	2.5×10^{-4}
	$BaCl_2$	30.73 (±2)	0.998	6	2×10^{-5}–3×10^{-4}	1.2×10^{-5}
Ig12	K_2SO_4	42.38 (±4)	0.996	6	6×10^{-5}–1×10^{-3}	2.9×10^{-5}
	KCl	46.97 (±3)	0.998	6	6×10^{-5}–1×10^{-3}	3.8×10^{-5}
	$BaCl_2$	21.25 (±1.1)	0.999	6	2×10^{-5}–3×10^{-4}	$1.3 \times \cdot 10^{-5}$

[a] Nonionic surfactant standard, Ig12; flow rate, 2.5 ml min^{-1}; injected volume, 200 μl; r^2, correlation coefficient; n, number of points. Values in parentheses correspond to uncertainly intervals expressed at a 95% confidence level.

[b] Calibration equation: $H = a + s \times \log$ [Ig12].

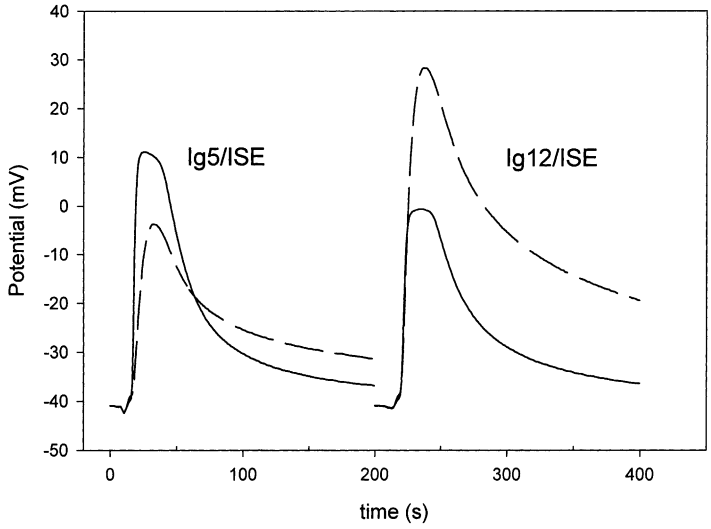

Fig. 2. Influence of the adjusting solution on the FIA peaks recorded. Adjusting solution: (—) $BaCl_2$ ($I = 0.1$ M); (— —) KCl ($I = 0.1$ M). Standard, 1×10^{-3} M Ig12; flow rate, 2.5 ml min^{-1}; injected volume, 200 μl.

divalent Ba^{2+} ion, the linear range is shifted to the lower range concentrations, obtaining lower detection limits. When potassium solutions were used, the linear range is wider and, especially with the Ig12/ISEs, the sensitivities obtained are much higher. The reason that causes the ULLR change is the CMC, a variable that is dependent on the media. We could conclude that the cation influence is much more significant for the Ig12/ISEs, because of possible changes in the adduct composition inside the membrane (Ba^{2+}–K^+ exchange) [13]. On the other hand, it was also observed that the return-to-baseline was quicker (2 min in all the concentration range) when using the barium solution. The shape of the obtained FIA peaks can be compared in Fig. 2.

Next, the effect of the ionic strength was studied. Fig. 3 shows the calibration plots obtained with an Ig12/ISE in potassium sulphate as the adjusting solution, where three different concentration levels were tested. Usually, the expected behaviour would be that when the ionic strength was increased, the interference effects would be higher and so the peak heights would be smaller. Despite this, we can see from this figure that the higher the ionic strength, the higher the system sensitivity (i.e. its slope). This is the way in which high potassium concentrations favour the Ig12/ISE performance. On the other hand, when working with a barium solution and varying the ionic strength from $I = 0.01$ to 0.1 M, the sensitivity does not improve noticeably for the Ig12/ISEs. The increase for the Ig5/ISEs is approximately 2 mV per decade. Consequently, the ionic strength chosen was 0.1 M in

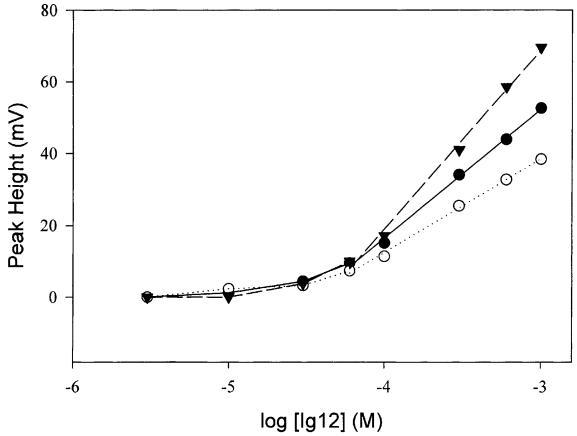

Fig. 3. Calibration curves for Ig12 using an Ig12/ISE. Adjusting solution, K_2SO_4; ionic strength: (○) 0.001 M; (●) 0.01 M; (▼) 0.1 M. The equation curves obtained are, respectively: $H = 116.80\,(\pm 9) + 26.09\,(\pm 2) \times \log[\mathrm{Ig12}]$ ($n = 5$, $r^2 = 0.997$); $H = 159.52\,(\pm 12) + 35.77\,(\pm 3) \times \log[\mathrm{Ig12}]$ ($n = 5$, $r^2 = 0.998$) and $H = 218.54\,(\pm 22) + 49.90\,(\pm 6) \times \log[\mathrm{Ig12}]$ ($n = 5$, $r^2 = 0.998$). Flow rate, 2.5 ml min^{-1}; injected volume, 200 μl.

Table 2
Characteristics of the optimised FI system

Optimised conditions	Ig5/ISE	Ig12/ISE
Adjusting solution	$BaCl_2$	K_2SO_4
Ionic strength	0.1 M	0.1 M
Flow rate	2.5 ml min^{-1}	2.5 ml min^{-1}
Injected volume	200 μl	200 μl
Return-to-baseline time[a] ($t_{90\%}$)	2 min	2–13 min
Sample throughput[b]	30 h^{-1}	30–5 h^{-1}

[a] Return-to-baseline times calculated for Ig12 standards from 2×10^{-5} to 1×10^{-3} M.

[b] Sample throughput calculated for Ig12 standards from 2×10^{-5} to 1×10^{-3} M.

order to obtain high sensitivities and a less noisy system.

Salts of other divalent ions and solutions using different proportions of barium and potassium were also tested, which did not yield any improvement.

The optimised conditions for the developed FI system are summarised in Table 2, with the observed return-to-baseline times when the Ig12 concentration standard went from 2×10^{-5} to 1×10^{-3} M. In this way, the sample throughput can be assumed to be 30 h^{-1} for the Ig5 system. For the Ig12 one, the sample throughput varied depending on the magnitude of the concentration. The different adjusting solutions selected for each ISE type ($BaCl_2$ or K_2SO_4) were further studied along time to evaluate their performance characteristics.

3.2. Evaluation of the FI system for the direct determination of NIS of the polyethoxylate type

Once the FI system was optimised, its evaluation was carried out. One main advantage of the developed system is the general response behaviour to different poyethoxylate NIS. This can allow the global determination of this group of surfactants. Table 3 shows the calibration parameters obtained with different NIS (Ig12, Triton X-100 and LAP). The data presented correspond to three electrode units and three calibrations realised per unit.

A first observation to the presented data is that the detection limit obtained with the system using Ig12/ISEs as detectors are worse than those obtained with the Ig5 devices. As expected, this responds to the different adjusting solutions used in each case. However, sensitivities of the Ig12 detectors are much higher. Therefore, the choice of the detector would depend on the nature of the sample to be analysed with the FI system. Apart from this, potassium sulphate is a commonly used salt in these systems, while the use of the barium solution may present problems related to the formation of precipitates.

In a work realised for the characterisation of the membranes [13], we found the interference effect of two ionic surfactants: sodium dodecylbenzenesulfonate (SDBS) (Carlo Erba) as anionic surfactant and cetyltrimethylammonium bromide (CTAB) (Panreac) as cationic surfactant. Hence, the response of the FI

Table 3
Calibration parameters obtained with the FI system in response to Ig12, Triton X-100 and LAP nonionic surfactants[a]

NIS	Parameters	Ig5/ISE	Ig12/ISE
Ig12	s (mV per decade)	29.65 (6)	50.34 (5)
	LR (M)	3.6×10^{-5}–3.0×10^{-4}	9.2×10^{-5}–9.0×10^{-4}
	DL (M)	1.1×10^{-5}	7.6×10^{-5}
	r^2 (n)	0.999 ($n = 5$)	0.996 ($n = 5$)
Triton X-100	s (mV per decade)	30.49 (7)	54.63 (1.6)
	LR (M)	6.1×10^{-5}–8.2×10^{-4}	1.1×10^{-4}–1.0×10^{-3}
	DL (M)	3.0×10^{-5}	9.1×10^{-5}
	r^2 (n)	0.996 ($n = 6$)	0.998 ($n = 5$)
LAP	s (mV per decade)	18.05 (6)	24.26 (7)
	LR (M)	2.9×10^{-5}–6.1×10^{-4}	1.1×10^{-4}–6.1×10^{-4}
	DL (M)	3.4×10^{-5}	7.9×10^{-5}
	r^2 (n)	0.998 ($n = 6$)	0.996 ($n = 4$)

[a] s, sensitivity; LR, linear response range; DL, detection limit; r^2, correlation coefficient; n, number of points. Values in parentheses correspond to absolute standard deviation values of three different units and three calibrations per unit.

system to these compounds was evaluated in this part of the study using the mixed solution procedure [30]. The study was done with the Ig12 standard solutions and the Ig12/ISE, with a constant added background of the interference substances: 1×10^{-5} M SDBS or 1.4×10^{-6} M CTAB. It is observed that CTAB was an important interference since the detection limit obtained in the presence of the cationic surfactant was 0.6 logarithmic units higher. However, the effect of SDBS could not be noticed at the concentrations levels tested. Although the estimate of selectivity coefficients (k^{pot}) from the Eisenman-Nikolskii formalism was not suitable due to the noncharged analyte [31], an approximation assuming single charged ions was made. The selectivity coefficients, calculated according [30] and taking into account the detection limit in absence of interferent, was $\log k^{pot}_{NIS,CTAB} = 0.81$. So, this can be considered a severe interference effect. Problems with cationic surfactants are related to interactions with the tetraphenylborate anion present in the membrane, as it has already been observed in batch studies [9,12].

The performance characteristics of the proposed system were studied over time. The lifetime of similar ISEs reported elsewhere was not longer than 1 month [9,10], working discontinuously. However, the response characteristics of the sensors used in the present work did not deteriorate after 3 months of use. This is a remarkable feature, considering wearing effects caused by the continuous flow.

Finally, the precision of the system was checked with repetitive determinations of a 3×10^{-4} M Ig12 standard. After 50 injections the system showed a relative standard deviation (R.S.D.) less than 3%.

3.3. FI system for the determination of NIS of the polyethoxylate type at trace levels

The main problems involved in the determination of NIS in the environment are its low concentration levels and the complexity of environmental sample matrices that call for sample preconcentration and purification. This has traditionally been carried out by off-line methodology, but recently the on-line mode has proved several advantages [32].

In our laboratories, we developed an automated FI system for the determination of trace levels of anionic surfactants in river water and wastewater using ISEs sensitive to these surfactants [29]. The system included an on-line preconcentration procedure, which also allowed the purification of the analytes. It was achieved by the use of an on-line laboratory-made microcolumn packed with a polymeric sorbent (LiChrolut EN, Merck). This sorbent, which is based on a styrene-divinylbenzene resin, establishes hydrophobic bonds with the analytes. So, the presence of potential interferents such as inorganic compounds was not a limitation because they do not present retention. The way to implement the manifold of this flow system is depicted in Fig. 4.

The previously developed system was used to check the low level NIS determination employing preconcentration of Ig12 standards. The flow conditions where those previously optimised (see Table 3), and 8 ml

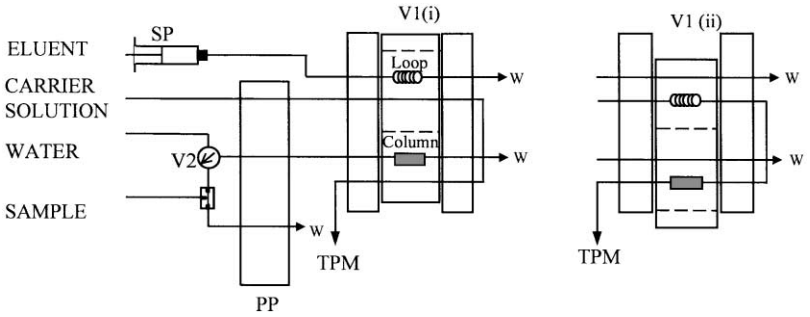

Fig. 4. Detail of the on-line preconcentration system used for the determination of low levels of NIS in environmental samples. SP, syringe pump; PP, peristaltic pump; V1, multifunctional rotary valve; V2, 3-way solenoid valve; W, waste; TPM, to the potentiometric measurements; carrier solution, distilled water. V1 operation: (i) preconcentration stage; (ii) elution and determination stage.

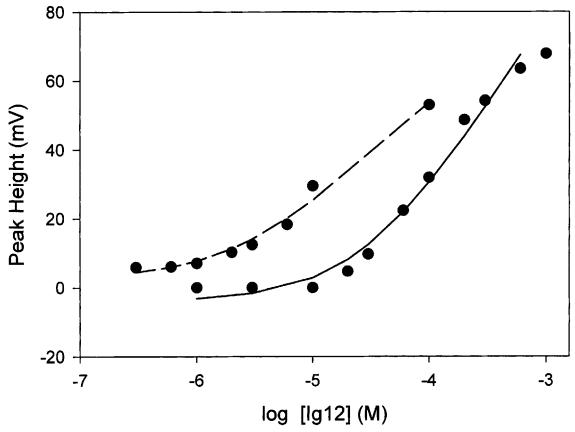

Fig. 5. Calibration curves for Ig12 standard using the Ig12/ISE system. The detection limits obtained with the direct determination system (—) and the on-line preconcentration system (— —) are 2.9×10^{-5} and 2.3×10^{-6} M, respectively. Preconcentration conditions: preconcentration volume, 8 ml; eluent, 75% acetonitrile; eluent volume, 100 μl (see Table 3 for the conditions of the direct system).

of standards were preconcentrated and then eluted by 100 μl of 75% acetonitrile. Fig. 5 shows the preliminary calibration curves obtained using the system with preconcentration and compared with the direct analysis system (Section 3.1). In this way, we can observe how the detection limit improves with the preconcentration step from 2.5×10^{-5} to 2.3×10^{-6} M Ig12.

Nevertheless, when working with these preconcentration conditions, the efficiency of the system for the determination of NIS is poorer than the previously developed system [29]. This is due to the worst detection limits of the ISEs sensitive to NIS. Therefore, nowadays we work towards the improvement of the detection limits of the on-line preconcentration FI system for the determination of NIS in environmental samples.

4. Conclusions

Two different automated FI systems for the direct determination of nonionic surfactants of the polyethoxylate type have been presented. Comparing them with the accepted spectrophotometric procedures for the global or group analysis of these compounds, this approach allows a simpler and more specific method. Selecting a proper ISE-adjusting solution, the manifold could be easily adapted to different applications, according to the characteristics of the samples.

With this simple approach, NIS can be determined down to ca. 10^{-5} M Ig12 with a sample throughput to up 30 per hour. The only critical interferences found are those of cationic surfactants or related compounds, which should be eliminated. In a final application of the determination of NIS in environmental surface waters, the presence of these substances is not expected, as the authors have checked with a related system [29].

The use of simple and stable reagents could enable an unattended, low-maintenance, automated water monitoring system to be developed. However, much work is necessary to improve the detection limit of the system to achieve environmental levels. Current efforts are directed in this way.

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Determination of polyethoxylated non-ionic surfactants using potentiometric flow injection systems. Improvement of the detection limits employing an on-line pre-concentration stage

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Abstract

In this paper, the universal determination of non-ionic surfactants (NIS) of the polyethoxylate type is attempted using flow-injection potentiometry. Two systems are proposed which use specifically developed tubular flow-through ion selective electrodes (ISEs). These are sensitive to NIS with an hydrophilic chain between 6 and 18 ethoxylate units, which are predominant species in the environment. An on-line pre-concentration system is designed with the aim of a possible application for the unattended monitoring of NIS in surface waters. This on-line pre-concentration is achieved by employing a column packed with a commercial solid phase extraction (SPE) sorbent for the enrichment and purification of the target analytes. The procedure outlined improves the detection limit of a direct system, decreasing it from 1×10^{-4} to 3×10^{-6} M by use of a pre-concentration volume of 40.0 ml and 200 μl of 75% acetonitrile in water as the eluent. Precision was estimated as 4% relative standard deviation (R.S.D.) ($n = 25$) for a 1×10^{-6} M (0.7 ppm) nonylphenol polyethoxylate with 12 ethoxylate units when 10.0 ml of sample are pre-concentrated. Finally, the on-line pre-concentration system is applied for the total NIS determination in environmental samples from Llobregat river basin of Barcelona area (NE Spain).

Keywords: Potentiometric flow injection system; On-line pre-concentration; Ion selective electrodes; Solid phase extraction; Alkylphenol polyethoxylates

1. Introduction

Non-ionic surfactants (NIS) are the second most produced surfactants after the anionic class, due to their increasing domestic and industrial applicability. They possess specific physicochemical properties, which make them particularly suited for use wherever interfacial effects of detergency, (de)foaming, (de)emulsification, dispersion or solubilisation, can enhance product or process performance. Among the wide range of NIS, alcohol ethoxylates (AE) and alkylphenol ethoxylates (APE) are the predominant types [1].

Environmental concern fostered the study of the presence and fate of these synthetic products. Studies have shown that the biodegraded metabolites are more persistent and toxic in the environment than their parent compounds. For instance, intensive research about

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the oestrogenic performance of nonylphenol has been done [2,3]. For this reason, the use of nonylphenol ethoxylates (NPEs) with an ethoxylate chain from $n = 3$ to $n = 20$ as NIS in laundry detergents was banned in 1986 in Switzerland. New regulations directed to phase out their use in industrial fields have been introduced in other European countries [4].

Several and different methods for the analysis of NIS of the polyethoxylate type are available. *Selective methods*, which include the chromatographic and spectrometric methods, prove to be very sensitive techniques, permitting the identification of individual surfactants. Preferred approaches are the chromatographic, as it was reviewed by Marcomini and Zanette [5].

A second approach is that of routine environmental monitoring. In this case, as it is not essential to know the complete surfactant profile speciation, a general, rapid, simple and inexpensive method is sufficient. *Group methods*, which include titrimetry, spectrophotometry and electrochemical methods, are suitable for environment and process control due to their characteristics. Among these, the bismuth active substances (BIAS) and cobalt thiocyanate active substances (CTAS) colorimetric methods are standard procedures accepted for the NIS determination in water and wastewater, although they possess recognised drawbacks [6,7]. Gerlache et al. presented two reviews about electrochemical [8] and potentiometric [9] methods available for surfactant determinations. The main interest there is focused on potentiometric titrations because of the advantages when compared to conventional methods [10,11]. But a problem with most of these methods is their inability to detect the low concentrations levels required for an environmental application.

Flow injection analysis (FIA) has proven to be a suitable alternative for the implementation of a variety of sample treatment procedures [12]. However, this technique has rarely been employed in the analysis of NIS. The described procedures are based on chemiluminiscence [13], fluorimetry [14] or spectrophotometric detection [15–18].

The use of ion-selective electrodes (ISEs) as potentiometric detectors for flow injection systems greatly simplifies the analytical procedure because of their ease of use, maintenance and robustness. Moreover, the analytical performance is also improved by the FIA technique [19]. Consequently, automated analysers can be based on FIA systems using potentiometric sensors due to the simplicity, low reagent consumption and high sample processing capability [20]. With respect to our case study, the unique antecedent of the presented work is that of Masadome et al. [21,22], who reported a FIA system for NIS employing especially developed ISEs. For these, it must be mentioned that their membranes were formed solely with polymer plus plasticizer. The absence of electroactive component yielded somewhat limited analytical features.

The work described here involves two potentiometric flow-injection systems for the global determination of NIS of the polyethoxylate type, a direct analysis system and a second one employing pre-concentration. All-solid-state electrodes selective to NIS are used as detectors, which were previously developed and optimised in batch studies [23]. Their main membrane components are poly(vinylchloride) (PVC) as polymeric matrix, *o*-nitrophenyloctyl ether as plasticizer and the electroactive component, which is formed by the tetraphenylborate salt of the complex between the barium ion and a polyethoxylate NIS [24,25]. A tubular flow-through configuration for a better implementation in a FIA system was adopted following existing technology in our laboratories [26]. The initial optimisation of the simpler potentiometric system has already been presented [27].

Due to the limitations in the detection limit of the ISEs, the incorporation of an on-line pre-concentration procedure based on solid phase extraction (SPE) could permit the environmental NIS determination. According to several works, SPE allows both trace enrichment and clean-up of these NIS [28–30]. As it was described in a FIA system for anionic surfactant determinations, a specially designed on-line minicolumn packed with commercial sorbents showed its suitability for the on-line pre-concentration procedure [31].

2. Experimental

2.1. Apparatus

A flow system design as described in previously related work [31] is also used here. Briefly this involved a potentiometric flow-injection system with on-line

pre-concentration for the monitoring of anionic type surfactants at low levels. A description of the analytical procedure may also be found in this paper. The aforementioned system, with slight modification, allows for direct use in the determination of NIS at higher concentrations, as it is depicted in Fig. 1. It is based on a two-channel flow manifold constructed with 0.7 mm i.d. PTFE tubing (Foss Tecator, Höganäs, Sweden) used to adjust the ionic strength of the sample. A four-channel peristaltic pump (Gilson Minipuls 2, Villiers le Bel, France) equipped with PVC pump tubing (Elkay, Boston, USA) was used for propelling the solutions.

An automated laboratory-made multifunctional slider valve [32] was used for both the pre-concentration procedure and the direct analysis system. In the on-line pre-concentration system, two channels of the multifunctional valve were used for the eluent loop

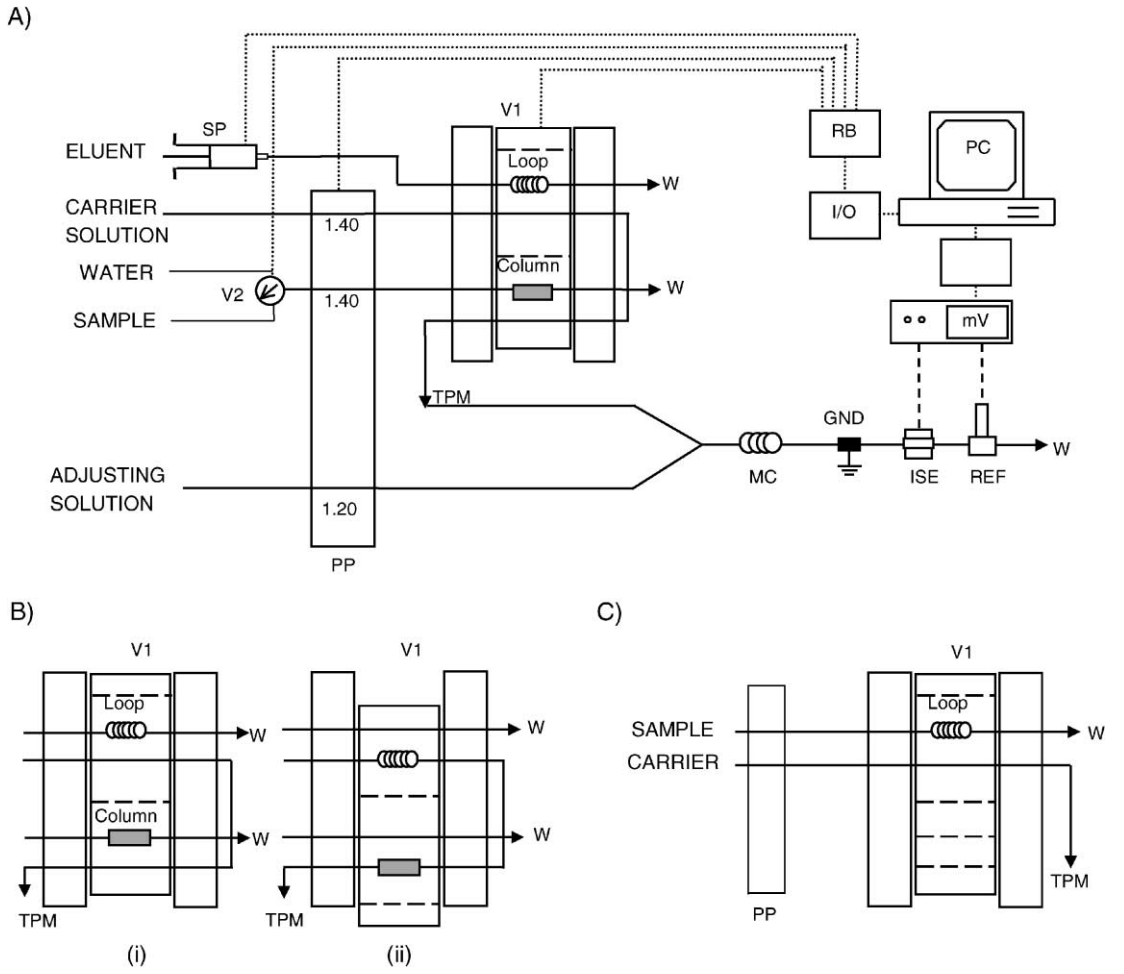

Fig. 1. (A) On-line pre-concentration system used for the determination of low levels of non-ionic surfactants. SP, syringe pump; PP, peristaltic pump (flow rates in ml/min are indicated); V1, multifunctional slider valve with a calibrated injection volume (loop) and the pre-concentration column; V2, three-way solenoid valve; W, waste; MC, mixing coil; GND, ground point; ISE, surfactant electrode; REF, reference electrode; PC, personal computer; A/D, data acquisition card; I/O, digital control card; RB, relay board; TPM, to the potentiometric measurements; (···) communication lines. Carrier solution, distilled water; adjusting solution, K_2SO_4 ($I = 0.1$ M). (B) The operation of valve V1 in the on-line pre-concentration system: (i) pre-concentration stage; (ii) elution and determination stage. (C) Modification used for the direct analysis system.

and the pre-concentration column. This arrangement permits the simultaneous switching of the column and the subsequent countercurrent elution to be performed with a single operation, as outlined in Fig. 1B (i) and (ii). The sample was introduced through a three-way solenoid valve (Bio-Chem Valve Inc., Boonton, USA) so that the sample volume was determined by the sampling interval (time-based method at a constant flow-rate). The eluent solution was loaded before the injection with the aid of a $1\,ml\,min^{-1}$ fixed speed syringe pump (Fisher Bioblock Scientific, Illkirch, France). Low-pressure Gilson connectors (P/N 810065, Villiers le Bel, France) were used in the pre-concentration/elution channels to increase the robustness of the system.

Laboratory-made micro columns (16.0 mm long × 1.8 mm i.d.) were used for the on-line pre-concentration. The columns were constructed and packed with suitable sorbent materials as described previously [30].The frits were of 35 mm pore polypropylene (MoBiTec, Göttingen, Germany).

Direct analysis system (Fig. 1C) was used to compare the pre-concentration efficiency and to study the ISEs' lifetime. The multifunctional valve was used as a standard injection valve, meaning only one of its circuits were employed. In this simpler system, the pre-concentration column was only used for the characterisation study of the enrichment materials, whereby it was inserted between the pump and the sample loop.

An optoisolated potentiometric ISE Amplifier (MBT Environmental, Barcelona, Spain) was employed to acquire the potentiometric measurements. The indicator electrode was an all-solid-state, tubular, flow-through electrode [26], with a PVC matrix membrane selective to polyethoxylate NIS. The tetraphenylborate salt of the complex between the barium ion and a polyethoxylate NIS with 12 ethoxylate units constitutes the electroactive recognition element. More details of the preparation and characterisation of this membrane are given in [23]. The reference device was a double junction Ag/AgCl electrode (Thermo Orion P/N 900200, Cambridge, UK) with a 0.1 M potassium sulfate solution in the salt bridge.

The system was computer-controlled, using a 40 MHz AT-386 computer with an A/D and I/O card (Advantech PC Lab 812 PG, Taiwan), and especially developed software using Microsoft QuickBASIC [33].

2.2. Reagents and solutions

The various polyethoxylate NIS used were of *puriss*. grade (99–100%), whose structural characteristics are presented in Table 1. Apart from Triton X-100 purchased from Fluka (Buchs, Switzerland)

Table 1
Structural characteristics of different non-ionic surfactants used in this work[a]

Non-ionic surfactant	Registered name	Abbreviation	No. of OEUs	No. of C
Polyethoxylated octylphenol	Triton X-100	(T9)	9	8
Polyethoxylated nonylphenol	Igepal CO-520	(Ig5)	5	9
	Findet 9Q/19	(F7)	7	9
	Findet 9Q/21.5	(F9I)	9	9
	Igepal CO-720	(Ig12)	12	9
	Igepal CO-890	(Ig40)	40	9
Polyethoxylated fatty alcohol	Findet 20/N	(F2)	2	12–14
	Findet 1214/16	(F4)	4	12–14
	Findet 13/18.5	(F6.5)	6.5	13
	Findet 10/18	(F8)	8	10
	Findet 1214N/21	(F9ii)	9	12–14
	Findet 1618 A/35-E	(F11)	11	16–18
	Findet 18/27	(F18/27)	–	18
	Findet AR/30	(F18)	18	30

[a] OEUs, number of ethoxylate units; C, number of carbon atoms in the hydrophobic chain.

and the different Igepals from Aldrich (Milwaukee, WI, USA), the rest were kindly donated by Kao Corporation (Barcelona, Spain). During the studies, Igepal CO-720 (Ig12) was taken as the reference NIS. Stock solutions 1×10^{-2} M were prepared every month by directly weighing the corresponding salt, and stored at 5 °C to prevent degradation. From these, standard solutions were made daily by dilution.

Reagents used for the preparation of the electrode membranes and the working solutions were of analytical reagent grade. Doubly distilled water was used throughout except for the carrier solution, which was distilled water. The adjusting solution was potassium sulfate with a 0.1 M ionic strength.

The sorbents assayed for the SPE process were Sep-Pak C_{18} (SP) and Oasis (O) from Waters (Barcelona, Spain), LiChrolut EN (LEN) from Merck (Darmstadt, Germany) and Discovery DSC-18 (DS) from Supelco (Bellefonte, PA, USA). SP and DS are silica gel-based bonded phase sorbents with C_{18} alkylic chains, LEN is a non-ionogenic highly-porous polystyrenedivinylbenzene resin and O, a macroporous copolymer of polydivinylbenzene-co-vinylpyrrolidone, which exhibits both hydrophilic and lipophilic retention characteristics.

2.3. Samples

The samples were collected from various locations at the Llobregat river basin (Barcelona, Spain) in glass bottles the day prior to analysis. They were immediately stored at 5 °C with a 2% formaldehyde addition to prevent degradation of the target analytes.

3. Results and discussion

3.1. Optimisation of the flow-system

The hydrodynamic parameters (flow rates, injected volume) and the composition of the adjusting solution were taken from the previously reported study [27]. Their values are indicated in Fig. 1 and Section 2.1. Other variables such as the SPE sorbent for the pre-concentration procedure, the eluent and the pre-concentration volume were studied for the best performance of the flow-system in the determination of NIS.

3.1.1. Sorbent characterisation

In order to choose the most appropriate sorbent for the on-line pre-concentration procedure, breakthrough curves for Ig12 were compared for four different resins (SP, O, LEN, DS). These curves were obtained by using the manifold described in Fig. 1C, where the pre-concentration column was included in the sample channel, prior to the valve. A surfactant concentration greater than that usually found in the samples (1.2×10^{-4} M Ig12) was used, therefore, accelerating the experiments. By forcing the solution to flow directly through the pre-concentration column at a rate of 0.3 ml min^{-1}, the surfactant may be retained.

Switching the injection valve every 5 min, allows the non-retained NIS to be detected by the ISE, resulting in the recording of a rising S-shaped profile. A calibration with Ig12 bypassing the column was performed prior to each experiment, allowing the concentration of the surfactant to be quantified.

By plotting the relative concentration of the analyte versus the sample volume passed through the column the breakthrough curves were obtained. The relative concentration was defined as the ratio between the concentration of surfactant in the effluent (C) and its concentration in the influent (C_0). Analysis of the breakthrough curves allows arbitrary definition of the breakthrough volume to be associated with the point corresponding to the ratio $C/C_0 = 0.05$ [34]. It can be seen that, the greater this volume, the greater the amount of analyte being retained by the column. Upon further analysis of the curves, it was realised that the capacity of the sorbent would be also qualitatively estimated to the point corresponding to a relative concentration (C/C_0) of 1.

Fig. 2 shows the curves obtained for the four sorbents. As may be seen from the extrapolation of the steady increase of the effluent/influent concentration ratio versus time, LEN presents the greatest capacity. Furthermore, its breakthrough volume for Ig12 was only 7.0 ml. On the other hand, the three remaining sorbents displayed typical S-shaped curves, with breakthrough volumes more than five-fold higher. For the SP curve, it was not observed until 46.0 ml and the sorbent showed a higher capacity than the other

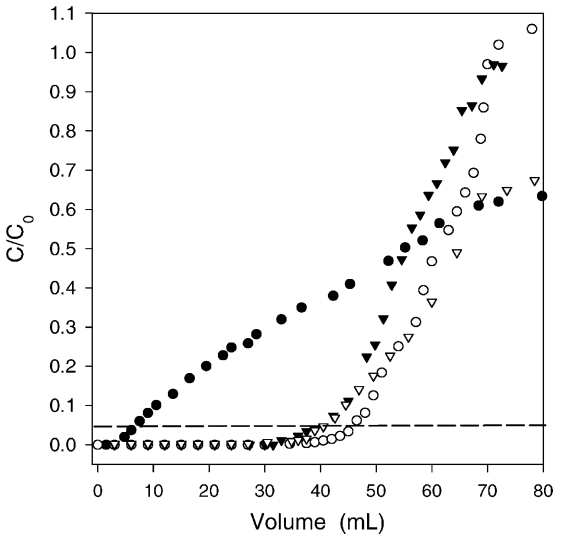

Fig. 2. Breakthrough curves for Ig12 surfactant on (○) SP; (●) LEN, (▽) O and (▼) DS sorbent materials. *C*, surfactant concentration in the effluent; C_0, surfactant concentration in the influent; (- - -) $C/C_0 = 0.05$ ratio.

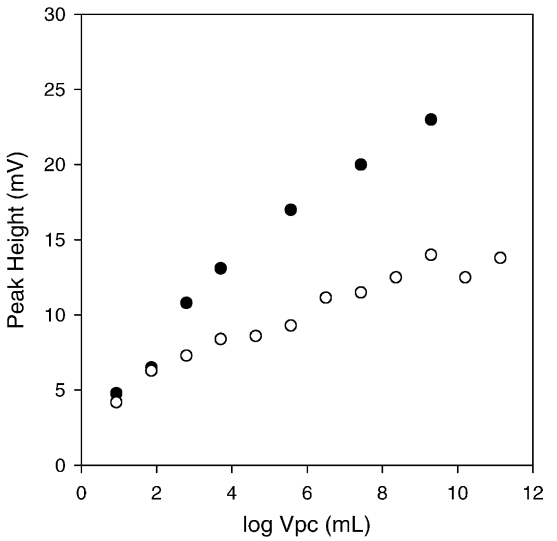

Fig. 3. Effect of the pre-concentration volume (V_{pc}) on the peak height for a (○) 0.5 ppm and a (●) 1.0 ppm Ig12 solution (6.0×10^{-7} and 1.2×10^{-6} M, respectively). Eluent volume, 200 μl acetonitrile 75% (v/v); SPE sorbent, SP.

two resins. For this reason, SP was found the most suitable sorbent for the pre-concentration of NIS.

3.1.2. Eluting parameters

As was demonstrated previously [31] optimum eluent was 75% (v/v) acetonitrile solution. The suitability of this solvent is partly due to its high efficiency in eluting and also the low interference effect for the ISE elasticised membrane, when compared with other organic eluents.

A slow increase of the elution volume such that an increase of the measured signal up to a steady value allows this parameter to be optimised. A volume of 200 μl for the elution was considered to be optimal as no distortion of the FIA peaks was observed, even though the steady value was confirmed as 300 μl. A preference for this lower value allows us to overcome problems associated with reduction of lifetime of the sensors.

3.1.3. Pre-concentration volume and pre-concentration factor

Response of the system may be determined directly from the pre-concentration volume (V_{pc}), since this volume affects other parameters such as the detection limit, the pre-concentration factor and the sample throughput. Hence, the pre-concentration factor is calculated as the quotient between the detection limit of the direct analysis system and the detection limit of the system incorporating the pre-concentration column [31]. This factor denotes the obtained gain in measured concentration when an analyte is treated with the system. This treatment is proposed as pre-concentration does not alter the sensitivity (the fixed potentiometry slope), rather it improves in the minimum detectable amount.

A study of the V_{pc} was achieved by varying it from 1 to 12 ml for a same standard solution. Fig. 3 shows the results for a 0.5 and 1.0 ppm Ig12 solutions, typical concentration values in surface waters (6.0×10^{-7} and 1.2×10^{-6} M, respectively). In all cases, the samples were eluted using 200 μl of 75% acetonitrile solution. It can be seen from the figure that a relationship exists between the logarithm of the V_{pc} and the peak height.

Adapting the V_{pc} to the analyte concentrations in the samples results in the system gaining a high versatility. Consequently, depending on this volume, the remaining parameters—detection limit, pre-concentration factor and sample throughput—would also vary.

3.1.4. Precision and carry-over effect

The precision of the system was evaluated by repetitive determinations. A 3.0×10^{-4} M Ig12 solution was used for the direct analysis system, showing a relative standard deviation (R.S.D.) lower than 3.0% after 50 injections. The repeatability of the on-line pre-concentration system was also checked by repeatedly pre-concentrating (25 times) a 1.0×10^{-6} M (0.7 ppm) Ig12 solution. The pre-concentration volume employed was 10.0 ml and an R.S.D. of 4.0% was obtained. When one considers the number of stages being performed by the automated analysis system, this value is remarkably low.

Carry-over effects are a particular problem of the on-line pre-concentration systems, i.e. the analytical signal of low concentration sample solutions could show higher values than those expected. This may occur for an incomplete elution of a previous and more concentrated sample. This problem is easily overcome by performing additional elutions after each analysis. For instance, after the pre-concentration of 6.0 ml of a 1.0×10^{-4} M Ig12 solution two extra elutions must be performed before the pre-concentration of the next sample. In any case, a value of 1.0×10^{-4} M (75 ppm Ig12) is not a usual concentration level for NIS in natural waters.

In summary, the optimised characteristics for both developed systems—the direct and the on-line pre-concentration systems—are shown in Table 2. The sample throughput for the direct analysis system depends on the peak height and, consequently, on the concentration of the sample. This is due to the high response time of the used ISEs and the required time to recover the baseline values [23]. On the other hand, the sample throughput for the on-line pre-concentration system depends mainly on the pre-concentration volume.

3.2. Evaluation of the flow-system

3.2.1. Calibration curves

Using the Nernst equation, $H = a + s \log[X]$, the calibration curves were obtained by plotting the peak heights (H) versus the logarithm of concentration, i.e. [X] for each standard, which ranges from 1.0×10^{-7} M (0.07 ppm Ig12) to 1.0×10^{-5} M (7.5 ppm Ig12). Concentrations greater than this were not tested, as they are unlikely to be found in environmental samples. Sensitivity of the electrodes (s) was estimated by linear regression whitin the response range. Detection limit was estimated from a non-linear curve fit, according to an expression derived from the Eisenman–Nikolskii equation, $H = A + B \log[X + C]$; where B is considered as the sensitivity of the ISE in all of the concentration range and C the modified detection limit that includes all the interference effects. This non-linear model allows the interpolation of samples belonging to the sub-Nernstian region [31].

Fig. 4 compares the peak heights of the direct analysis system with those of the on-line pre-concentration system. From the figure, an improvement of the monitored signal with the pre-concentration system can be clearly seen. This fact indicates the utility of the proposed system for samples with low concentration levels. However, it should also be noticed the appreciable signal given by the eluent (the blank).

For instance, the Nernst equations and the detection limits obtained with the direct system and the pre-concentration system for F7 standards using a pre-concentration volume of 14.0 ml are, respectively,

Table 2
Characteristics of the optimised flow injection systems

Parameters	Direct analysis system	On-line pre-concentration system
Adjusting solution	K_2SO_4 ($I = 0.1$ M)	K_2SO_4 ($I = 0.1$ M)
Injected/elution volume	200 μl	200 μl
Pre-concentration volume	–	Variable
Precision	3.0% ($n = 50$)	4.0% ($n = 25$)[b]
Additional elutions	–	2
Sample throughput	30–5 h^{-1}[a]	4–5 h^{-1}[b]

[a] Sample throughput calculated for Ig12 standards from 1×10^{-5} to 1×10^{-3} M, respectively.
[b] Pre-concentration volume used, 10.0 ml.

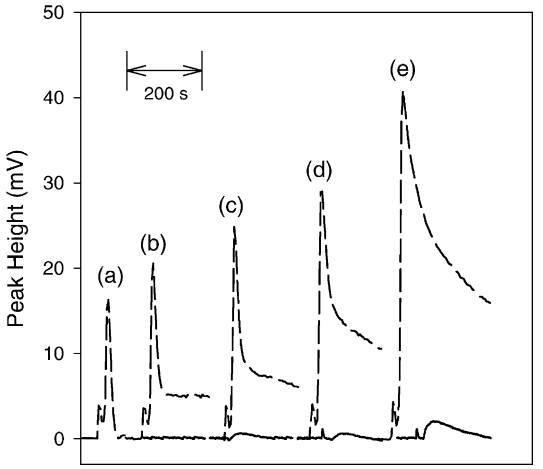

Fig. 4. FIA peaks recorded during Ig12 calibration runs, performed with the direct analysis system (—) and with the on-line pre-concentration system (- - -). Surfactant concentration: (a) blank; (b) 1.0×10^{-6} M; (c) 2.0×10^{-6} M; (d) 3.0×10^{-6} M and (e) 6.0×10^{-6} M. Pre-concentration volume, 8.0 ml; eluent volume, 200 μl acetonitrile 75% (v/v); SPE sorbent, SP.

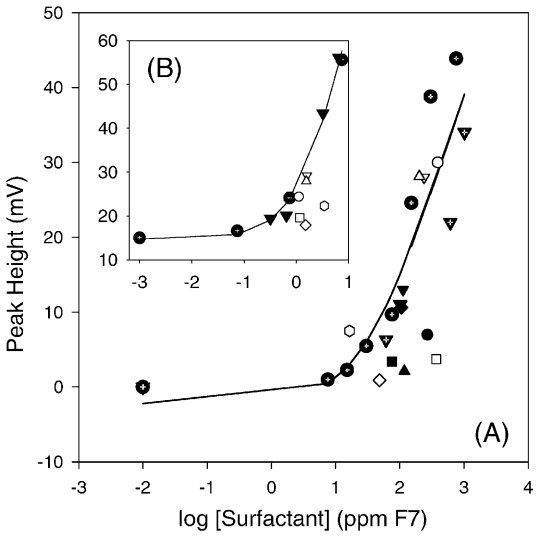

Fig. 5. Calibration curves obtained in (A) direct analysis system; (B) on-line pre-concentration system for different non-ionic surfactants (see Table 1): (❁) Ig12, (▼) F7, (○) F9i, (▽) F9ii, (□) F2, (◇) F18, (△) F6.5, (⬡) F11, (●) Ig5, (▼) T9, (■) Ig40, (◆) F8 and (▲) F18/27. In (B), pre-concentration volume, 10 ml; eluent volume 200 μl acetonitrile 75% (v/v); SPE sorbent, SP. All concentrations are expressed as ppm F7 polyethoxylated surfactant.

H (mV) $= -38(\pm 9) + 27(\pm 4)\log[X]$, $C = 67.5$ (ppm F7), and H (mV) $= 11(\pm 6) + 22(\pm 5)\log[X]$, $C' = 2.52$ (ppm F7). Thus, the pre-concentration factor, which can be estimated from the equations, is $C/C' = 26.8$.

In Fig. 5, the calibration curves may be seen. These were obtained for both systems using different NIS and a pre-concentration volume of 10.0 ml for the on-line pre-concentration system. General calibration equations corresponding to reference NIS standards were calculated employing a non-linear least squares fit. For the direct analysis system, Ig12 and T9 surfactants (expressed as ppm F7) were employed in the calculation and the equation was H (mV) $= -41.2 + 27\log[X + 29.3]$ (ppm F7). Similarly, for the on-line pre-concentration system, and using Ig12 and F7 as reference standards, the equation was H (mV) $= -1.2 + 58.5\log[X + 1.70]$ (ppm F7). An estimation of the pre-concentration factor in this case is 17.2. As a measure of the efficiency of the systems with respect to NIS, other available surfactants were analysed (see Table 1). From this graph, it can be seen that some of the tested surfactants show the behaviour expected from the calibration (F7, F8, F9i, F9ii, T9 and Ig12). However, some others (F2, Ig5, F11, F18, F18/27 and Ig40) give an answer lower than the estimated. In this way, the conclusion is that both systems are sensitive to NIS with a number of OEUs between 6.5 and 12. But as other *group methods* such as titrimetric or colorimetric techniques, NIS with <6 OEUs are difficult to be measured [7].

3.2.2. Interferences

In addition to sensitivity and detection limit, lack of selectivity is a problem hampering the sensor-based direct determinations. For this reason, where the NIS concentrations are not very low, the most important role of the column is not the enrichment factor, but the purification of the analyte. Undoubtedly, the removal of interferences also enhances the detection limits with real samples.

The interference effect of some typical salts at usual environmental concentration levels was evaluated. The salts tested were: 2×10^{-4} M KNO_3, 1×10^{-2} M NaCl, 2×10^{-3} M $MgSO_4$ and 4×10^{-3} M $NaHCO_3$. The response of the direct flow injection system for the two different standard solutions was compared: first, a 6.0×10^{-5} M Ig12 solution and secondly, a standard with the same concentration of surfactant, but

containing the potentially interfering species. Apart from $NaHCO_3$, identical shape and peak height were obtained for both solutions. From these results, it may be said that these compounds do not show any interference effect for the ISE system. However, when $NaHCO_3$ was tested, the signal obtained was 18 mV higher than the reference value. Using the on-line pre-concentration system with a 1.0×10^{-6} M Ig12 solution, the removal of the observed distortion is not complete: in the presence of a 4×10^{-3} and a 8×10^{-3} M $NaHCO_3$ the peak height were 3 and 9 mV higher, respectively. The ineffective separation of the interference by the column could be due to the polar affinities. A possible solution for elimination of the interferent is to adjust the conditioning solution to pH = 2.5 with H_2SO_4 50%, although in this case the system sensitivity diminished from 34.3 to 30.1 mV/dec.

The interference effect of two ionic surfactants was also checked with the direct analysis system: dodecylbenzenesulfonate (SDBS, Carlo Erba) as anionic and cetyltrimethylammoniumbromide (CTAB, Panreac) as cationic surfactant at concentration levels of 1.0×10^{-5} and 1.4×10^{-6} M, respectively. In this study, it was demonstrated that only the cationic surfactant created an interference for the system [23]. However, their concentration in the environment is much lower when compared with other types of surfactants [31].

The addition of a percentage of formaldehyde to the samples is a well known procedure used to minimise the biodegradation [1]. Hence, its interference effect must be studied. Results show that for direct analysis system, the presence of 2% formaldehyde causes a decrease of the response and a distortion of the peak shape. However, using the on-line pre-concentration system the substance is eliminated and, additionally, the preservation of the sample is achieved.

From above, it can be summarised that the predominant features of the proposed on-line pre-concentration FIA system is not only the diminishing of the detection limit, but the successful elimination of interferences, hence, improving the selectivity limitations of ISEs.

3.2.3. Reproducibility and lifetime

The performance characteristics of the proposed systems—electrode and pre-concentration behaviour—were studied over time. During the study of the ISEs, which was carried out in the direct analysis system, two constructed electrode units were thoroughly used.

It was observed that the sensing membrane needed a time to be conditioned, due to a re-equilibration between the Ba^{2+} present in the membrane and the K^+ of the adjusting solution. This exchange in the membrane makes the sensitivities change from ca. 30 to ca. 50 mV/dec, as it was also reviewed by Okada [35]. For both electrode units, the sensitivities increase from 36 mV/dec in the first use to 57 mV/dec in the 12th day. Further studies showed that this sensitivity diminished slowly over the time with a progressive increase in the time required to return to baseline for the same standard concentration (recovery time). Accordingly, the limit of detection and the lower limit of linear response (LLLR) also diminished, which was

Table 3
Calibration parameters of the Ig12/1 electrode unit using the Ig12 surfactant as NIS standard[a]

Day	B[b] (mV/dec)	n	Linear range (M)	C[b] (M)
2	44.9	5	6×10^{-5} to 1×10^{-3}	3×10^{-5}
10	51.0	6	6×10^{-5} to 1×10^{-3}	3×10^{-5}
12	57.3	5	6×10^{-5} to 1×10^{-3}	3×10^{-5}
15	55.1	6	6×10^{-5} to 1×10^{-3}	6×10^{-5}
20	45.8	6	3×10^{-5} to 6×10^{-4}	3×10^{-5}
23	(44.8)[c]	(3)	(3×10^{-5} to 3×10^{-4})	(5×10^{-5})
28	(46.7)	(3)	(3×10^{-5} to 3×10^{-4})	(6×10^{-5})
35	(37.8)	(3)	(3×10^{-5} to 3×10^{-4})	(3×10^{-5})
43	(39.2)	(3)	(1×10^{-5} to 1×10^{-4})	(4×10^{-6})
55	16.2	4	1×10^{-5} to 1×10^{-4}	6×10^{-6}

[a] Sensitivity: B; number of points in the linear range: n; detection limit: C.
[b] Calibration equation: $H = A + B \log [\text{Ig12} + C]$.
[c] Values in parenthesis are estimative.

a favourable feature. The results corresponding to one of these NIS units are summarised in Table 3. The correlation coefficients, r^2, were in all the cases >0.99. From the table, it must be pointed out that from the 16th day, the ISEs were used continuously (24 h per day). Thus, the lifetime evaluated for these electrodes was around 2 months, but it could be higher depending of the frequency of use.

A typical pre-concentration column lasts for 13 days when performs one analysis per 90 min during 24 h per day, degraded by back-pressure effects due to the progressive packing of sorbent material. Even with the use of countercurrent elution, the large difference between the sample and eluent volumes lead to this effect. A further shortening of this lifetime occurs when samples come from natural waters due to the occlusion of the frit's pores by particulate matter present in the samples. However, the substitution for a new frit is easy due to the quick and simple method for the construction and re-packing of the columns. A filtration stage could help in this point.

3.3. Application of the on-line pre-concentration flow-system with surface waters and waste waters

Once the on-line pre-concentration method was shown to be suitable for the determination of some NIS, it was applied to surface water samples. Samples corresponding to different points of the Llobregat river (Catalonia, Spain) were simultaneously analysed with the proposed FIA system and the electrospray-mass spectrometry (ESI-MS) method [36] in order to compare the two procedures. The analysis using ESI-MS was performed in the laboratories of CSIC (Spanish Research Council) by Palacios [37]. A calibration of the system was performed prior to the analysis with a pre-concentration volume of 40 ml. After each sample, a second elution without enrichment was performed to avoid carry-over effects. For instance, the Nernst equations obtained with the direct system and the pre-concentration system for F7 standards were, $H\,(\mathrm{mV}) = -34(\pm 9) + 26(\pm 4)\log[X]$, (ppm F7), and $H\,(\mathrm{mV}) = 21(\pm 5) + 27(\pm 9)\log[X]$ (ppm F7), respectively.

From Table 4, an observable relationship between both series of data can be observed when one considers that both methods are instrumentally very different. No significance statistical tests were performed as many of the results values were too close to the detection limits. Although the results from CSIC are slightly higher, it can be taken into account that ESI-MS measures all the NIS, independent of the number of OEUs, while the FIA method is sensitive to a limited range of OEUs. Additionally, the simplicity of the developed system makes it ideal to be used as a routine and alert system for environmental monitoring.

Table 4
Validation results obtained by the on-line pre-concentration flow-injection system (FIA) and the electrospray-mass spectrometry (EI-MS)

Sampling points	[FIA] (ppm Ig12)	[EI-MS] (ppm Ig12)
Abrera, Llobregat river	<0.1	0.34
Cubellet Torrent	0.14	0.28
Llobregat river before Martorell	0.14	0.15
Molins de Rei, Llobregat river	<0.1	0.35
Cardona, Cardener tributary	<0.1	0.04
Solsona, Cardener tributary	<0.1	0.25
Manresa, Cardener tributary	<0.1	0.13
St. Fruitós, Llobregat river	0.19	0.22
Súria, Cardener tributary	<0.1	0.41

4. Conclusions

Two different automated FIA systems for the global determination of NIS of the polyethoxylate type have been presented. With the direct simple approach, NIS can be determined down to ca. 10^{-5} M with a sample throughput of up to 30 samples per hour.

The use of simple and stable reagents could enable an unattended, low-maintenance, automated water monitoring system to be developed. Consequently, a second automated FIA system for the determination of trace levels of NIS in surface water which employs pre-concentration is optimised. One of the main advantages of this system is its great instrumental simplicity, achieved by integrating the SPE process for the trace enrichment and clean-up. Such a system would work unattended for periods up to 2 weeks.

The validation of the FIA system with the ESI-MS method for samples from Llobregat river basin has been attempted. Although the results could be improved, a relationship between them can be noticed.

As a consequence of this study, the possibility exists to develop a combined system capable of the monitoring of anionic and NIS using special ISEs for each type.

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