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Determination of Trace Levels of Anionic Surfactants in River Water and Wastewater by a Flow Injection Analysis System with On-Line Preconcentration and Potentiometric Detection

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The authors present an automated flow injection analysis (FIA) system for the determination of low levels of anionic surfactants in river water and wastewater. The system uses especially constructed tubular flow-through ion-selective electrodes (ISEs) as potentiometric sensors and on-line preconcentration techniques. The anionic surfactant ISEs employed are of the all-solid-state type with a plasticized PVC membrane. They show a general response to anionic surfactants with a lower limit of linear response of $\sim 10^{-5}$ M, when used in direct determinations. However, their specificity is limited, which hampers their direct use with environmental samples. Therefore, the FIA system presented here includes a solid-phase extraction procedure for purification and preconcentration of analytes. Breakthrough curves were constructed to characterize different sorbents and different eluents were tested to optimize the preconcentration process. The FIA system was first applied to the determination of different types of anionic surfactant standards. Potentially interfering substances such as chloride, nitrate, and nonionic surfactants were checked to verify that they did not interfere on the response of the system. Concentrations of $\sim 10^{-7}$ M (0.03 ppm) of sodium dodecyl sulfate could be detected in the nonlinear response region when 3 mL of sample was preconcentrated and eluted with 50 μ L of a 75% acetonitrile/water (v/v) solution. Precision was 2% RSD ($n = 31$) for a 1×10^{-6} M sodium dodecyl sulfate standard solution and the sample throughput was 10 h⁻¹. The FIA system was then used for the determination of total anionic surfactants in river water and wastewater.

Anionic surfactants are widely used both in technological processes and as household cleaners, being then expelled as sometimes untreated municipal and industrial wastes to natural water reservoirs. Linear alkylbenzenesulfonates (LAS), alkylbenzenesulfonates (ABS), and alkyl sulfates (AS) are some of the most common examples of this group of substances.

Nowadays, environmental legislation does not permit surfactant products with less than 90% biodegradability to be marketed.¹ Even so, their continued presence in the environment causes a toxic fate in aquatic organisms, distortion of the ionic transport in invertebrate animals, and a decrease of the self-purification capability of surface waters. The determination of surfactants in environmental samples is thus of great interest, after maximum priority pollutants such as pesticides or polychlorobiphenyls.

A simple and automated analysis system would be very useful in environmental monitoring, both to check normal concentration levels and to work as an early warning system for runoff situations.

The main problems involved in the determination of anionic surfactants are the low concentration levels of analytes and the complexity of environmental sample matrixes, which makes sample preconcentration and purification necessary. This has traditionally been carried out by liquid–liquid extraction, although lately solid-phase extraction (SPE) has taken on great importance.^{2,3} Though the sample preconcentration is traditionally performed off-line, the on-line methodology has several advantages, including a decrease in the number of manually operated stages and an increase in sensitivity, reproducibility, and sample processing speed.⁴

Although there are different accepted procedures for the determination of anionic surfactants, none of these have the optimal combination of simplicity, rapidity, specificity, and sensitivity. Gas chromatography,⁵ gas chromatography/mass spectrometry,⁶ and high-performance liquid chromatography (HPLC)^{7–11} are very sensitive techniques permitting the identification of

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surfactants, but they require large sample preparation times and are not versatile enough for control applications.

The widely accepted method for the analysis of anionic surfactants in environmental samples is the Methylene Blue active substances (MBAS) method, due to its high sensitivity and simplicity. This spectrophotometric method is based on the formation of an ionic pair between the surfactant and the cationic dye, an adduct that is extracted into chloroform. A recognized drawback of this method, however, lies in its questionable specificity.¹²

The use of ion-selective electrodes (ISEs) sensitive to anionic surfactants has been reported by several authors.^{13–15} It has proven to be a good alternative to the two-phase titration, the standard procedure for high concentration levels.¹⁶ Some surfactant electrodes were commercially introduced a short time ago,^{17,18} but difficulties related to their detection limit and low specificity prevent their use in environmental samples. The demand for sensing procedures has stimulated continued research in the biosensor field as well.^{19,20}

Flow injection analysis (FIA) has proven to be a suitable alternative for the implementation of a variety of sample treatment procedures.²¹ The first FIA system for the determination of low concentration levels of anionic surfactants in water was reported by Kawase et al.²² Since then, other FIA systems have been proposed, most of them based on the MBAS method with liquid–liquid solvent extraction and spectrophotometric^{23–25} or surface tension²⁶ detection. The drawbacks of these systems are related to their complex experimental setups or the need for large amounts of organic solvents.

This paper presents a new analytical procedure for the unattended automated determination of trace levels of total anionic surfactants in river water and wastewater. It is based on a flow injection system that incorporates on-line preconcentration techniques and potentiometric detection. Based on an SPE procedure, trace enrichment and cleanup are performed by a specially designed on-line minicolumn packed with commercial sorbents. The column's miniaturized design allows the characteristic low dispersion of an FIA system to be maintained with a minimum dead volume.

The use of potentiometric detection greatly simplifies the procedure due to its easy maintenance, the use of common and

stable reagents, and a simple yet robust apparatus. Besides, functional ISE characteristics are improved by the FIA technique.²⁷ For all these reasons, ISEs responding to the global presence of anionic surfactants already developed in our laboratories²⁸ and applied with good results in an FIA system²⁹ were used as detectors in the system presented here. The points related to specificity and the low detection limits required for the environmental application were treated with the SPE methodology, which were further improved when working in the sub-Nernstian region using a nonlinear model.

EXPERIMENTAL SECTION

Apparatus. Potentiometric measurements were taken with an optoisolated potentiometric ISE amplifier (MBT Environmental, Barcelona, Spain). The indicator electrode was an all-solid-state tubular flow-through electrode, with a PVC matrix membrane selective to anionic surfactants,^{16,28,29} constructed according to the technology in our laboratories.³⁰ The electrode resembles a coated wire type, but with the selective membrane fixed on the inner wall of a cylindrical hole defined on a conductive graphite–epoxy resin. The plasticized membrane employed a quaternary ammonium salt of dodecylbenzenesulfonate as the ion pair responsible for selectivity. As reference electrode, a double-junction Ag/AgCl electrode (Orion 900200) with a 0.1 M potassium sulfate solution in the salt bridge was used. Adaptors for the reference electrode and stabilizing devices have been previously described.³¹ A piece of stainless steel tubing was used as the grounding electrode to suppress the streaming potentials created by the fluids propelled by the pump.

The FIA system used for the determination of anionic surfactants in environmental samples is depicted in Figure 1A. Figure 1C shows a modification of this system, used for the direct determination of surfactants. A laboratory-made multifunctional rotary valve³² was used for the preconcentration procedure and, with a different arrangement, in the direct analysis system. In the on-line preconcentration system (OPS), the multifunctional valve has an eluent loop and the preconcentration column is arranged in the rotor. This arrangement permits the simultaneous switching of the column and the subsequent countercurrent elution to be performed with a single operation, as outlined in the cutouts i and ii of Figure 1B. The sample was introduced through a three-way solenoid valve (Bio-Chem Valve Inc., Boonton, NJ) so that the sample volume was determined by the sampling interval (time-based method at a constant flow rate). Additionally, a laboratory-made tee connection with a short input tubing was used to ensure the renewal of the sample. The eluent solution was loaded before the injection with the aid of a 1 mL/min fixed-speed syringe pump (Bioblock, Illkirch, France).

In the direct analysis system (DAS) (Figure 1C), the column was used during the characterization study of the enrichment

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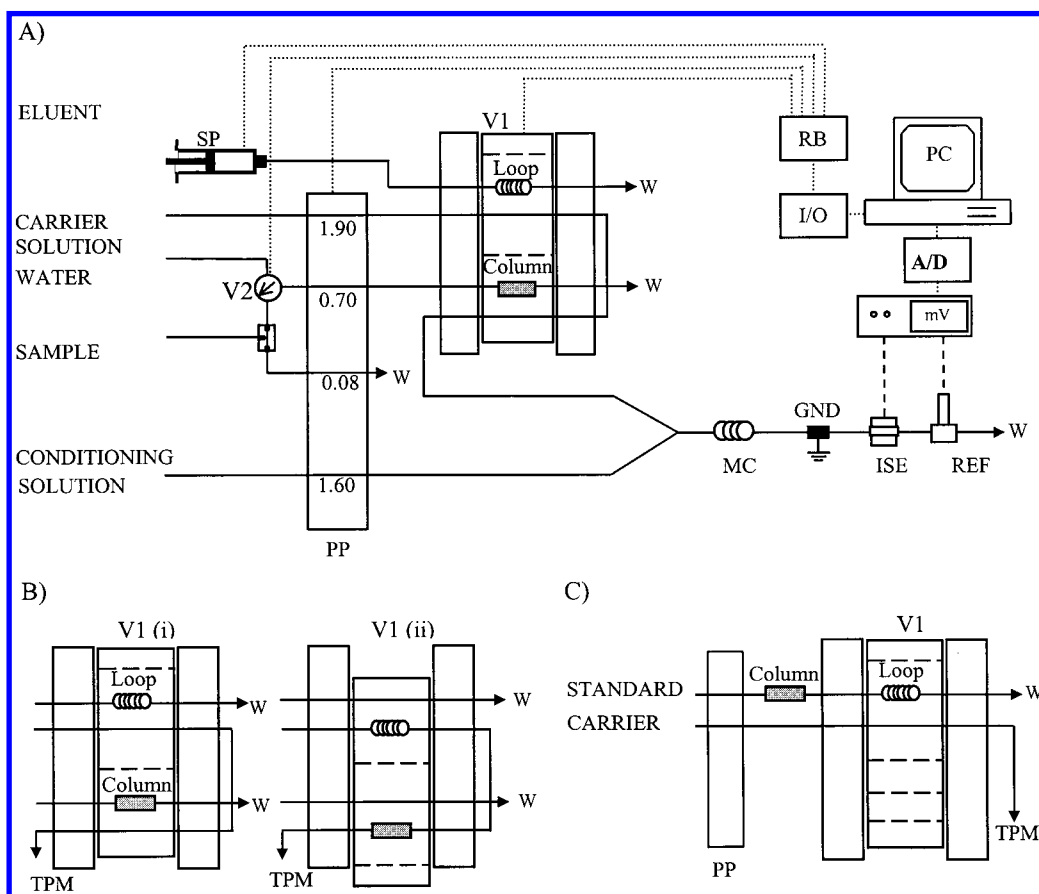


Figure 1. (A) On-line preconcentration system (OPS) used for the determination of low levels of anionic surfactants in environmental samples. SP, syringe pump; PP, peristaltic pump (flow rates in mL/min are indicated); V1, multifunctional rotary valve with a calibrated injection volume (Loop); V2, three-way 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; conditioning solution, K_2SO_4 ($I = 0.01$ M). (B) V1 operation in the OPS: (i) preconcentration stage; (ii) elution and determination stage. (C) V1 arrangement in the direct analysis system (DAS) used during the characterization of the sorbent materials.

materials. Without the column, this system was used to compare the preconcentration efficiency. In this case, the multifunctional valve was used as a standard injection valve so only one of the two circuits was employed.

All tubing used had 0.7 mm i.d. (Tecator, Hoganas, Sweden), and the four-channel peristaltic pump used was a Gilson-Minipuls-2 equipped with PVC pump tubing (Elkay, Boston, MA).

Reagents. Analytical reagent-grade sodium dodecyl sulfate (SDS; Fluka, Basel, Switzerland), standard-grade sodium dodecylbenzenesulfonate (SDBS), and sodium tetrapropylenebenzenesulfonate (STBS; both from Carlo Erba, Milano, Italy) were used as standards. The standard solutions were prepared daily by dilution of a 1×10^{-2} M stock solution. Stock solutions were prepared every 3 months by direct weighing of the corresponding salt and were stored at 5 °C to prevent degradation. SDBS and STBS were standardized by a two-phase titration method with a 4 mM Hyamine 1622 solution (Merck, Darmstadt, Germany) using disulphine-blue and dimidium bromide mixed indicator.³³

Reagents used for the preparation of the electrode membranes and working solutions were of analytical reagent grade. Standard and reagent solutions were prepared using doubly distilled water.

For the flow system, the conditioning solution was potassium sulfate with a 0.01 M ionic strength and the carrier solution was distilled water.

Samples. The samples were collected from different points of the Llobregat river basin (Barcelona, Spain) in polyethylene bottles the day before the analysis. They were immediately stored at 5 °C and kept under these conditions until analysis to avoid degradation of the target analytes. All samples were filtered before the analysis using 0.7- μ m glass fiber filters (Schleicher & Schuell, Dassel, Germany) and then conditioned to room temperature.

Column Preparation. Laboratory-made microcolumns (16.0 mm long \times 1.8 mm i.d., 41 μ L internal volume) were used for the on-line preconcentration. The columns were constructed in Perspex and adapted to the flow system using conventional low-pressure chromatography fittings. The polymeric sorbents assayed, originally packed as cartridges, were Sep-Pak C_{18} (SP), LiChrolut EN (LEN), and LiChrolut RP-18e (LC), obtained from Millipore (Barcelona, Spain) and Merck. Sorbents were repacked into the columns by the aspiration of a methanol suspension of these, with a plastic frit placed in one end. The frits were 90- μ m pore polypropylene frits (MoBiTec, Göttingen, Germany). After packing, a second frit was placed in the open end and the column was kept wet.

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Procedures. The analytical procedure for the determination of trace levels of anionic surfactants consists of a preconcentration stage followed by the determination step (Figure 1A and B). First, the sample was continuously pumped through the manifold so that the analyte was retained on the column, while the sample matrix was driven to waste (Figure 1B cutout i). By suitable selection of sample flow rate and solenoid valve switching time, the sample volume could be accurately controlled. After the sample preconcentration, the solenoid valve was switched to allow the circulation of distilled water through the system to drag the remaining sample in the manifold. In the elution or determination step, the multifunctional rotary valve previously loaded with the eluent was switched and a defined volume of eluent passed through the column to desorb the analyte. Thereafter it was detected by the surfactant ISE (Figure 1B cutout ii). The elution took place in the countercurrent mode to avoid the development of back pressure due to the sorbent packing and to minimize the broadening of the detected sample zone.

The complete sequence was computer-controlled, using a 40-MHz AT-386 computer with an A/D and I/O card (Advantech PC-Lab 812 PG, Taipei, Taiwan) and especially developed software (QuickBASIC).²⁹

Calibration curves were constructed by plotting the obtained peak heights versus the logarithm of concentration (assimilated to activity) for each standard. The sensitivity of the electrodes was obtained by linear regression in the linear response range and corresponds to Nernstian behavior:

$$H = K + s \log(X)$$

where H , K , s , and X are, respectively, the peak height, the ordinate, the sensitivity of the electrode, and the analyte concentration. The detection limit was estimated from a nonlinear curve fit of all the experimental data, according to an expression derived from the Eisenman–Nikolskii equation:

$$H = A + B \log(X + C)$$

where A and B are considered, respectively, as the ordinate and the sensitivity of the ISE in all of the concentration range. The parameter C is a modified detection limit that includes all interference effects. If we consider that, at the preconcentration stage, the main interferences are separated, the parameter C can then be considered the detection limit of the system according to the accepted terminology in potentiometry. For its practical application, the model describing the nonlinear region of the potentiometric response was used. This allowed the working range to be extended so that in the interpolation of unknown samples, concentration values of approximately one-tenth of the C value could be still estimated. Calculations were made with SIGMA-PLOT 4.0 software, using the Marquardt–Levenberg algorithm³⁴ to fit the nonlinear region of the potentiometric response.

RESULTS AND DISCUSSION

Sorbent Characterization. To choose the most appropriate sorbent for the on-line preconcentration, the breakthrough curves

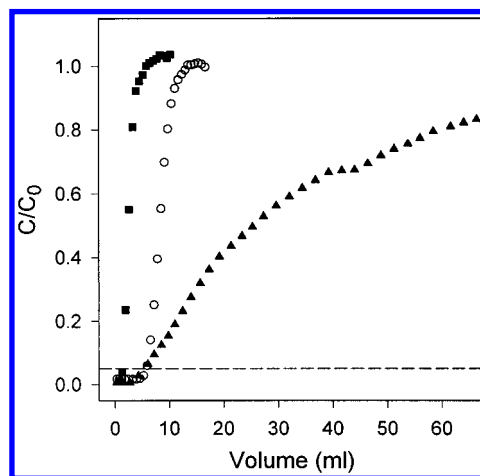


Figure 2. Breakthrough curves for SDS on (○) SP, (▲) LEN, and (■) LC. C , surfactant concentration in the effluent; C_0 , surfactant concentration in the influent. (---) ratio $C/C_0 = 0.05$. For details see text.

for SDS were compared for three different sorbents (SP, LEN, LC). These curves were obtained by using the manifold described in Figure 1C, where the preconcentration column was included in the sample channel, prior to the valve. To accelerate the experiments, a surfactant concentration notably higher than that usually found in the samples (5×10^{-5} M SDS) was used and was forced to flow directly through the preconcentration column at 0.16 mL/min so that the surfactant could be retained.

By switching the multifunctional valve (now used as a standard injection valve) every 4 min, the SDS passing the column was detected by the surfactant ISE and a rising S-shaped profile recorded. To quantify the surfactant concentration in the effluent, a calibration with SDS standards bypassing the column was performed just before the experiment. To regenerate the column, it was eluted with 3 mL of methanol, which made it clean for use again.

The breakthrough curves were constructed by plotting the relative concentration of the analyte versus the sample volume passed through the column. 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). From the breakthrough curves, the breakthrough volume was arbitrarily defined as the point corresponding to the ratio $C/C_0 = 0.05$. A large value means a large amount of analyte totally retained by the column. The capacity of the sorbent, defined as the amount of analyte retained by a dry weight of sorbent, was also estimated from the curves, corresponding to a relative concentration (C/C_0) reaching 1.

The breakthrough curves for the three sorbents are shown in Figure 2. SP and LC display typical S-shaped curves, with a breakthrough volume of only 0.6 mL for the LC curve and a 10-fold value (6.8 mL) for the SP curve. On the other hand, LEN showed a steady increase of effluent concentration as the surfactant passed through, and the breakthrough volume for SDS was not observed before 5 mL and did not exceed 80% of the inlet concentration after 60 mL. It can be concluded that both SP and LEN are suitable for efficient preconcentration of anionic surfactants. Of the two, LEN was preferred, due to its 5-fold greater capacity.

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Table 1. Elution Yields Relative to the Total Retained Amount Obtained with Different Eluent Solutions

elution no. ^a	75% acetonitrile	75% methanol	50% 2-propanol
1	74	58	30
2	12	21	21
3	6	7	15
4	3	4	7

^a Eluent volume, 20 μ L.

Eluting Solvent. The eluent needed to provide maximum elution of the anionic surfactants retained on the column with minimum interference to the potentiometric sensor. The eluents tested were different water mixtures of methanol, 2-propanol, and acetonitrile at concentration levels that did not distort the profiles of the FIA peaks and did not shorten the lifetime of the sensor. With each eluent, a sample volume of 1 mL of 1×10^{-4} M SDS was preconcentrated on the column, and successive elutions were carried out. Each elution employed only 20 μ L, an insufficient volume for the total removal of the retained surfactant. This feature allowed the efficiency of each eluent to be compared (Table 1). To calculate the elution percentage values, the peak heights were corrected by subtracting the signal obtained with a blank (the same volume of eluent solution). The optimal eluent was chosen as 75% (v/v) acetonitrile solution. This was the eluent solution with a low interference level for the surfactant ISE and higher efficiency.

The modification of the pH value of the eluent solution to acidic or alkaline values did not improve its performance.

Optimization of the Flow System. The hydrodynamic parameters (tube lengths and flow rates) and the composition of the conditioning solution were taken from a previously reported study.²⁹ The conditioning solution contained a background level of STBS (1×10^{-6} M) to reduce the broadening of the peaks and to minimize the time needed to return to the baseline.

First, the elution volume was optimized. Increasing the volume of eluent, an increase of the measured signal up to a steady value for injected volumes greater than 60 μ L was confirmed, with 50 μ L considered the optimal volume for the elution. A low value is preferred here in order to avoid the degradation of the response of the electrodes. The flow rate should also be studied, but it was maintained at its previously stated value because it had a direct effect on the detection elements.

The influent flow rate is a significant parameter, as an excessive high value could prevent the optimum adsorption of the analyte. To study the influent flow rate, an extra pump with variable speed was necessary. A change in the influent flow rate from 0.3 to 1.7 mL/min caused a 20% decrease in the peak height and a large reduction of the preconcentration time. As a compromise between the preconcentration time and flow rate, the latter was kept constant at 0.7 mL/min in all subsequent experiments (4-min preconcentration time for 3 mL of sample volume).

It is useful to study the preconcentrated sample volume, as it directly determines the response of the system. Moreover, the preconcentration ratio can be adapted to the concentration levels in the samples. Where the anionic surfactant concentrations are not very low, the most important role of the column is not the enrichment factor but the purification of the analyte. Undoubtedly,

Table 2. Effect of the Sample/Eluent Ratio on the On-Line Preconcentration System^a

preconcn vol (mL)	detection limit C_{OPS} (M)	preconcn factor, C_{DAS}/C_{OPS}	sample throughput (h ⁻¹)
1.0	2×10^{-6}	4	20
3.0	5×10^{-7}	16	10
5.0	4×10^{-7}	20	7

^a The detection limit of the direct analysis system, $C_{DAS} = 8 \times 10^{-6}$ M; eluent volume, 50 μ L.

the removal of this interference also helps to improve the detection limits with real samples. The sample volume was studied by comparing the calibrations of the system using preconcentration volumes of 1, 3, and 5 mL. In all cases, the samples were eluted using 50 μ L of 75% acetonitrile solution. Table 2 shows the results, including the detection limit, the preconcentration factor, and the sample throughput. Briefly, the preconcentration factor denotes the obtained gain in measured concentration when an analyte is treated with the system. It was necessary to redefine the intuitive factor, which is normally used with on-line preconcentration systems using spectrophotometric detection.³⁵ In fact, to our knowledge, no related work with potentiometric detection has been published. For the present study, the preconcentration factor was calculated as the quotient between the detection limit of the direct analysis system and the detection limit of the system incorporating the preconcentration column. Defined in this way, the preconcentration factor compares the detection limits of the two systems instead of their sensitivities, as is done with spectrophotometric detection. This comparison is justified since potentiometric systems have a fixed sensitivity, with the Nernstian slope value, so the intuitive preconcentration factor always approximates 1. Table 2 shows how the increase of the preconcentrated volume is followed by an increase in the preconcentration factor and the reduction of the sample throughput. The system can thus be made more versatile by adapting the preconcentrated volume to the concentrations expected in the samples. The value preferred for the environmental application under normal conditions was 3.0 mL.

The precision of the system with on-line preconcentration was also checked with repetitive determinations. A 1×10^{-6} M SDS solution preconcentrated 31 times had a relative standard deviation (RSD) of 2.0%, an outstanding value when considering the number of stages being performed by the automated analysis system.

A particular concern here is that the preconcentration of a sample solution at a high concentration level could result in a higher reading in the next measurement because of an incomplete elution (carry-over effect). An increase of ~ 10 mV in the expected peak height of 0.05 ppm SDS standard was observed when the previous sample had a 10-fold concentration value. However, this problem can be solved by an additional elution before the preconcentration of the next sample.

Determination of Anionic Surfactants. The calibration curves were constructed with SDS standards ranging from 1×10^{-7} (0.03 ppm) to 1×10^{-5} M (2.66 ppm). Concentrations greater than 1×10^{-5} M were not tested as they are not likely to be found

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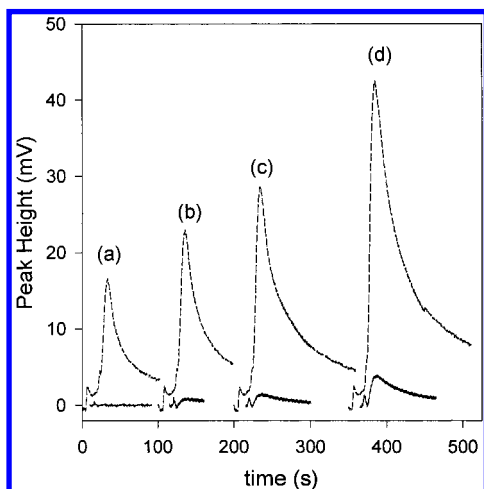


Figure 3. FIA peaks recorded during SDS calibration runs, performed with the direct analysis system (—) and with the on-line preconcentration system (---). Surfactant concentration: (a) 5×10^{-7} , (b) 1×10^{-6} , (c) 2×10^{-6} , and (d) 5×10^{-6} M. Preconcentration volume, 2 mL; eluent volume, 50 μ L; sorbent, LEN.

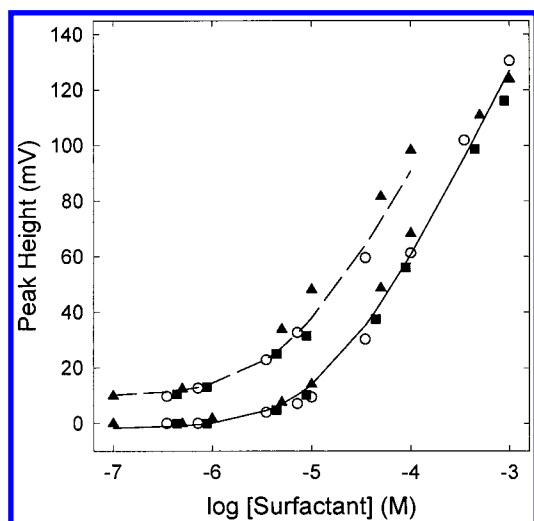


Figure 4. Calibration curves for three different anionic surfactants: (○) dodecylbenzenesulfonate; (▲) dodecyl sulfate; (■) tetrapropylenebenzenesulfonate. The equation's curves obtained with the direct analysis system (—) and the on-line preconcentration system (---) are, respectively, $H = 336 + 70 \log[X + 1.4 \times 10^{-5}]$ and $H = 343 + 63 \log[X + 6 \times 10^{-6}]$. Preconcentration volume, 2 mL; eluent volume 50 mL; sorbent, LEN.

in environmental samples. Figure 3 compares the peak heights of the direct analysis system with those of the on-line preconcentration system. The improvement of the monitored signal with the preconcentration system can be clearly seen, indicating the utility of the proposed system for samples with low concentration levels.

Figure 4 shows the calibration curves obtained with three different anionic surfactants [SDBS (LAS), STBS (ABS), and SDS (AS)] with the FIA system and a preconcentration volume of 2 mL. The nonlinear fit of the data is also presented in Figure 4. The preconcentration effect is visualized; two parallel curves are obtained, and the net gain is expressed as the improvement of the detection limit. The high correlation of the experimental data with a common calibration fit demonstrates that the measurement does not depend on the type of anionic surfactants. In fact, the

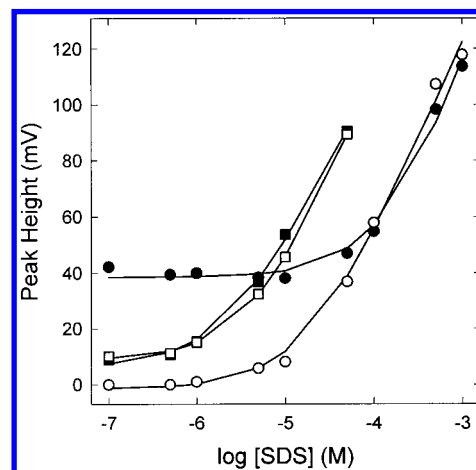


Figure 5. Calibration curve for SDS to demonstrate the elimination of interference effects from expected anions in river waters: (○, ●) direct analysis system; (□, ■) on-line preconcentration system; (○, □) no interferences; (●, ■) with interferences. Preconcentration volume, 1 mL; eluent volume, 50 μ L; sorbent, LEN.

success demonstrated with the different types of anionic surfactants tested suggests that the procedure may be applicable to the analysis of anionic surfactants in general and the proposed FIA system could be applied to the monitoring of these pollutants in surface water.

Interferences. In addition to sensitivity and detection limit, lack of selectivity is a problem hampering the sensor-based direct determination of organic substances such as anionic surfactants in freshwater. In the determination considered here, certain naturally occurring inorganic species are potential interferences to surfactant ISEs.²⁸ The high concentration levels feasible for some of these species, and the low concentrations of the target analyte make their removal necessary. Some of the most abundant interfering substances in the analyzed samples were chloride and nitrate. The selectivity coefficients, calculated according to the mixed solution procedure,³⁶ were $\log k^{\text{pot}}_{\text{SDS,Cl}} = -2.95$ (1×10^{-2} M potassium chloride) and $\log k^{\text{pot}}_{\text{SDS,NO}_3} = -1.29$ (2×10^{-4} M potassium nitrate). The response of the system was evaluated with surfactant standard solutions, with a constant added background of the two substances: 3×10^{-4} M chloride and 7×10^{-4} nitrate, ~ 4 times the expected value in normal samples. Figure 5 shows the different calibrations, with and without interferences or preconcentration. The results of the different calibrations are summarized in Table 3. We can see that, with the direct analysis system, the presence of interferences causes a large increase in the detection limit, raising values from 1.9×10^{-5} to 1.7×10^{-4} M. In contrast, with the FIA system with on-line preconcentration, there is no significant difference between the results with or without interferences. The elimination of interferences is thus useful for the direct determination of anionic surfactants.

The interference effect of two common nonionic surfactants was also checked: Triton X-100 (Fluka) and ethoxylated lauryl alcohol (KaoSoap, Barcelona, Spain), at concentration levels of 1.6×10^{-6} and 2×10^{-4} M, respectively. The study demonstrated that the presence of nonionic surfactants neither interferes with the surfactant ISEs nor varies the preconcentration properties of the column.

(36) Vesely, J.; Weiss, D.; Stulik, K. *Ion Selective Electrodes*; Ellis Horwood: Chichester, 1978; Chapter 1.

Table 3. Calibration Parameters Obtained in the Nonlinear Curve Fit of the Data: $H = A + B \log(X + C)$

conditions	B^b (mV/decade)	C^b (M)
DAS-NI	71 (7)	1.9×10^{-5} (26)
DAS-I	94 (20)	1.7×10^{-4} (42)
OPS-NI	77 (3)	5×10^{-6} (7)
OPS-I	62 (6)	2×10^{-6} (19)

^a DAS-NI, direct analysis system with no interferences; DAS-I, direct analysis system with interferences; OPS-NI, on-line preconcentration system with no interferences; OPS-I, on-line preconcentration system with interferences. ^b Values in parentheses correspond to relative standard deviation values (%).

Table 4. Calibration Parameters of the On-Line Preconcentration System Using Four Different Columns^a

column	K (mV)	s (mV/decade)	C ($\times 10^7$ M)	n
C0	388 (3)	58 (3)	5 (24)	5
C1	377	56	7	1
C2	392 (6)	59 (6)	7 (49)	4
C3	385	58	5	1

^a Linear fit, $H = K + s \log(X)$; nonlinear fit, $H = A + B \log(X + C)$; C , detection limit; n , number of calibrations realized per column; preconcentration volume, 3 mL; sorbent, LEN. Values in parentheses correspond to relative standard deviation values (%).

These results indicate that the most fruitful feature of the proposed FIA system is not the lowering of detection limits to an extreme, which would be counterbalanced by worse sample throughput, but the successful elimination of interferences, which solves the selectivity limitations of the ISEs.

Reproducibility. The performance characteristics of the proposed system were studied over time, as regards both electrode data and preconcentration behavior. The lifetime of the ISEs was estimated as the time it took for Nernstian sensitivity to decrease 5% from the values observed on the first days. The lifetime evaluated for the six ISEs used in this study was greater than 10 months, with an average slope of 57 mV/decade. Relative standard deviation of this slope was 1.9%.

A typical preconcentration column lasts for 3 months when working with standard solutions prepared in the laboratory, degraded by back-pressure effects due to the progressive packing of sorbent material. This lifetime is further shortened when samples come from natural waters due to the occlusion of the frit's pores by particulate matter present in the samples. During a 45-day study using a single column, the average slope was 59 mV/decade with a relative standard deviation of 6%, and the average lower limit of linear response (LLLR) observed was 8×10^{-7} M when the preconcentrated volume was 3 mL. Using four different columns during a period of 6 months with the same ISE, 56–59 mV/decade sensitivities and 5×10^{-7} – 7×10^{-7} M detection limits were observed. These values and other parameters relative to the sensitivities and detection limits obtained with different columns are summarized in Table 4.

Validation. Once the proposed method was shown to be suitable for the determination of ABS, LAS, and AS, it was applied to surface water samples. On different days, different series of samples were simultaneously analyzed with both the proposed

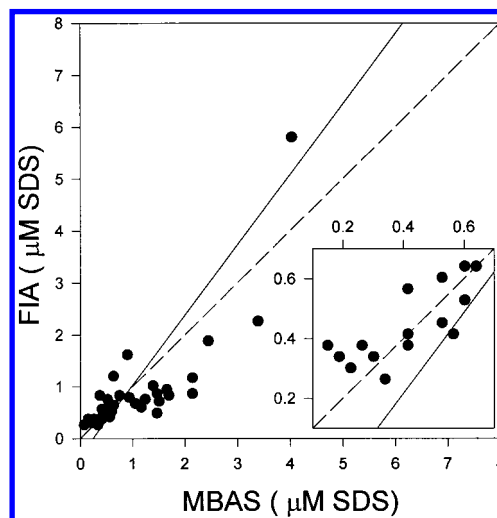


Figure 6. Regression test for the comparison of the surfactant concentrations obtained with two analytical methods (proposed FIA method and standard MBAS method). (—) $y = 1.35(\pm 0.38)x - 0.086(\pm 0.17)$; $r = 0.75$ ($n = 41$ samples); (---) expected identity line $y = x$ ($1 \mu\text{M} = 0.288 \text{ ppm SDS}$).

FIA system and the standard MBAS methods in order to compare the two procedures. A calibration of the system was performed prior to the analysis. The sample volume used for preconcentration was 3 mL. After each sample, a second elution without enrichment was done to avoid carry-over effects, especially with the more highly concentrated samples. In the analysis of 47 samples, 6 of them (wastewater samples) gave results clearly lower than those of the standard method. A potentiometric standard addition procedure was performed with these samples.³⁷ Concentration values obtained with this procedure were close to interpolated values, adding confidence to the values obtained with the proposed system as compared to the MBAS methodology.

The results were compared using statistical tests at the 95% confidence level. The results of the regression test are summarized in Figure 6. No significant differences were found when a paired Student's t -test was applied to the data (calculated t -value, $t_{\text{exp}} = 0.207$, is lower than the tabulated value, 41 degrees of freedom, 95% confidence level, $t_{\text{tab}} = 2.02$).

The results are especially rewarding at the lower concentration level, as can be seen in the excerpt in Figure 6. The results of the regression test can be considered acceptable considering the different specificities of the two methods. In fact, the standard MBAS method yielded a measure of the methylene blue active substances, which could include possible interfering compounds.¹² The FIA system proposed here proved to be particularly selective for the anionic surfactant group of substances.

CONCLUSIONS

This paper presents an automated FIA system for the determination of trace levels of anionic surfactants in river water and wastewater. One of the main advantages of this system is its great instrumental simplicity, achieved by integrating the solid-phase extraction process and the potentiometric detection stage with the FIA methodology. The use of simple and stable reagents could enable an unattended low-maintenance surface water monitoring

(37) Mascini, M. *Ion-Sel. Electrode Rev.* **1980**, 2, 17.

system to be developed, to be used as a pollution alert system. The overall response obtained with potentiometric detection and on-line preconcentration can provide a valid measure of the global presence of anionic surfactants. The mathematical model used allows for the interpolation of samples with low levels of anionic surfactants in the nonlinear region of the potentiometric response.

The main feature of the FIA system presented here is not so much the sample preconcentration, which has not been forced to a maximum level, but the elimination of inorganic interferences from the sample matrix.

The on-line preconcentration techniques used, which have only rarely been used for analytes other than metals, have been shown to be successful also for organic pollutants. The work presented leads us to recommend this methodology for sorbent characterization in a continuous FIA system with potentiometric detection.

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