Determination of anionic surfactants in sea sand using a multicommutation approach

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Abstract

It has been employed a mechanized procedure for the spectrophotometric determination of anionic surfactants in sea sand samples. The method is based on a batch leaching of surfactants from sand with two hot water successive treatments followed by on-line reaction of the extracted surfactants with methylene blue (MB) and extraction in chloroform using the multicommutation approach. The dynamic linear range was evaluated till 8.7×10^{-6} mol L^{-1} (2.48 mg L^{-1}) sodium dodecyl sulphate (SDS). A solvent consumption of 0.7 mL per determination, a sampling throughput of 40 measurements per hour, a relative standard deviation of 4.2% (*n*=10) for a 2×10^{-6} mol L^{-1} (576 µg L^{-1}) surfactant standard and a limit of detection of 1.4×10^{-7} mol L^{-1} (0.04 mg L^{-1}) were the analytical parameters obtained for the on-line reaction. Quantitative recoveries, between 92.2 and 100.0%, were found for the determination of anionic surfactants in sand samples spiked with amounts of SDS from 0.75 to 3 µg g^{-1}.

Keywords: anionic surfactants, multicommutation, spectrophotometry, sand.

Determinación de tensoactivos aniónicos en arena de mar empleando un sistema multiconmutado

Resumen

Se ha empleado un procedimiento mecanizado para la determinación espectrofotométrica de tensoactivos aniónicos en muestras de arena de mar. El método se basa en el lixiviado de los tensoactivos de las arenas mediante dos extracciones sucesivas con agua caliente seguida de la reacción en línea de los tensoactivos lixiviados con azul de metileno y extraction en cloroformo empleando un sistema multiconmutado. El intervalo lineal se ha evaluado hasta una concentración de $8,7 \times 10^{-6}$ mol L^{-1} (2,48 mg L^{-1}) de dodecilsulfato sódico (SDS). Un consumo de disolvente de 0,7 mL por determinación, una velocidad de muestreo de 40 medidas por hora, una desviación estándar relativa de 4,2% (*n*=10) para un patrón de 2×10^{-6} mol L^{-1} (576 µg L^{-1}) de tensoactivo y un límite de detección de $1,4 \times 10^{-7}$ mol L^{-1} (0,04 mg L^{-1}) fueron los parámetros analíticos obtenidos para la reacción en línea. Las recuperaciones conseguidas en la determinación

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de los tensoactivos aniónicos en muestras de arena enriquecidas con cantidades de SDS entre 0,75 y 3 µg g^{-1} fueron entre 92,2 y 100,0%.

Keywords: tensoactivos aniónicos, multiconmutación, espectrofotometría, arena.

1. Introduction

Anionic surfactants comprise a set of chemical compounds widely used for several purposes in products as shampoos, soaps, detergents cosmetics, etc. (1). The extensive use of surfactants means they can become a problem of contamination from wastewater and makes necessary their determination in environmental matrices, like water or sand. Anionic surfactants can be retained in the sea sand and should be leached from it to determine their concentration. Therefore, its determination is interesting for both, environmental and health studies (2).

The official method for anionic surfactants determination in water is based on the reaction of these compounds with methylene blue (MB) followed by extraction with chloroform prior to the spectrophotometric determination at 656 nm (3, 4). However, manual extractions present a series of drawbacks such as high consumption of sample and toxic organic solvent, low sampling frequency, loss of analyte through manipulation and contamination of atmosphere by organic vapours.

Many efforts have been made to overcome these inherent drawbacks. Among them, one of the most successful techniques is the on-line liquid-liquid extraction using flow systems (5-8). Flow injection liquid-liquid extraction was proposed in 1978 by Karlberg and Thelander (9) and Bergamin et al. (10). By using the aforementioned approach, consumption of reagents and organic solvents is lower than those required in manual procedures and consequently the waste generation is reduced. However a more recent methodology, which used computer-controlled solenoid valves, has been able to further reduce reagent con-

sumption and waste generation and minimized manipulation of the system, with consequent benefits for precision measures and for the operator (11). A fully-mechanized multicommutated procedure for the determination of anionic surfactants in waters employing the methylene blue spectrophotometric method was proposed in 2005 by Rodenas-Torralba et al. (12) achieving an improvement of throughput and drastic reduction of organic solvent consumption without any significant loss of sensitivity.

Multicommutation presents a significant reduction on reagent consumption and waste production and in the present work it has been employed this fast and clean procedure to determine anionic surfactants in spiked sea sand samples.

2. Materials and Methods

2.1. Apparatus and flow set-up

The equipment set-up comprised a Hewlett-Packard Model 8452A diode array spectrophotometer (Waldbronn, Germany) equipped with a 10 mm optical pathway flow cell, with 50 µL inner volume, a Gilson Minipuls P2 peristaltic pump (Villiers Lebel, France) furnished with Viton© (Iso-Versinic) pumping tubes, a PC 486 microcomputer furnished with a PCL711S Advantec electronic interface card and running software written in QUICK BASIC 4.5. Six three-way solenoid valves NResearch, 161T031 (West Caldwell, USA), three home-made Mariotte vessels of 1000 mL and a home-made water/organic phase separation chamber complete the manifold. Reactor coils and conducts were of PTFE (0.8 mm i.d.). Coils employed for the connection between Mariotte vessels and solenoid valves were of PTFE (1.6 mm i.d.). The peristaltic pump was operated to provide a flow rate of 3.2 mL min^{-1}

and the Mariotte vessels located 100 cm over the top of the separation chamber provided constant flows of 180 µL s⁻¹ for sample and standards, 60 µL s⁻¹ for the MB solution and 70 µL s⁻¹ for $CHCl_3$.

The manifold employed for the mechanization of the anionic surfactant determination is indicated in figure 1. Samples and standards containing sodium dodecylsulphate (SDS), the MB solution and $CHCl_3$ were supplied through switching ON valves V_1, V_2 and V_3, respectively, and using the

Mariotte flask for reagent delivery. PTFE fragments were used to fill the bottom 16 cm of the separation chamber in order to provide a turbulent flow which can improve the reaction between MB and SDS and the mass transfer process during extraction. Additionally, an air flow of 106 µL s⁻¹ was counter current introduced through the base of the separation chamber for shaking the mixture of phases, using V_6 valve. Two additional solenoid valves, V_4 and V_5, were employed to take the organic phase to be measured in the detector.
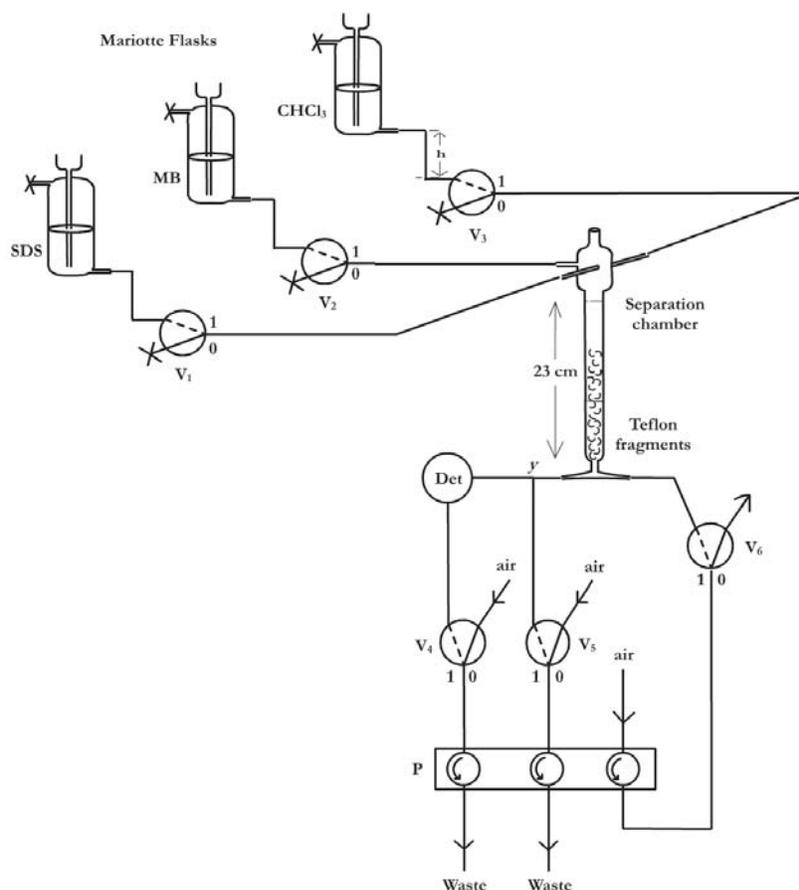
Figure 1.   Manifold employed for the multicommutation determination of anionic surfactants. Note: SDS: sodium dodecylsulfate; MB: methylene blue; $CHCl_3$: chloroform used as organic solvent extractant; V_1, V_2, V_3, V_4, V_5 and V_6: three-way solenoid valves; h: height necessary for the gravity flow (100 cm); y: Y type joint devices machined in acrylic; Det: detector; P: peristaltic pump; (------) Valve switched ON (bit 1 electronic position); (—) Valve switched OFF (bit 0 electronic position). Separation column of 23 cm length.

A vortex *2x³ Velp Scientifica* (Milano, Italy) and an ultrasound water bath *J. P. Selecta* (Barcelona, Spain) were used to do the leaching of anionic surfactants from sand samples.

2.2. Reagents and samples

Sodium dodecylsulphate (SDS [$CH_3(CH_2)_{11}OSO_3Na$], purity 99.0% or higher) was employed as a representative anionic surfactant for calibration. It was obtained from Sigma (St. Louis, USA). Methylene Blue (MB [$C_{16}H_{18}N_3SCl\cdot3H_2O$], purity 98.5% or higher) was used as a cationic dye and obtained from Merck (Steinheim, Germany). Chloroform stabilized with ethanol from Scharlau (Barcelona, Spain) was used as extractant of the SDS-MB ion pair. For these products, analytical grade reagents were used.

Five sand samples were collected from different points of the Valencia Region (Spain) at the Mediterranean coast. Samples 1, 2 and 3 were collected from Benidorm coast at 10, 20 and 25 m deep. Sample 4 was obtained from the seaside in the Malvarrosa beach and sample 5 was collected from an irrigation channel in Port Saplaya at 1 m deep. A previous analysis of all these samples, by using the reference procedure (3), provided anionic surfactant concentrations bellow the limit of detection of the method and after that, samples were spiked with known amounts of SDS in order to evaluate the recovery percentage of the methodology.

2.3. Recommended leaching procedure for surfactants from sand samples

Experimental procedure consisted in the extraction of surfactants from 5 g of sand with 5 mL of hot water (90 °C) using 5 min stirring with vortex and 5 min with soni-cation. After that, water and sand were let to separate few seconds and the aqueous phase, aspirated by a peristaltic pump, was introduced into the manifold to carry the out on-line colorimetric reaction with MB and extraction in chloroform.

The aforementioned procedure was repeated twice for each sample and data found combined to obtain the concentration of anionic surfactants in real samples.

2.4. Measurement procedure

Using the manifold depicted in figure 1 and the experimental steps shown in table 1, a total volume of sample, or standard, of 3.60 mL, corresponding to 20 pulses of 1.0 second, was placed in the separation chamber through valve V_1. At the same time a total volume of 0.24 mL of a 10^{-3} mol L^{-1} MB solution, corresponding to 20 pulses of 0.2 seconds, was added through valve V_2. A time of 3.0 s was programmed as mixing step between the aforementioned solutions inside the separation chamber. An air flow of 106 µL s^{-1}, introduced using valve V_6, was bubbled in counter current inside the extraction chamber to favour the reaction between anionic surfactant and MB to form an ion pair. After the mixing step valve V_3 was switched ON/OFF, for 10 cycles of 1.0 second, in order to introduce 0.70 mL of chloroform inside the mixing chamber. During this time, an additional 7.0 seconds air flow was also bubbled through the chamber to improve the mass transfer of the ion pair to the organic phase. To provide phase separation all valves were switched OFF during 7.0 s. Afterwards, valve V_5 was switched ON for 3.0 s to eliminate the rests of aqueous phase which could remain at the bottom of the separation chamber. After switching OFF V_5, V_4 was switched ON to let the organic layer to reach the detector for 10.0 seconds. After that, V_4 was switched OFF and V_5 was switched ON for 10.0 s to displace the aqueous phase from the separation chamber to the waste making during this time the absorbance measurements in the stopped-flow mode. At the end of the process, V_4 and V_5 were switched ON for 10.0 s to clean the set-up.

Absorbance values at 656 nm were corrected, with the absorbance at 750 nm, to compensate base-line shift. These measure-

Table 1

Multicommutated program employed to determine anionic surfactants

Step	Parameter	Valves switched ON	Settled time (s)
1	Inserting sample solution	V_1	1.0 (20 cycles)
	Inserting reagent solution	V_2	0.2 (20 cycles)
2	Mixing	V_6	3.0
3	Inserting organic solvent	$V_3 + V_6$	1.0 (10 cycles)
4	Extraction	V_6	7.0
5	Separation	-	7.0
6	First portion delivering	V_5	3.0
7	Displacing organic phase	V_4	10.0
8	Aqueous phase delivering	V_5	10.0
9	Flow cell empting	$V_4 + V_5$	10.0

Step 1 involves the sequential injection of small volumes of sample or standards and reagent solution through a series of 20 cycles of 1.0 s and 0.2 s duration, respectively.

ments were taken for both, samples and SDS aqueous standards; and employed for anionic surfactant determination using CHCl3 stabilized with ethanol as a blank.

3. Results and discussion

3.1. Experimental conditions for multicommutation analysis

In the experimental set-up indicated in table 1, sample and reagent volumes were inserted sequentially into the separation chamber. The ion pair extraction occurred by falling down chloroform and bubbling air in counter current from the bottom of the separation chamber. Good mixing conditions were attained by this way. Some experimental parameters as the study of the effect of reagents and sample volumes and the effect of the sampling cycles in multi-commutation were assayed in a previous work (12) and the optimal parameters were selected to carry out the measurements in this study. The concentration of anionic surfactant can be determined by measuring the corrected absorbance of the chloroform phase at 656 nm.

3.2. Effect of the stirring time for surfactants leaching

It was studied the effect of the shaking time of sand sample with hot water on the absorbance signal by using a vortex and an ultrasound water bath. As can be seen in figure 2 it was observed that 5 minutes of vortex shaking and 5 min of sonication were the best option to extract the anionic surfactants from the sand, taking into account the compromise between absorbance signal (sensitivity), absorbance dispersion (repeatability) and extraction time (throughput). The use of a shaking time lower than 5 minutes not assures a complete extraction of the anionic surfactants, and times higher than 5 minutes provided comparable results.

3.3. Recovery of the anionic surfactants added to the sand

Five mililiters of a 3.5 10^{-6} mol L^{-1} SDS concentration were added to 5 g of Malvar-rosa beach sand sample. After that, retained surfactant was leached with 5 mL hot water, shaken for 5 min plus 5 min using vortex and ultrasound bath respectively, and

measured spectrophotometrically the signal obtained after on-line reaction and extraction. The aim of this procedure was to find out the retention percentage of the anionic surfactants in the sand. Furthermore, this procedure was repeated in different days (from day 1 to 8) on a series of portions of the same sand. As can be seen in figure 3, the first leaching step provided, for all the days studied, leached percentages of around 80 ± 5%. So, it would be necessary successive extractions to leach quantitatively the surfactant that remains adsorbed among the sand particles. It was proved that two leaching steps were enough to obtain the quantitative (>90%) recovery of the surfactant.

3.4. Analytical figures of merit

Using the setup shown in figure 1 and under the conditions selected in the 2.4 section, an extraction calibration line was obtained for SDS in the concentration range from 0.4×10^{-6} to 8.7×10^{-6} mol L^{-1} (0.11 to 2.48 mg L^{-1}) being found the regression equation $A = (119000 \pm 2000)$ C + (0.047 ± 0.006) (C in mol L^{-1}) with a correlation coefficient of 0.996, as shown in table 2. The LOD of the procedure was 1.4×10^{-7} mol L^{-1} (0.04 mg L^{-1}) and a RSD of 4.2% was found for n=10, at 2×10^{-6} mol L^{-1} concentration.
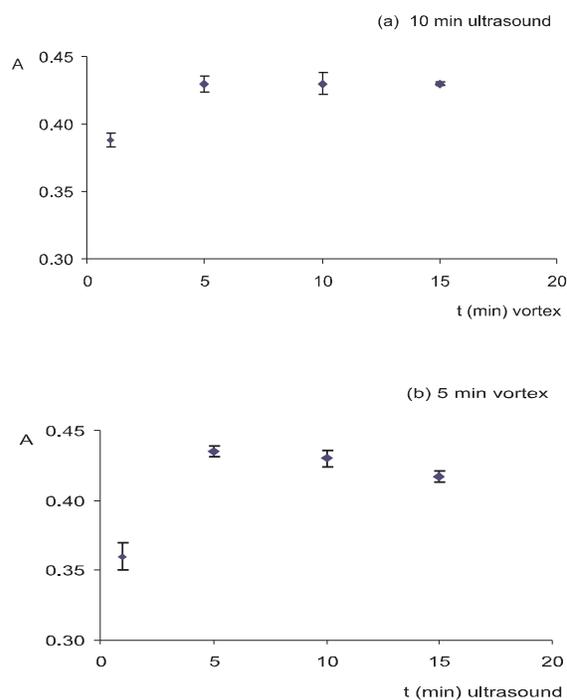
Figure 2. Effect of the stirring time on the absorbance signal. (a) Variation of the shaking time in vortex. (b) Variation of the stirring time in the ultrasound water bath. 3.5×10^{-6} mol L^{-1} anionic surfactant.
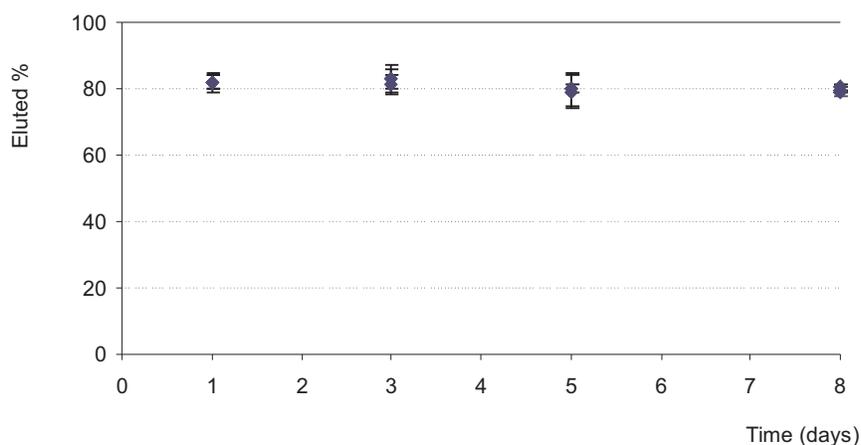
Figure 3. Study of the eluted percentage of the anionic surfactant in a sand sample from Malvarrosa beach. 3.5×10^{-6} mol L^{-1} anionic surfactant. They were made three series of three replicates each day.

Table 2

Analytical parameters of SDS-MB spectrophotometric determination by using the reference and the proposed multicommutated methods

	Reference method (3)	Multicommutation
Calibration line [a]	y = (79000 ± 3000) x + + (0.062 ± 0.003)	$y = (119000 ± 2000)\, x^{\,d}$ + + (0.047 ± 0.006)
Correlation coefficient (r)	0.998	0.996
Linear range (mol L^{-1})	0.4×10^{-6} - 1.8×10^{-6}	0.4×10^{-6} - 8.7×10^{-6}
Linear range (mg L^{-1})	0.11-0.50	0.11-2.48
RSD (%) [b]	6.2	4.2
LOD (mol L^{-1}) [a]	3.9×10^{-8}	1.4×10^{-7}
LOD (mg L^{-1}) [a]	0.011	0.04
LOD (µg g^{-1})	0.011	0.04
Sample consumption (mL) [c]	10000	360
Dye consumption (mL) [c]	1000	24
Solvent consumption (mL) [c]	4500	70
Waste (mL) [c]	15500	450
Throughput Determination (h^{-1})	1	40
Throughput Analyis (h^{-1})	0.75	3

[a] Concentrations and LOD values are related to the organic phase.   [b] RSD (%): relative standard deviation corresponding to ten independent measurements of a solution containing 2×10^{-6} mol L^{-1}.   [c] Sample and reagent consumptions and waste generation corresponding to 100 analysis.   [d] Concentration in mol L^{-1}.

Table 2 shows the main characteristics of anionic surfactants determination by using multicommutation compared with those found by the reference procedure. It can be concluded that multicommutation provided comparables analytical basic properties to those obtained by the reference procedure.

The sampling determination throughput, of the on-line measurement, was 40 injections per hour, providing a total waste volume of 4.5 mL per determination. So, it means a 40 times enhancement of the laboratory productivity and a 34 times reduction of laboratory wastes as compared with the reference batch procedures. Concerning sample and reagent consumptions, it can be seen that the reference method involves a total consumption of 10 L of sample, 1 L of dye solution and 4.5 L of CHCl$_3$ for 100 determinations being required 360 mL, 24 mL and 70 mL, respectively, for the multicommutation approach, thus reducing the consumptions by a factor of 28, 42 and 64 for sample, MB and CHCl$_3$, respectively. So, it can be concluded that the developed procedure is a sustainable and environmentally friendly alternative to the reference procedure.

For an evaluation of the accuracy of the recommended procedure, five actual samples of sand taken from different parts of the Valencia coast were spiked with different amounts of SDS and then analyzed by the developed procedure.

Data reported in table 3 show that a single extraction was not enough to obtain a complete recovery of added SDS. It meant about 79.97 ± 0.13% recovery in the first extraction and ca. an additional 15 ± 3% in the

Table 3
Total anionic surfactant concentrations found in spiked sea sand samples

Sand sample	First extraction (μg g^{-1})*	Second extraction (μg g^{-1})*	Third extraction (μg g^{-1})*	Total recovery percentage (%)	Anionic surfactant added to the sand (μg g^{-1})*
Irrigation channel	2.40 ± 0.02 (80.0%) **	0.49 ± 0.04 (16.3%) **	< LOD	96.3±1.5	3.00
Beach (shore sea)	1.42 ± 0.01 (79.8%)	0.25 ± 0.02 (14.0%)	< LOD	93.8±1.3	1.78
Deep sea 1	1.17 ± 0.02 (80.1%)	0.21 ± 0.01 (14.4%)	< LOD	94.5±1.5	1.46
Deep sea 2	1.03 ± 0.02 (79.8%)	0.16 ± 0.01 (12.4%)	< LOD	92.2±1.7	1.29
Deep sea 3	0.60 ± 0.04 (80.0%)	0.15 ± 0.01 (20.0%)	< LOD	100±5	0.75

* Results in μg anionic surfactant / g sand. ** Results in brackets correspond to eluted percentages referred to added surfactant. Results indicated are the average of 3 independent determinations ± the corresponding standard deviation.

second extraction step. For all the samples a third extraction provided concentration values under the LOD of the method.

It can be concluded that it is necessary to do two sequential extractions with hot water to assure the complete leaching of anionic surfactants from sand samples and that demonstrates that the method is free from systematic errors.

4. Conclusions

A multicommutated approach for on-line reaction with MB and liquid-liquid extraction for anionic surfactants determination was exploited for the determination of these analytes in sand samples previously treated twice with hot water. Consumption of reagents and organic solvent, also waste generation, can be tremendously reduced as compared with the in batch procedure. Leaching of anionic surfactants from sand samples has been successfully carried out taking two successive treatments with hot water for 5 min with vortex treatment and 5 min of sonication.

The proposed method is simple and reliable. Extraction, of the ion pair of surfactants with MB, and detection is integrated in the same manifold and all the operations can be controlled from the computer. Additionally, as it has been indicated, multicommutation offers an environmentally friendly alternative to do this kind of determinations.

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