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An environmentally friendly multicommutated alternative to the reference method for anionic surfactant determination in water

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Abstract

It has been developed a fully mechanized procedure for the spectrophotometric determination of anionic surfactants in water expressed in terms of SDS concentration. The reference method, based on the reaction of SDS with methylene blue (MB) followed by extraction in chloroform, was mechanized in order to reduce the consumption of organic solvents. The system was based on the multicommutation approach and provided a 35 times reduction of the waste production without sacrificing the figures of merit of the method in terms of sensitivity and repeatability, for a dynamic linear range from 0.2 to 1.7 mg l^{-1}. Results obtained for washing water samples were comparable with those obtained using the reference method and no significant differences, at 95% confidence level, were observed. Other useful characteristics are a solvent consumption of 0.7 ml per determination, a sampling throughput of 40 determinations per hour, a relative standard deviation of 5.9% ($n = 10$) for a sample containing 2×10^{-6} mol l^{-1} (576 μg l^{-1}) surfactant and a limit of detection of 6.1×10^{-9} mol l^{-1} (1.7 μg l^{-1}).

Keywords: Multicommutation; Flow; Spectrophotometry; Surfactant; Washing water

1. Introduction

Anionic surfactants comprise a series of products widely used for washing proposals, both for personal hygiene and industrial cleaning applications. The extensive use of surfactants makes necessary their determination in natural waters as potential contaminants. In this sense, the authorities of the European Union established a maximum tolerated limit of 200 μg l^{-1} for anionic surfactants in water supplies for human consumption [1].

The official method for anionic surfactants determination in water is based on the reaction of these compounds with methylene blue (MB) followed by an extraction with chloroform prior to the spectrophotometric determination at 654 nm [2]. This analytical procedure, carried out manually, is very tedious. The use of large volumes of chloroform (45 ml per determination) and a lot of laboratory glassware, make these operations extremely expensive, time consuming and uncomfortable for the operator. So it seems necessary to search for alternatives of the aforementioned method in order to increase the laboratory productivity and operator safety and comfort and to reduce drastically the reagents consumption and waste production.

Koga et al. [3] proposed a reduction of the size of sample employed for anionic surfactant determination in water, being modified this method to use only 50 ml of water and 5 ml $CHCl_3$, having obtained a six times increase of the laboratory productivity.

On the other hand, the use of small tubes and Pasteur pipettes to do the solvent extraction and phase separation of the ion pair between anionic surfactants and MB provided a 20 times reduction of the sample size, a five times reduction

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of $CHCl_3$ consumption and avoids the use of expensive glassware [4].

Probably, the most innovation approach was that developed by Agudo et al. [5] based on the continuous solvent extraction inside the measurement cell by flow injection analysis, which provides a sampling throughput of 20 h^{-1} and a $CHCl_3$ consumption of 200 μl per determination.

In the last years, multicommutation has opened a new way for the mechanization of analytical procedures [6]. Multicommutation could be understood as a means to handle solutions in flow system by inserting sequentially small aliquots of sample and reagent solutions into the reacting device (coiled reactor or chamber). The figures of merit of the procedures based on multicommutation are usually similar to those observed employing ordinary flow process, nevertheless presenting a significant reduction on reagent consumption and waste production [7].

In this work, a multicommutation automated procedure for the determination of anionic surfactants in water employing the methylene blue spectrophotometric method has been developed.

2. Experimental

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 386 microcomputer furnished with a PCL711S Advantec electronic interface card and running software in QUICK BASIC 4.5, 6 three-way solenoid valves NResearch, 161T031 (West Caldwell, USA), three home-made Mariotte vessels of 1000 ml and home-made water/organic phase separation chambers. 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 Fig. 1. Samples and standards containing sodium dodecylsulphate (SDS), the MB solution and $CHCl_3$ were supplied through the 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 lower part 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 select the organic phase to be measured in the detector.

Different designs of the separation chamber were home-made and assayed for this study. Fig. 2 indicates the five ones which provided the best results. Basically, the separation chamber was constructed in glass from cylindrical pieces with three reagent intakes located at the top for the introduction of SDS, MB and $CHCl_3$ and two outsides located at the bottom, one for air bubbling in counter current and the second one for aspiration of the separated phases. This basic design (A) was modified to let open the system to favour phases separation (B–E) and additionally, in the case of B, a single outside was employed for liquid aspiration, shaking the phases with a magnetic bar. The final design was improved by using different volumes of the thin part to increase the volume of the aqueous phase employed for extraction thus enhancing the preconcentration from a maximum volume of 35 ml (C and D) to a volume of 100 ml (E).

2.2. Reagent solutions

Sodium dodecylsulphate was employed as a representative anionic surfactant for calibration. It was obtained from Sigma (St. Louis, USA) (SDS [$CH_3(CH_2)_{11}OSO_3Na$], purity 99.0% or higher). Methylene blue (trihydrates) was used as a cationic dye and obtained from Merck (Steinheim, Germany) (MB [$C_{16}H_{18}N_3SCl{\cdot}3H_2O$], purity 98.5% or higher). Chloroform stabilized with ethanol (Scharlau, Barcelona, Spain) was used as extractant. For other products, analytical grade reagents were used.

2.3. Reference procedure

Hundred millilitre of sample was placed into a 250 ml separating funnel and 10 ml of a 1×10^{-3} mol l^{-1} methylene blue solution and 15 ml chloroform were added. After shaking the mixture vigorously for 1 min, the two phases were let to separate and chloroform layer taken for analysis. Each sample was extracted additionally three times using 10 ml portion of chloroform and absorbance measurements were made at 654 nm in front of an external calibration prepared from SDS. Solutions in the range between 0.1 and 0.5 mg l^{-1} were extracted in the same way than samples [2].

2.4. Recommended procedure

Using the manifold depicted in Fig. 1 and the experimental steps shown in Table 1, a total volume of sample of 3.60 ml, corresponding to 20 pulses of 1.0 s was placed in the separation chamber through valve V_1, at the same time than a total volume of 0.24 ml of a 1×10^{-3} mol l^{-1} MB solution,

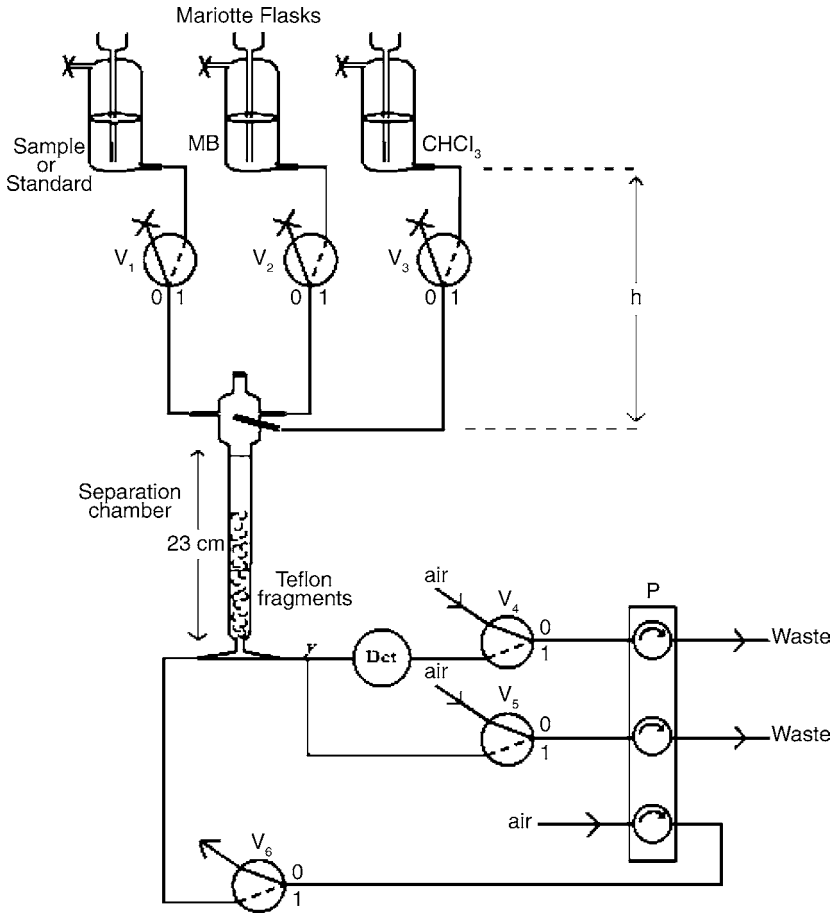

Fig. 1. Manifold employed for the multicommutation determination of anionic surfactants. Note—SDS: sodium dodecylsulfate; MB: methylene blue; $CHCl_3$: organic solvent extractant; V_1, V_2, V_3, V_4, V_5 and V_6: three-way solenoid valves; *h*: height necessary for the gravity flow (100 cm); *y*: Y type 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.

corresponding to 20 pulses of 0.2 s 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 $\mu l\,s^{-1}$ (through the use of valve V_6) was bubbled in counter current to favour the reaction between anionic surfactant and MB to form an ionic pair. After the mixing step, valve V_3 was switched ON/OFF for 10 cycles of 1.0 s in order to introduce 0.70 ml of chloroform inside the mixing chamber. During this time, and additional 7.0 s, air was also bubbled through the chamber to improve the mass transfer of the ionic pair to the organic phase. To provide phase separation, all valves were switched OFF during 7.0 s.

Table 1
Multicommutated program employed to determine anionic surfactants

Event sequence	Parameter	Valves switched ON	Settled time (s)
1	Inserting sample solution (is)	V_1	1.0 (20 cycles)
	Inserting reagent solution (is)	V_2	0.2 (20 cycles)
2	Mixing step (ms)	V_6	3.0
3	Inserting organic solvent step (ios)	$V_3 + V_6$	1.0 (10 cycles)
4	Extraction step (es)	V_6	7.0
5	Separation step (sp)	–	7.0
6	First portion delivering step (fd)	V_5	3.0
7	Displacing organic phase step (dos)	V_4	10.0
8	Aqueous phase delivering step (aq)	V_5	10.0
9	Flow cell empting step (fs)	$V_4 + V_5$	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 and 0.2 s duration, respectively.

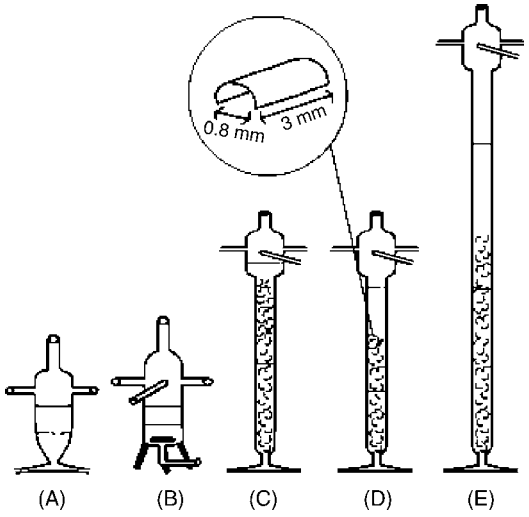

Fig. 2. Extraction cell designs. (A) Separation chamber of 4 cm length and 1.2 cm internal diameter. (B) Separation chamber of 3 cm length and 2 cm internal diameter, with a magnetic bar stirring inside. (C) Separation chamber of 35 ml upper part and 23 cm length, 0.7 cm internal diameter with 23 cm filled with fragments of Teflon separation area. (D) Separation chamber of 35 ml upper part and 23 cm length, 0.7 cm internal diameter with 16 cm filled with fragments of Teflon separation area. (E) Separation chamber of 100 ml upper part and 65 cm length, 0.7 cm internal diameter with 27 cm filled with fragments of Teflon separation area. Inset: PTFE packed pieces.

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 s. 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 654 nm, were corrected with the absorbance at 750 nm, to compensate base-line shift. These measurements were taken for both, samples and aqueous standards of SDS and used for anionic surfactant determination using $CHCl_3$ stabilized with ethanol as a blank.

3. Results and discussion

3.1. Reaction of SDS and MB

The equilibrium between SDS and MB and the distribution of SDS–MB ion pair in water and chloroform has been qualitatively reported in the literature [3]. The SDS, and other anionic detergents, dissolved in water are slightly soluble in $CHCl_3$. On the other hand, MB dissolves well in both, $CHCl_3$ and water, providing a blue colour solution in all the cases. When pure water is mixed with a $CHCl_3$ solution of MB, the blue colour is rapidly transferred to the water phase.

3.2. Experimental conditions for multicommutation analysis

In the experimental set-up indicated in Fig. 1, sample and reagent volumes were inserted sequentially into the separation chamber. The ionic pair extraction occurred by falling down chloroform and bubbling air in counter current. Good mixing conditions were attained by this way.

Therefore, to attain maximum sensitivity it is necessary to consider the separation chamber length and geometry, additionally than the sampling cycles and the use of a packing material to create a turbulent flow which can favour the reaction between MB and SDS and the mass transfer process.

3.2.1. Selection of the separation chamber

Two empty separation chambers and two packed ones (see Fig. 2) were assayed for making the on-line extraction of the SDS–MB ion pair into $CHCl_3$ using in all the cases, except for chamber B, the manifold depicted in Fig. 1 (for chamber B, V_6 and air line were unnecessary).

In these experiments, SDS and MB solutions were merged by using V_1 and V_2 pulses and let to stand before the introduction of $CHCl_3$.

When thin separation area chambers were employed (C–E), it was also evaluated the use of different portions of the chamber filled with PTFE fragments from the total height (23 cm for C) to 16 cm in the case of D and 23 cm over a total length of 65 cm for E.

Different sample volumes from 3.6 to 21.6 ml were assayed through the use of different inserting times and cycles for a fixed 1×10^{-3} mol l^{-1} MB solution and a $CHCl_3$ volume from 0.7 to 1.4 ml was used for extraction.

Table 2 shows the absorbance values found in each case for a solution of 576 μg l^{-1} SDS with the corresponding standard deviation and the typical calibration line obtained for each system in terms of absorbance units of the extracted chloroformic solution per mol^{-1} l SDS.

As can be seen in Table 2, separation chambers A and B provided a reduced sensitivity and a poor repeatability, especially in the case of A, due to the difficulties on making a quantitative extraction. Separation chambers with a thin separation area provided sensitive and reproducible data, based on the quantitative extraction of SDS and easy phase separation in case D and E and a high aqueous/organic phase ratio of 10.3 in case C. However, as it can be seen in the case of C and D both, the volume of sample and the relation between sample and $CHCl_3$ volumes together with the use of packing materials control the analytical sensitivity to be obtained. In fact aqueous/organic phase ratios from 2.6 to 5.1 could be found on using separation chamber D filled partially with PTFE fragments and a 26 times preconcentration was found on using a big separation chamber (E).

The best results in terms of sensitivity in the organic phase and precision were found on using chamber D and for 20 cycles of 1.0 s for samples and 20 cycles of 0.2 s for MB and using 0.7 ml of $CHCl_3$. However, for highly diluted samples,

Table 2
Effect of the extraction cell design on the analytical sensitivity and reproducibility

Cell	Loading plugs			Total volume (ml)	$A \pm s$[a]	Calibration curve	R	LOD and RSD
A	SDS	45 s	1 cycle	8.10	0.17 ± 0.03	$y = (80000 \pm 2000)x + (0.01 \pm 0.02)$	0.997	LOD = 1.1×10^{-7} mol l^{-1} (31.7 ng ml^{-1}), RSD = 17.6%
	MB	2 s	1 cycle	0.12				
	$CHCl_3$	15 s	1 cycle	1.05				
B	SDS	40 s	1 cycle	7.20	0.123 ± 0.005	$y = (53700 \pm 500)x + (0.015 \pm 0.003)$	0.999	LOD = 2.8×10^{-7} mol l^{-1} (80.6 ng ml^{-1}), RSD = 4.1%
	MB	2 s	1 cycle	0.12				
	$CHCl_3$	15 s	1 cycle	1.05				
C	SDS	2 s	20 cycles	7.20	0.22 ± 0.01	$y = (101000 \pm 1000)x + (0.023 \pm 0.007)$	0.997	LOD = 3.0×10^{-7} mol l^{-1} (86.4 ng ml^{-1}), RSD = 4.5%
	MB	0.2 s	20 cycles	0.24				
	$CHCl_3$	1 s	10 cycles	0.70				
D	SDS	1 s	20 cycles	3.60	0.21 ± 0.01	$y = (141000 \pm 7000)x - (0.06 \pm 0.02)$	0.997	LOD = 6.1×10^{-9} mol l^{-1} (1.7 ng ml^{-1}), RSD = 4.8%
	MB	0.2 s	20 cycles	0.24				
	$CHCl_3$	1 s	10 cycles	0.70				
	SDS	2 s	10 cycles	3.60	0.116 ± 0.009	$y = (61800 \pm 700)x - (0.014 \pm 0.004)$	0.9998	LOD = 5.0×10^{-8} mol l^{-1} (14.2 ng ml^{-1}), RSD = 7.7%
	MB	0.2 s	10 cycles	0.12				
	$CHCl_3$	2 s	10 cycles	1.40				
E	SDS	2 s	60 cycles	21.60	0.22 ± 0.01	$y = (127000 \pm 4000)x - (0.02 \pm 0.01)$	0.998	LOD = 5.0×10^{-10} mol l^{-1} (0.14 ng ml^{-1}), RSD = 4.5%
	MB	0.2 s	60 cycles	0.72				
	$CHCl_3$	2 s	6 cycles	0.84				

SDS: anionic surfactant; MB: methylene blue; $CHCl_3$: solvent extractant. % RSD: relative standard deviation of the reference standard solution; LOD: limit of detection. Measurements for $k = 3$ in the original sample.

[a] Absorbance corresponding to six measurements of a solution containing 2×10^{-6} mol l^{-1} (576 μg l^{-1}) of SDS in the aqueous phase.

design E, which involves the use of a maximum sample volume of 21.6 ml for a $CHCl_3$ volume of 0.84 ml, provided a limit of detection of 0.14 μg l^{-1} anionic surfactant in the original sample, thus offering the best alternative.

3.2.2. Study of the effect of reagents and sample volumes

Sample or standard, reagents and air flow rates were fixed by using different positions of the Mariotte flasks and different rotation speeds and pump tubes.

Flow rates of 180, 60, 70 and 106 μl s^{-1} for sample, dye, solvent and air streams, respectively, were found to be convenient for introducing ml volumes on using short insertion times from 3 to 10 s.

On using the separation chamber C and D indicated in Fig. 2, it was evaluated the effect of the volumes of sample, MB and $CHCl_3$ on the extract absorbance measurements.

The total sample volume to be employed strongly depends on the volume of the separation chamber. Total volumes from 3.6 to 21.6 ml were assayed on varying the chamber design (see Table 2).

The volume of the organic plug introduced in the separation chamber is one of the most important variables in order to obtain a good aqueous/organic phase ratio for a fixed sample volume. It is clear that small $CHCl_3$ volumes are highly convenient in order to reduce the reagent consumption and side effects of toxic reagents. However, volumes smaller than about 0.5 ml $CHCl_3$ create practical difficulties to fill the detection cell and provided a poor precision. A volume of 0.7 ml per determination (10 cycles of 1.0 s) was finally selected as a compromise between technical difficulties and sensitivity.

The best MB amount in the separation chamber was obtained for a 1×10^{-3} mol l^{-1} solution and 0.24 ml insertion through the use of 20 cycles of 0.2 s. Higher MB amounts than that led to molecular aggregations of the reagent which can be extracted by chloroform, thus increasing the blank signal and adversely affecting the sensitivity. Moreover, a high concentration of MB involved long times for the washing step between samples.

3.2.3. Study of the sampling cycles in multicommutation

The analytical sensitivity of multicommutation methods increases on increasing the total sample volume introduced in the system [8].

For a fixed MB concentration and $CHCl_3$ volume, it was evaluated the effect of increasing volumes of SDS solutions as a function of the use of an increasing number of cycles of 1.0 s insertion time (see Fig. 3).

It can be seen that on using separation chamber D the absorbance signals increase linearly till to reach a plateau for 20 sampling cycles, which corresponds to 3.6 ml of sample, independently on the use of different SDS concentrations, thus indicating a limited extraction of SDS in the experimental conditions selected based on the shaking of both aqueous SDS and $CHCl_3$ MB solutions (see Fig. 3a).

On the other hand, on using the separation chamber E, the plateau was reached for 60 sampling cycles, corresponding to 21.6 ml (Fig. 3b). These data indicated that, in spite of the

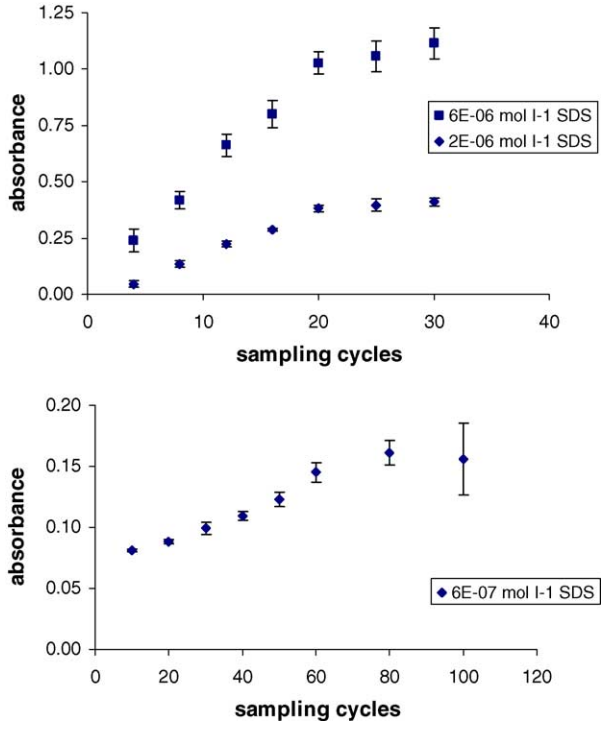

Fig. 3. Effect of the number of sampling cycles on the absorbance signal of SDS determined with MB. Note: each cycle corresponds to 1 s of loading time. Experiments were carried out for 2×10^{-6} and 6×10^{-6} mol l^{-1} SDS using the separation chamber D with 20 cycles of 0.2 s for 1×10^{-3} mol l^{-1} MB and 10 cycles of 1 s $CHCl_3$ (a) and for a concentration of 6×10^{-7} mol l^{-1} SDS in the separation chamber E using 60 cycles of 0.2 s 1×10^{-3} mol l^{-1} MB and 6 cycles of 2 s of $CHCl_3$ (b).

use of excess concentration of MB, the extraction efficiency, for a fixed mass of SDS strongly depends on the geometry and shaking characteristics of the system.

On comparing with in batch experiments, it was confirmed that the extraction efficiency of the ion pair between SDS and MB in $CHCl_3$ was 78 ± 3% and that this value is reproducible for both, sample and standard solutions.

3.3. Analytical figures of merit

In the best operational conditions determined previously, additional experiments were performed in order to establish the linear dynamic range and limit of detection. These assays were done running a set of anionic surfactant reference solutions and the blank solution.

Table 3 shows the main characteristics of anionic surfactants determination by using multicommutation compared with those found by the reference procedure. As can be seen, the slope of a typical calibration graph obtained by multicommutation is 1.8 times higher than that found in the reference method. The limits of detection obtained by both reference method and multicommutation were 1.8×10^{-8} and 6.1×10^{-9} mol l^{-1}, respectively, related to the original sample. The coefficient of variation of eight independent analysis of a solution containing 2×10^{-6} mol l^{-1} surfactant was of the same order for both the reference (6.2%) and the multicommutation approach (5.9%). So it can be concluded that multicommutation does not sacrifice any of the analytical basic properties of the method as compared with the reference procedure.

The sampling throughput 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 procedures. Concerning sample and reagent consumptions, it can be seen in Table 3 that the reference method involves a total consumption of samples and reagents for 100 determinations of 10 l of sample, 1 l of dye solution and 4.5 l of $CHCl_3$ being required 360, 24 and 70 ml, respectively, for the multicommutation approach,

Table 3
Analytical parameters of SDS–MB spectrophotometric determination by using the reference and the proposed multicommutated methods

	Reference method	Multicommutation[a]
Calibration line[b]	$y = (79000 \pm 3000)x + (0.062 \pm 0.003)$	$y = (141000 \pm 7000)x - (0.06 \pm 0.02)$
Correlation coefficient (r)	0.998	0.997
Linear range (mol l^{-1})	0.4×10^{-6} to 1.8×10^{-6}	0.7×10^{-6} to 6.1×10^{-6}
Linear range (mg l^{-1})	0.1–0.5	0.2–1.7
RSD (%)[c]	6.2	5.9
LOD (mol l^{-1})[b]	3.9×10^{-8}	3.1×10^{-8}
LOD (mol l^{-1})[d]	1.8×10^{-8}	6.1×10^{-9}
LOD (μg l^{-1})[b]	11.4	8.8
LOD (μg l^{-1})[d]	5.2	1.7
Sample consumption (ml)[e]	10000	360
Dye consumption (ml)[e]	1000	24
Solvent consumption (ml)[e]	4500	70
Waste (ml)[e]	15500	450
Throughput (h^{-1})	1	40

[a] Multicommutation measurements were made on using separation chamber D.
[b] Concentrations and LOD values are related to the organic phase.
[c] RSD (%): relative standard deviation corresponding to 10 independent measurements of a solution containing 2×10^{-6} mol l^{-1}.
[d] LOD values are related to the original sample.
[e] Sample and reagent consumptions and waste generation corresponding to 100 analysis.

Table 4
Analytical comparison of the proposed method with previous ones

	Proposed method	Previously reported methods						
		[3]	[4]	[5]	[9]	[10]	[11]	[12]
Correlation coefficient (r)	0.997	0.9993	0.997–0.999	0.990	0.999	–	0.9999	0.999
Linear range (mg l^{-1})	0.2–1.7	0.02–0.5	0–2	–	0–20	0.01–0.4	1.4–2.5	0–1.5
RSD %	5.9	7.2–7.5	6	6.7	0.5	2	0.4	1.5
LOD (μg l^{-1})	1.7	20–50	–	20	100	5	200	20
Sample consumption (ml)	3.6	50	15	50	0.2	50	0.18	0.15
Throughput (h^{-1})	40	–	–	20	50	–	90	30

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.

On comparing the proposed method with previous spectrophotometric procedures available in the scientific literature (see Table 4), it can be concluded that all these methods work in the linear range till 0.4 to 2.5 mg l^{-1}, except a method which covers till 20 mg l^{-1} [9]. RSD values range comprises from 0.4 to 7.5% but not so many data are available about the criterion and concentration levels employed to establish the repeatability. Concerning the LOD, it can be concluded that the method developed is one of the most sensitive and it must be emphasized that a sample consumption of 3.6 ml of the proposed method is clearly lower than 50 ml [3,5,10] or 15 ml [4] required for previous procedures and that methods involving less than 1 ml of sample [9,11,12] only provided LOD values between 20 and 200 μg l^{-1}. So, it can be concluded that the proposed method clearly improves the reference ones and provides comparable or better performance than that offered by precedent studies.

3.4. Study of interferences

It was evaluated the effect of Ca^{2+}, Mg^{2+}, Cd^{2+}, Cl^-, $NO_3{}^-$, $C_2O_4{}^{2-}$ and Triton X-100 on the determination of anionic surfactants by the developed procedure. For a fixed concentration of 2×10^{-6} mol l^{-1} (576 μg l^{-1}) SDS, the maximum tolerance levels which do not modify the absorbance values of SDS, beyond the limits of $\bar{A} \pm 3$ s of those obtained in the absence of interferences, were established and results reported in Table 5 were found. In this table, there are also indicated the tolerance levels described in the literature for foreign ions [9–14] on using different procedures for anionic surfactants determination. As can be seen, only Cd^{2+} and Mg^{2+} interfere at concentration levels under the 1000 mg l^{-1}. It can be seen that the method developed clearly enhances the selectivity of this determination as compared with some of the reported methods [9,12,13]. On the other hand, the method proposed inhibits the Triton X-100 interference reported before [11,13] and improves the selectivity of $NO_3{}^-$ [9,10,12,13] and Cl^- [9,12–14].

3.5. Evaluation of the accuracy

The evaluation of the developed procedure was made by two ways: (i) making recovery studies on washing water samples spiked with known concentrations of SDS from 5 to 30 mg l^{-1} and on natural irrigation channels waters spiked at a concentration level of 0.2 mg l^{-1} and (ii) by the comparison of results found by both, the reference and the developed procedure, on the analysis of a series of different actual samples.

Recovery studies on washing samples were made by using both methods, the reference and the proposed one, in order to evidence the absence of losses or contaminations on the determination of anionic surfactants. Data found for different

Table 5
Tolerance levels of foreign ions in mg l^{-1} for a SDS concentration of 2×10^{-6} mol l^{-1}

Ion	Developed method	Previously reported methods					
		[9]	[10]	[11]	[12]	[13]	[14]
Ca^{2+}	>1000	200	400	1000	–	300	4000
Mg^{2+}	>500	100	1500	1000	–	300	2430
Cd^{2+}	>500	–	–	–	–	30	–
Cl^-	>1800	100	24900	>16000	1000	300	1750
$NO_3{}^-$	>1000	400	6.2	>16000	100	30	–
$C_2O_4{}^{2-}$	>1000	–	–	8000	–	–	–
Triton X-100	>10000	–	–	400	–	0.3	–

Note: Reported methods are based on: [9] FIA reaction in water with different dyes; [10] in batch extraction in toluene of the reaction product with a Co(III) complex; [11] FIA displacement of the ion pair between methyl orange and cetyl pyridine in waters; [12] FIA extraction of MB and SDS in $CHCl_3$; [13] in batch extraction in benzene or toluene of the ion pair with ethyl violet; [14] in batch extraction in different solvents of the reaction product between a Co(III) complex and SDS.

Table 6
(a) Total anionic surfactant recoveries (%) found in washing samples[a]; (b) recovery of SDS added to natural irrigation channel waters at a spiked level of 0.2 mg l^{-1} on using the multicommutation developed procedure

Water	SDS added (mg l^{-1})	Reference method (%)	Multicommutation (%)
Tap	5	99 ± 9	91 ± 5
Clothes washing	10	105 ± 9	97 ± 7
Washing machine	20	102 ± 9	98 ± 2
Crockery washing	30	101 ± 5	95 ± 4

Irrigation channel	Concentration (mg l^{-1})	Recovery (%)
Port Saplaya	0.31 ± 0.01	94 ± 3
Pobla de Farnals	0.73 ± 0.03	103 ± 6
Puig	0.24 ± 0.02	95 ± 3

[a] Measurements were carried out by the reference method and by the multicommutation developed procedure. Standard deviation values correspond to three independent analysis.

Table 7
Total anionic surfactant concentrations found in washing waste water samples

Water sample	Reference method (mg l^{-1})	RSD (%)	Multicommutation (mg l^{-1})	RSD (%)
Crockery washing	860 ± 50	5.8	870 ± 10	1.1
Clothes washing	42 ± 4	9.5	43 ± 2	4.7
Clothes washing	15 ± 2	13.3	17 ± 1	5.9
Washing machine	15 ± 2	13.3	14.7 ± 0.8	5.4
Hand washing	1110 ± 50	4.5	1140 ± 30	2.6
Glassware washing	20 ± 2	10.0	21.0 ± 0.5	2.4
Soil washing	33 ± 2	6.1	33 ± 1	3.0
Car washing	12 ± 2	16.7	13.5 ± 0.3	2.2

Results indicated are the average of three independent determinations (six measurements) ± the corresponding standard deviation.

kind of samples spiked with SDS concentrations ranging from 5 to 30 mg l^{-1} are presented in Table 6a.

Average recoveries of 95% for multicommutation and 102% for the reference procedure were found.

Water samples collected from three irrigation channels near the city of Valencia containing from 0.24 to 0.73 mg l^{-1} of anionic surfactants, were spiked with a 0.2 mg l^{-1} concentration of SDS and recovery values reported in Table 6b evidenced that SDS was recovered between the 94 and 103%.

Anionic surfactants were determined by the developed procedure in eight different washing waste water samples, and the results obtained are shown in Table 7 also indicating data found by the reference standard method.

Data reported evidenced the presence of concentrations of anionic surfactants from 12 (car washing waste water) to 1140 mg l^{-1} (hand washing waste water).

Precision (RSD values) found for real sample analysis varied from 1.1 to 5.9% in the case of multicommutation measurements and from 4.5 to 16.7% for the reference method being average RSD values 3.4 and 9.9%, respectively. These data indicate the good repeatability obtained by the developed procedure.

The comparison of data found by multicommutation with those found by the reference method provided an equation $y = (1.02 \pm 0.08)x + (0 \pm 4)$ with a regression coefficient of 0.999 and Student's t calculated values for the slope (0.322) and for the intercept (0.107) which were in both cases lower than the theoretical t value (1.682) for a 95% probability level and 46 freedom degrees, thus showing a good comparability of the results, which evidences that both procedures provide statistically comparable results.

4. Conclusions

The proposed method, for the determination of anionic surfactants in waters, offers several advantages over the reference procedure [2] and previously developed alternatives [3–5]. It has been reduced the sample size from 100 ml [2], 50 ml [3,5] or 15 ml [4] to only 3.6 ml. In terms of $CHCl_3$ consumption, the 700 μl required per determination are clearly lower than the 45 ml of the reference method [2] and the 30 ml [4] and 5 ml [3] required by the simplified methods, being only higher than that employed in continuous liquid–liquid extraction, which was 200 μl [5].

Separatory funnels and expensive glassware were avoided as in the case for some of the previous alternatives [4,5].

On the other hand, the multicommutation approach offers a sampling throughput of 40 h^{-1}, two times better than the FIA procedure [5] and provides the best limit of detection reported, 1.7 μg l^{-1} as compared with the 20 μg l^{-1} indicated in previous papers [3,5].

The proposed method is characterized by its simplicity and reliability. Extraction and detection are 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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