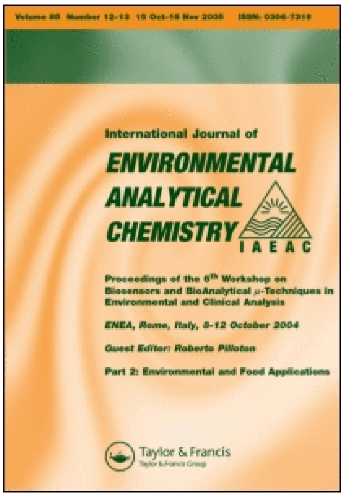

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A spectrophotometric flow procedure for the determination of cationic surfactants in natural waters using a solenoid micro-pump for fluid propulsion

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A spectrophotometric flow procedure for the determination of cationic surfactants in natural waters using a solenoid micro-pump for fluid propulsion

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An automatic flow-analysis procedure for spectrophotometric determination of cationic surfactants in surface water using a solenoid micro-pump for propelling solutions of reagents and sample is described. The proposed method is based on a ternary formation complex between chromazurol S, the Fe(III) ion, and the cationic surfactant. The flow network comprised four solenoid micro-pumps controlled by a microcomputer, which performed the sampling step by loading a reaction coil with sample and reagent solutions and displacing the sample zone through the analytical path. The system is simple, easy to operate, and very flexible, with sufficient sensitivity to determine cationic surfactants in water without any pre-concentration or separation step. After determining the best operational conditions, favourable features such as a linear response between 0.34 and $10.2\,\mathrm{mg\,L^{-1}}$ of surfactant ($R = 0.999$), a relative standard deviation of 0.6% ($n = 11$) for a sample containing $3.4\,\mathrm{mg\,L^{-1}}$ of surfactant, a detection limit of $0.035\,\mathrm{mg\,L^{-1}}$ of surfactant, and a sampling throughput of 72 determinations per hour were achieved. The system was used to determine cationic surfactant in river-water samples, and recovery values between 91 and 106% were achieved.

Keywords: Flow-injection analysis; Multicommutation; Micro-pump; Cationic surfactants; Spectrophotometry; Multi-pumping system

1. Introduction

Nowadays, attention has focused on surface water for both human consumption and economical activities. Under this context, water-quality maintenance and its mitigation after use could be considered as an essential condition. In this sense, considerations concerning water quality have been highlighted by several researchers [1–4], including the determination of several chemical substances [5–7] and cationic surfactant (CS) among the chemical substances that could be monitored. This substance had been

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commonly used in several manufactured products, which have usually been utilized for rinsing and disinfecting, including industrial and domestic environments; therefore, the generalized use increased its pollutant risk [8, 9], mainly for aquatic organisms [10]. Subsequently, the determination of CS in surface water could be considered as a necessary requirement to prevent contamination. Furthermore, in water-treatment plants, for human consumption prior determination of the CS concentration may help in the implementation of the purification process.

Spectrophotometric methods for CS determination based on the formation of ion pairs with anionic dyes such as Disulphine Blue, Orange II, and Bromophenol Blue have usually been used [11–13]. These procedures require an extraction step with an organic solvent such as chloroform, which should be avoided due to its toxicity for life organisms. The procedures are very slow, requiring a time interval of 5–15 min to allow adsorption of the compound on the wall of a PTFE vessel. The volumes of sample solution and solvent were at least 10 mL and 5 mL, respectively, thus generating a large volume of waste, which could become an additional difficulty concerning residue management. In this way, a spectrophotometric procedure using less aggressive reagents should be considered, and a reagent based on ion-pair formation between zephiramine and tetraphenylporphinetetrasulphonic acid [14], or tetrabromophenolphthalein ethyl ester [15] may be a good alternative.

Other analytical procedures exploiting two-phase titration [16–18], adsorption on silica gel and detection by spectrophotometry [19], potentiometric titration [20], and an ion-selective electrode [21] have also been proposed. These procedures do not use organic solvents but involve tedious manual processes. This drawback could be surpassed by using procedures based on flow-injection analysis (FIA) [22–25].

The continuous pumping of reagent solutions is a feature of the classical FIA process [26], thus affording a high degree of reagent consumption and also generating a large volume of waste. These disadvantages can be easily minimized by using flow manifolds based on sequential injection analysis [27] or multicommutation [28, 29]. The flow-analysis module based on the multicommutation approach involves the use of a set of solenoid valves nested to work as an independent commutation unit. This feature has been explored to design a versatile flow system using low-cost devices [29].

Solenoid micro-pumps controlled by a microcomputer were introduced as a new device for fluid propulsion that could be used to replace peristaltic pump [30–32]. It was demonstrated that a solenoid micro-pump could be assembled to accomplish fluid propulsion, and a multicommutation approach used to replace the peristaltic pump and solenoid valves, thus simplifying the flow-system network. In this case, different flow rates should be easily achieved by varying the on/off switching pattern of the micro-pumps. The electronic hardware required to drive the micro-pump is similar to that usually used in a multicommuted flow system [28, 29].

The present work develops an automatic flow-analysis procedure for spectrophotometric determination of cationic surfactants in natural water using chromoazurol S as a chromogenic reagent forming a ternary compound with iron(III) and a cationic surfactant. The flow system designed using a solenoid micro-pump to propel the sample and reagent solutions should provide a facility to obtain a reduction in reagent consumption and waste generation without compromising the main analytical features. Considering that the Schlieren effect should occur in flow-injection procedures and that their correction was demonstrated by using dual-wavelength measurements [33], the software was designed with the ability to read a signal at two wavelengths to allow its correction. In this sense, measurement disturbance that could be caused by small bubbles retained in the inner wall of the flow cell will also be corrected using this strategy.

2. Experimental

2.1 *Reagents and samples*

All chemicals used were of analytical grade, and all solutions were prepared with purified water ($18.2\,\mathrm{M\Omega\,cm^{-1}}$). A $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ hexadecylpyridiniun chloride monohydrate (CPC) ($C_{21}H_{38}ClN$) stock solution was prepared by dissolving the appropriate amount of reagent (purity 99%) from Sigma-Aldrich (St Louis, MO) in water. Working standard solutions with concentrations between 1.0×10^{-6} and $5.0 \times 10^{-5}\,\mathrm{mg\,L^{-1}}$ (0.34–$17\,\mathrm{mg\,L^{-1}}$) CPC were prepared daily by with the appropriate dilution from the stock solution with water.

A $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ chromazurol S (CAS) ($C_{23}H_{13}ClO_9SNa_3$) stock solution was prepared by dissolving the appropriate amount of reagent (purity 65%) purchased from Sigma-Aldrich in water. Working standard solutions with concentrations ranging from 0.25×10^{-4} to $2.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ CAS were prepared daily by dilution in a $0.1\,\mathrm{mol\,L^{-1}}$ acetate buffer solution at pH 4.5.

The stock solution ($1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ Fe(III)) was prepared by dissolving 2.4 mg of $FeCl_36H_2O$ (purity 99%) purchased from Merck (Darmstadt, Germany) in 5 mL of concentrated HCl and diluting to 500 mL with water. Working solutions (0.5×10^{-4} to $4.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ Fe(III)) were prepared by dilution from the stock solution with water.

Water samples were collected on different sites of Piracicaba River. Before use, samples were filtered through a 0.42 µm filter to remove the suspended solids, which could impair the diaphragm of the solenoid micro-pumps.

2.2 *Apparatus*

The equipment set-up comprised four solenoid micro-pumps (Bio-chem, 090SP, nominal volume of 8 µL per stroke); a Pentium microcomputer; an optical-fibre CCD-array spectrophotometer (Ocean Optics, PC 1000 equipped with a glass home-made flow cell (225 µL inner volume, 37 mm optical pathway); reaction coils and flow lines made of PTFE tubing (0.8 mm i.d.); two *T*-type home made flow-line joint devices machined in acrylic; and a homemade electronic control interface based the on the ULM2803A integrated circuit. The control interface was coupled to the outlet printer port of the microcomputer (address = &H378) using a multi-vial flat cable. The software to drive the micro-pumps and to perform data acquisition was written in Visual Basic 3.0.

2.3 *Procedure*

The selected method was based on the reaction between CAS and iron(III) to form an ionic pair followed reaction with the cationic surfactant to produce a ternary

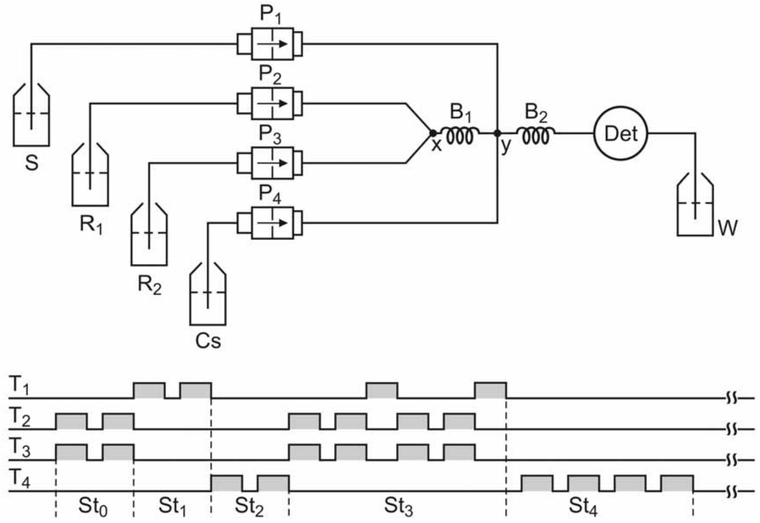

Figure 1. Diagram of the flow system. S: sample or standard solution; R_1: 1.0×10^{-4} mol L^{-1} of CAS in 0.1 mol L^{-1} of acetate buffer solution, pH 4.5; R_2: 2.0×10^{-4} mol L^{-1} of Fe(III) solution; Cs: carrier fluid, water; P_1, P_2, P_3 and P_4: solenoid micro-pumps; B_1 and B_2: reaction coils, length 10 cm, 0.8 mm i.d. TPFE tubing; x and y: joint devices; Det: spectrophotometer at 650 and 750 nm; W: waste. T_1, T_2, T_3, and T_4: timing pattern to switch on/off micro-pumps P_1, P_2, P_3, and P_4, respectively; St_0: filling step of coil B_1; St_1: line filling step; St_2: washing filling; St_3: sampling cycle; St_4: signal reading step. The shadow surfaces beneath the time lines indicate that the corresponding solenoid micro-pumps were switched on. The flow rates of the sample, carrier fluid, and reagent solutions were maintained at 37 µL s^{-1}.

complex [34]. The flow system was designed, considering the feature of the reaction; a diagram of the system manifold is shown in figure 1. When the analytical procedure was started, the microcomputer sent electric pulses through the control interface to switch the micro-pumps P_1, P_2, P_3, and P_4 on/off following the switching pattern depicted in figure 1. To fill the coil reaction B_1 with a mixing of the reagent solutions R_1 and R_2, the filling step (St_0) was repeated 50 times. Afterwards, the line-filling step (St_1) was performed and repeated 50 times to fill the flow line from the sample vessel (S) up to the joint y with sample or standard solution. Afterwards, the washing step (St_2) was carried out sequentially 50 times to wash the coil (B_2) with carrier solution (Cs). The sets of events comprising St_1 and St_2 steps were carried out only when a new sample or standard solution was processed. Afterwards, the sampling step (St_3) was performed to load coil B_2 with aliquots of sample and the mixture of reagent solution. As shown in figure 1, the signal reading step (St_4) was the last step to be carried out. The micro-pump pulsation frequency was maintained at 5 Hz, settling equal time intervals of 0.1 s to maintain each micro-pump switched on and switched off.

The micro-pump switching pattern (figure 1) shows that micro-pumps P_2 and P_3 were always switched on/off at the same time alternately with the micro-pump P_1 switching step. This set of events comprised one sampling step (St_3), which could be repeated several times in accordance with the requirement of the analytical procedure. Under this condition, the reaction coil B_2 was loaded with a string comprising slugs of sample solution in tandem with slugs of the CAS and Fe(III) solution mixture. The micro-pump switching pattern can be modified, varying the number of on/off switching events for either P_1 or P_2 and P_3. Assays to define the volume of the sample zone inserted into the reaction coil B_2 were performed by varying the number of sampling steps (St_3). Afterwards, the signal reading step (St_4) was repeated 50 times to propel the carrier solution (Cs), thus displacing the sample zone through the reaction coil (B_2) towards the detector (Det). The mixing between sample and reagent solution and reaction to form the ternary complex occurred during the displacement. The software was designed to acquire data at two wavelengths (650 and 750 nm) to compensate for some noise that could occur.

The experiments described below were implemented to determine the best operational conditions concerning sensitivity and precision and carried out using a set of cationic surfactant standard solutions with concentrations ranging from 0 to $17.0\,\mathrm{mg\,L^{-1}}$.

Because pH could affect the reaction for ternary complex formation, it was the first parameter assayed. This was done by varying the pH of the CAS solution using a $0.1\,\mathrm{mol\,L^{-1}}$ acetate solution and adjusting the pH from 4.0 to 8.0 with acetic acid. The length of both reaction coils B_1 and B_2 was fixed at 50 cm and the number of sampling steps (St_3) was fixed at 15 times, thus maintaining the switching pattern shown in figure 1. In this study, the concentrations of both CAS and Fe(III) solutions were maintained at $1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$.

The concentration of the Fe(III) solution was varied from 0.5×10^{-4} to $4.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$, maintaining the CAS solution at $0.25 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$. Additional experiments were carried out using these two Fe(III) solutions and changing the concentration of the CAS solution between 0.25×10^{-4} and $2.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$.

The micro-pumps delivered 8 μL per stroke, thus the experiments to find the best ratio between the volume of CPC and CAS–Fe(III) solutions mixture were done by varying the micro-pumps on/off switching pattern of sampling step (St_3). In this sense, the micro-pumps P_2 and P_3 were turned on/off once, and the micro-pump P_1 on/off switching was changed from one to four times per sampling step (St_3). A similar assay was carried out, maintaining one on/off pulse for the micro-pump P_1 and changing the on/off pulsation of P_2 and P_3 from one to four per sampling step (St_3). In these assays, each run comprised 10 sampling steps. The experiments described above were carried out, maintaining the lengths of the coils B_1 and B_2 at 50 cm (250 μL inner volume).

To complete the studies of the system parameters, the lengths of the coils B_1 and B_2 were varied from 10 to 120 cm, and the volume of sample zone from 80 to 400 μL. After determining the best operational conditions, river-water samples were analysed. To ascertain the accuracy, recovery and standard addition methods were used. In the first case, samples were spiked with two cationic surfactant solutions, and in the second case, before processing the water sample, a set of standard solutions (0.5×10^{-5}–$2.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) was added to each one.

3. Results and discussion

3.1 *Ternary complex CAS–Fe(III)–CS formation*

The spectral absorptions of the complex formed between CAS–Fe(III) and CAS–Fe(III)–CS in aqueous solutions at pH 4.5 are shown in figure 2. As can be seen,

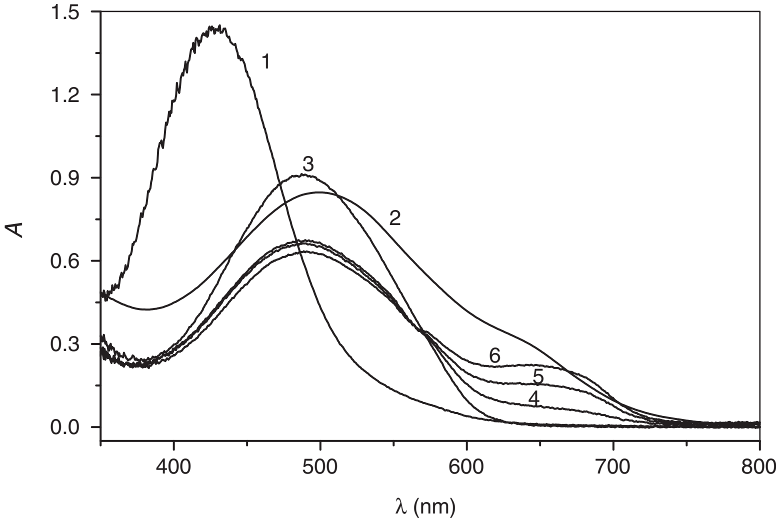

Figure 2. Absorption spectra of CAS–Fe(III)–CPC system. (1) CAS; (2) CAS–CPC (CPC = 1.0×10^{-4} mol L^{-1}); (3) CAS–Fe(III); (4) CAS–Fe(III)–CPC (CPC = 1.0×10^{-5} mol L^{-1}); (5) CAS–Fe(III)–CPC (CPC = 3.0×10^{-5} mol L^{-1}); (6) CAS–Fe(III)–CPC (CPC = 5.0×10^{-5} mol L^{-1}). CAS: 1.0×10^{-4} mol L^{-1}; Fe(III): 2.0×10^{-5} mol L^{-1}; pH 4.5.

the maximum absorption of the CAS solution is around 430 nm (curve 1), while for the CAS–CPC ion pair, the maximum absorption occurred at 500 nm (curve 2). The curve 3 shows that the maximum absorption of the CAS–Fe(III) ion-pair complex occurred at 490 nm. The other curves (4, 5, and 6) were obtained by adding three different concentrations of CPC to the CAS–Fe(III) ion-pair solution previously formed into the reaction coil B_1 (figure 1). As shown in figure 2, an increase in absorbance occurred around 650 nm. Additional assays reveal that a linear relationship between CPC concentration and the light-absorbing effect occurred at this wavelength. This effect was exploited to develop the procedure for the cationic-surfactant determination in water. When the CPC concentration was higher than 1.0×10^{-4} mol L^{-1} the signal monitored at 650 nm decreased, while an increase in signals around 500 nm was observed. In this sense, we presumed that the decomposition of CAS–Fe(III)–CPC ternary complex occurred.

3.2 *Effect of pH and reagent concentration*

The effect of the pH on the reaction was verified using a 1.0×10^{-4} mol L^{-1} CAS solution that was prepared in a 0.1 mol L^{-1} acetate solution with a pH in the range of 4.0–8.0. Considering the slope, linear response coefficient, and intercept, no significant variations were observed, so a pH 4.5 acetate buffer solution was selected.

Assays to verify the effects concerning to CAS and Fe(III) solutions concentration were performed, yielding results shown in table 1. Considering linearity as the main parameter, a better result was obtained using CAS and Fe(III) solutions presenting concentrations of 1.0×10^{-4} mol L^{-1} and 2.0×10^{-4} mol L^{-1}, respectively.

Table 1. Effect of the concentration of CAS and Fe(III) solutions.[a]

10^{-4} mol L^{-1}			
CAS	Fe(III)	Equation	Correlation coefficient (*R*)
0.25	4.0	$A = (0.011 \pm 0.003) + (4119 \pm 181)$ mol L^{-1} CS	0.993
0.5	4.0	$A = (0.019 \pm 0.003) + (4121 \pm 159)$ mol L^{-1} CS	0.995
1.0	2.0	$A = (0.021 \pm 0.002) + (4063 \pm 96)$ mol L^{-1} CS	0.999
1.5	2.5	$A = (0.032 \pm 0.002) + (3735 \pm 113)$ mol L^{-1} CS	0.997
2.0	3.5	$A = (0.042 \pm 0.002) + (3606 \pm 104)$ mol L^{-1} CS	0.997

[a] *A*: absorbance.

3.3 *Effect of the manifold operational parameters*

The effects concerning sample and reagent solution ratios were investigated by varying the micro-pump switching pattern of the sampling step (St_3, figure 1) yielding the results shown in table 2. Considering the linear regression coefficient and slope as the evaluated parameters, we found that better results were achieved when the ratio between the volumes of sample solution and the mixture of CAS and Fe(III) solutions was 1 : 2. This ratio was obtained by sending one switching signal (electric pulse) to micro-pump P_1 and two for the micro-pumps P_2 and P_3, respectively. As depicted in the pump switching pattern (figure 1), the micro-pumps P_2 and P_3 were turned on/off at the same time. This volume ratio was maintained to carry out additional assays.

Because the length of the reactor could affect the reaction development and sensitivity, an experiment to define its dimension was performed. The lengths of reaction coils B_1 and B_2 were varied from 10 to 120 cm, so the inner volumes of both coils varied from 50 to 600 μL. The volume of the sample zone was maintained at 480 μL ($St_3 = 10$) in order to minimize the dispersion effect. In this experiment, a 1.0×10^{-5} mol L^{-1} CPC standard solution, 1.0×10^{-4} mol L^{-1} CAS, and 2.0×10^{-4} mol L^{-1} Fe(III) were used. No significant differences for both reaction coils were observed, thus indicating that the mixing of the solutions was efficient and that the involved reactions were very fast. Considering these results and in order to save time, the lengths of both coils B_1 and B_2 were fixed at 10 cm.

The volume sample zone was increased from 240 to 720 μL by varying the number of sampling steps (St_3) from 5 to 15, and as expected, the analytical signal was augmented with sample volume. Nevertheless, when the number of sampling steps (St_3) was higher than 10, no significant increase in signal was observed, thus indicating that the system attained a steady-state condition. In this case, the inserted volumes of sample and mixture of CAS and Fe(III) solutions were 160 μL and 640 μL, respectively, and selected for further experiments. Considering the results mentioned in the previous sections, the best operational conditions selected are shown in table 3. The sequence of events was organized according to the micro-pump switching pattern depicted in figure 1.

3.4 *Studies of potential interfering*

To ascertain whether chemical species such as Na^+, K^+, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, Triton X-100, and lauryl sulphate sodium (LAS) normally found in surface water interfere with cationic surfactant determination,

Table 2. Response of the system as a function of the sample and reagent solution volumes.[a]

mL			
V_R	V_A	Equation	Correlation coefficient (R)
0.16	0.64	$A = (0.037 \pm 0.009) + (2521 \pm 555)\ \mathrm{mol\,L^{-1}}$ CS	0.864
0.16	0.48	$A = (0.037 \pm 0.009) + (3049 \pm 568)\ \mathrm{mol\,L^{-1}}$ CS	0.897
0.16	0.32	$A = (0.036 \pm 0.008) + (3773 \pm 517)\ \mathrm{mol\,L^{-1}}$ CS	0.940
0.16	0.16	$A = (0.026 \pm 0.004) + (4688 \pm 271)\ \mathrm{mol\,L^{-1}}$ CS	0.988
0.32	0.16	$A = (0.025 \pm 0.001) + (3595 \pm 69)\ \mathrm{mol\,L^{-1}}$ CS	0.999
0.48	0.16	$A = (0.026 \pm 0.001) + (2722 \pm 61)\ \mathrm{mol\,L^{-1}}$ CS	0.999
0.64	0.16	$A = (0.025 \pm 0.001) + (2272 \pm 64)\ \mathrm{mol\,L^{-1}}$ CS	0.997

[a] V_R: volume of reagents (CAS + Fe(III)); V_A: volume of sample; A: absorbance.

Table 3. Control parameters of the flow system.

Parameter	P_1	P_2	P_3	P_4	Cycle
Coil B_1 filling step (St_0)	Off	On/off	On/off	Off	10
Line filling step (St_1)	On/off	Off	Off	Off	15
Washing step (St_2)	Off	Off	Off	On/off	15
Sampling step (St_3)	On/off	On/off	On/off	Off	10
Signal reading step (St_4)	Off	Off	Off	On/off	25

Table 4. Effect of the potential interfering chemical species.

Chemical species	Tolerance limit (mg L^{-1})
Ni^{2+}, Al^{3+}	10
Lauryl sulphate sodium, Cu^{2+}	20
Triton X-100, Mn^{2+}, Ca^{2+}, Mg^{2+}, NO_2^-	50
Na^+, K^+, Zn^{2+}, NO_3^-, PO_4^{3-}	100
SO_4^{2-}	1000[a]

[a] Maximum tested concentration.

experiments were performed using a 3.4 mg L^{-1} cationic surfactant standard solution (CPC). Table 4 shows the concentration limits that could cause an absorbance variation around 5%. The values listed are higher than the concentrations normally found in surface water.

3.5 *Accuracy evaluation and figures of merit*

After determining the best operational conditions and to demonstrate the feasibility of the proposed system, a set of river-water samples was processed using two methodologies. In the first case, prior to analysis, samples were spiked using two cationic surfactant concentrations, yielding the results shown in table 5; here, it can be seen that recoveries within the range of 91–106% were achieved. In the second case, the standard addition method was used, and the results obtained (table 5) are identical to those achieved in the proposed procedure.

Table 5. Results obtained of CS in natural waters, expressed as CPC.

Sample	CS	Amount found (mg L^{-1})[a]		CS added	CS recovered[a]	Recovery (%)
		Proposed method	Method: standard addition			
1	–	0.778 ± 0.009	0.741 ± 0.009	5.1	5.70 ± 0.03	97
				6.8	7.27 ± 0.02	96
2	–	ND[b]	ND[b]	5.1	4.85 ± 0.02	95
				6.8	6.19 ± 0.03	91
3	–	0.479 ± 0.007	0.439 ± 0.003	3.4	3.80 ± 0.02	98
				5.1	5.63 ± 0.02	101
4	–	ND[b]	ND[b]	3.4	3.37 ± 0.01	99
				5.1	4.64 ± 0.02	91
5	–	0.504 ± 0.006	0.487 ± 0.005	1.7	2.14 ± 0.02	97
				3.4	3.86 ± 0.01	99
6	–	0.485 ± 0.004	0.544 ± 0.004	1.7	2.32 ± 0.03	106
				3.4	3.85 ± 0.02	99
7	1	1.08 ± 0.01	0.985 ± 0.009	1.7	2.70 ± 0.02	97
				6.8	7.41 ± 0.01	94
8	1.5	1.78 ± 0.03	1.43 ± 0.02	1.7	3.58 ± 0.04	103
				6.8	8.07 ± 0.03	94
9	3	3.25 ± 0.04	3.65 ± 0.03	3.4	6.38 ± 0.03	96
				6.8	9.55 ± 0.02	95
10	4	4.33 ± 0.02	4.64 ± 0.05	3.4	7.27 ± 0.02	94
				6.8	10.91 ± 0.03	98

[a] Results average of three consecutive determinations ± standard deviation.
[b] Not detected.

Table 6. Analytical performance comparison.

Parameter	Proposed procedure	Reference [34]	Reference [35]
Correlation coefficient (R)	0.999	0.999	0.99
Dynamic range (mg L^{-1})	0.34–10.2	0.28–12.8	0.5–30
RSD (%)	2.0–0.4	4.4–0.5	1.5
LOD (mg L^{-1})	0.035	0.085	0.25
Sample consumption (mL)[a]	0.16	0.25	0.6
Reagents consumption (mL)[a]	0.64	1.75	0.84
Waste (mL)[a]	2.0	2.0	2.88
Throughput (per hour)	72	120	100

[a] Sample and reagent consumptions and waste corresponding to one analysis.

The main parameters of the proposed system are summarized in table 6; here, we can see that the limit of detection obtained by the proposed method is 2.4 and 7.1 times smaller than that found in other procedures [34, 35]. Comparison concerning to sample and reagents consumption are also favourably to the proposed procedures. These features could be considered to be indicative of the feasibility of the proposed system.

4. Conclusions

The flow-system network based on solenoid micro-pumps is simple, easy to operate, very versatile, and robust with facilities for automation. The system developed here provided a long-term stability, as demonstrated by working continuously for 4 h. No significant variation in response range and precision of measurements was observed. The limit of detection (0.035 mg L^{-1} of surfactant) means that water samples can be analysed without any prior treatment except filtration. This feature can be considered an advantage over usual procedures, which require an organic-solvent extraction step. The solenoid micro-pump can be viewed as a commuting device, and in this sense a set of these can be easily assembled to comprise an active hardware with several reagent solutions controlled using software.

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References

[1] K. Exall, J. Marsalek, K. Schaefer. *Water Qual. Res. J. Can.*, **3**, 1 (2004).
[2] P.J. Hancock. *Environ. Manage.*, **29**, 763 (2002).
[3] C. MacNeil, J.T.A. Dick, R.W. Elwood, W.I. Montgomery. *Arch. Hydrobiol.*, **151**, 591 (2001).
[4] V.H. Smith. *Environ. Sci. Pollut. Res.*, **10**, 126 (2003).
[5] V. Cerda, J.M. Estela. *Int. J. Environ. Anal. Chem.*, **85**, 231 (2005).
[6] M. Yaqoob, M. Anwar, A. Nabi. *Int. J. Environ. Anal. Chem.*, **85**, 451 (2005).
[7] A. Salinas, J.F. Fernandez-Sanchez, A. Segura, A. Fernandez-Gutierrez. *Int. J. Environ. Anal. Chem.*, **85**, 443 (2005).
[8] S.L. Feng, X.G. Chen, J. Fan, Z.D. Hu. *Int. J. Environ. Anal. Chem.*, **85**, 63 (2005).
[9] S.T. Li, S.L. Zhao. *Anal. Chim. Acta*, **501**, 99 (2004).
[10] H.P. Drobeck. *Surfact. Sci. Ser.*, **53**, 61 (1994).
[11] H.K. Biswas, B.M. Mandal. *Anal. Chem.*, **44**, 1636 (1972).
[12] G.V. Scott. *Anal. Chem.*, **40**, 768 (1968).
[13] T. Sakai, N. Ohmo, T. Kawamoto, H. Sasaki. *Mikrochim. Acta*, **106**, 45 (1992).
[14] M. Kanaya, J. Takahashi, K. Nagashima. *Microchim. Acta*, **144**, 35 (2004).
[15] M. Kanaya, Y. Kaneko, K. Nagashima. *Anal. Chim. Acta*, **384**, 215 (1999).
[16] M. Tsubouchi, H. Mitsushio, N. Yamasaky. *Anal. Chem.*, **53**, 1957 (1981).
[17] S. Motomizu, Y.H. Gao, K. Uemura, S. Ishihara. *Analyst*, **119**, 473 (1994).
[18] T. Masadome. *Anal. Lett.*, **37**, 499 (2004).
[19] A.N. Chebotarev, T.V. Paladenko, T.M. Shcherbakova. *J. Anal. Chem.*, **59**, 309 (2004).
[20] T. Masadome, T. Imato. *Talanta*, **60**, 663 (2003).
[21] T. Masadome. *Microchim. Acta*, **140**, 227 (2002).
[22] K. Yamamoto, S. Motomizu. *Anal. Chim. Acta*, **246**, 333 (1991).
[23] S. Motomizu, M. Oshima, Y. Hosoi. *Mikrochim. Acta*, **106**, 67 (1992).
[24] S. Motomizu, Y. Gao. *Microchem. J.*, **49**, 326 (1994).
[25] J. Kawase. *Anal. Chem.*, **52**, 2124 (1980).
[26] E.P. Borges, A.F. Lavorante, B.F. Reis. *Anal. Chim. Acta*, **528**, 115 (2005).
[27] A.N. Araujo, R.C.C. Conta, J.L.F.C. Lima, B.F. Reis. *Anal. Chim. Acta*, **358**, 111 (1998).
[28] B.F. Reis, M.F. Giné, E.A.G. Zagatto, J.F.l.C. Lima, R.A.S. Lapa. *Anal. Chim. Acta*, **193**, 129 (1994).
[29] F.R.P. Rocha, B.F. Reis, E.A.G. Zagatto, J.F.l.C. Lima, R.A.S. Lapa, J.L.M. Santos. *Anal. Chim. Acta*, **468**, 119 (2002).
[30] R.A.S. Lapa, J.F.l.C. Lima, B.F. Reis, J.L.M. Santos, E.A.G. Zagatto. *Anal. Chim. Acta*, **466**, 125 (2002).
[31] J.M.T. Carneiro, E.A.G. Zagatto, J.L.M. Santos, J.F.l.C. Lima. *Anal. Chim. Acta*, **474**, 161 (2002).
[32] A.F. Lavorante, A. Morales-Rubio, M. de la Guardia, B.F. Reis. *Anal. Bioanal. Chem.*, **381**, 1305 (2005).
[33] E.A.G. Zagatto, M.A.Z. Arruda, A.O. Jacintho, I.L. Mattos. *Anal. Chim. Acta*, **234**, 153 (1990).
[34] I. Nemcová, V. Tománková, P. Rychlovsky. *Talanta*, **52**, 111 (2000).
[35] R. Patel, K.S. Patel. *Talanta*, **48**, 923 (1999).