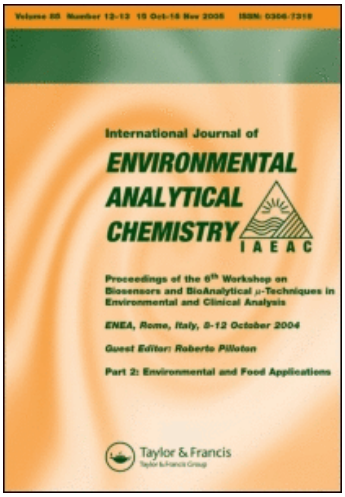

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Spectrophotometric method for the determination of trace cationic surfactants using sequential injection

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This paper presents a sequential injection spectrophotometric method for the determination of cationic surfactants (CS) on the basis of forming a coloured ion-associate complex of anionic dye, Bromophenol Blue (BB) with cationic surfactants, including zephiramine (Zeph), cyltrimethylammonium bromide (CTMAB) and cetylpyridinium bromide (CPB), and causing a red shift of λ_{max} from 585 nm for Bromophenol Blue to 634 nm for $CS^+ \cdot BB^-$ associate. The increased absorbance value is proportional to the concentration of cationic surfactant. Various chemical and physical parameters for the sequential injection spectrophotometric method were optimized. The linear ranges were 6.34–50.8 μg/mL for Zeph, 7.29–32.8 μg/mL for CTMAB and 7.50–40.0 μg/mL for CPB. The detection limits were 0.22 μg/mL, 0.29 μg/mL and 0.25 μg/mL for Zeph, CTMAB and CPB, respectively. The proposed system can be used to analyse 28 samples per hour with a relative standard deviation (RSD) lower than 4.1%. The method was applied to the determination of cationic surfactants in both synthetic and spiked water.

Keywords: Sequential injection; Spectrophotometry; Cationic surfactants; Bromophenol blue

1. Introduction

Cationic surfactants are widely used in mineral and oil processing, households and separation science, and they are mainly used as fabric softeners, disinfectants, foam depressants and antistatic agents, but they have also been reported as pollutants [1]. Various methods, such as spectrophotometry [2–8], high-performance liquid chromatography [9–11] and capillary electrophoresis [12–15], have been reported for the determination of cationic surfactants. Most methods used are based on the formation of an ion pair with an intensely coloured counterion and extraction of the ion pair into a suitable organic solvent, followed by measurements of the absorbance of the counterion [2–8]. The solvent extraction-spectrophotometry method is tedious and inaccurate owing to incomplete extraction or the formation of emulsions in the extraction solvent.

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However, many of the solvents used in solvent extraction are harmful to health and environment.

In addition, FIA coupled with spectrophotometry [16–20] or fluorimetry [21, 22] for the determination of cationic surfactants was also reported. A FIA spectrophotometry was described for the determination of cationic surfactants in terms of cetylpyridinium chloride (CPC) based on the enhancement of colour intensity of the Fe(III)-SCN^- complex [20]. Masadome *et al.* [22] proposed FIA fluorimetry for the determination of cationic surfactants, such as Zeph with low sample throughput. One of the disadvantages of FIA is the relatively high reagent consumption per analysis.

Sequential injection analysis (SIA) was introduced by Ruzicka *et al.* in 1990 [23]. The significant advantages of SIA include its versatility, high analytical throughput, low sample and reagent consumption and on-line process measurements. Sequential injection analysis has been reviewed and applied to the determination of organic and inorganic materials [24]. To our knowledge, there is only one report on the determination of surfactants (Tween-80) by SIA, which was based on the fluorescence enhancement effect of Tween-80 on the probe Eosin B [25]. This paper proposed a simple, rapid and organic-solvent-free analytical procedure for the automated determination of trace amount of cationic surfactants in synthetic and spiked water. Zeph, CTMAB and CPB can be determined in the ranges 6.34–50.8 μg/mL, 7.29–32.8 μg/mL and 7.50–40.0 μg/mL, respectively. And the detection limits were 0.22 μg/mL for Zeph, 0.29 μg/mL for CTMAB and 0.25 μg/mL for CPB. The sampling frequency was 28 samples per hour.

However, the development of methods and techniques that reduce and/or eliminate hazardous substances in analytical chemistry is of interest to avoid threats to human health and the environment [26]. The total amount waste is low in a full cycle for the proposed system, and the procedure does not involve toxic reagents. Therefore, the method for the determination of cationic surfactants can be considered as a contribution to the development of green analytical chemistry.

2. Experimental

2.1 *Reagents*

All chemicals used were of analytical reagent grade and redistilled water was used throughout. Zeph standard stock solution of 3.172 mg/mL was prepared by dissolute 0.3172 g of Zeph in 100 mL of water. CTMAB solution of 0.40 mg/mL was prepared by dissolving 0.0400 g of CTMAB in water and made up to 100 mL. CPB solution of 0.50 mg/mL was prepared by dissolving 0.0500 g of CPB in water and made up to 100 mL. Working solutions were prepared by appropriate dilution of the stock solution before use.

Bromophenol Blue solution of 1.0×10^{-3} mol/L was prepared by dissolving 0.1675 g of Bromophenol Blue in 250 mL of water. Bromophenol Red solution of 1.0×10^{-3} mol/L was prepared by dissolving 0.0256 g of Bromophenol Red in 50 mL of ethanol absolute. Working solutions were prepared by suitable dilution with water. Eriochrome Black T solution of 1.0×10^{-3} mol/L was prepared by dissolving 0.1153 g of Eriochrome Black T in 250 mL of water.

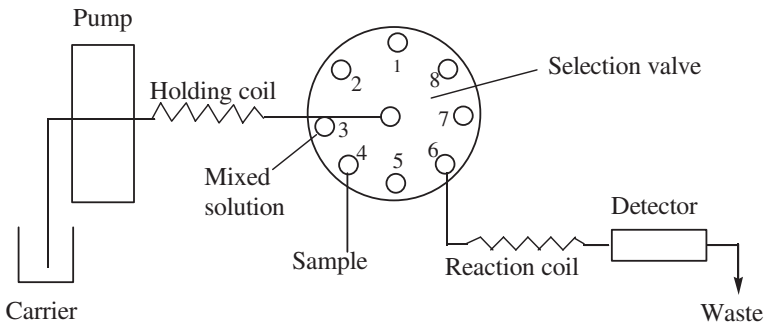


Figure 1. Schematic diagram of the sequential injection system for the determination of Zeph.

Britton–Robinson buffer solution of pH 5.80 was prepared by mixing 100 mL of 0.04 M acid (3.92 g of H_3PO_4 + 2.40 g of ethanoic acid + 2.47 g of H_3BO_3) with appropriate volumes of 0.2 mol/L of NaOH, and adjusting to pH 5.80.

A mixed solution of Bromophenol Blue and Britton–Robinson buffer was prepared by adding 1.0 mL of 1.0×10^{-3} mol/L of Bromophenol Blue and 1.0 mL of pH 5.80 Britton–Robinson buffer into a 10 mL flask, and diluting to the mark with water.

2.2 *Apparatus*

A Fialab 3500 (FIAlab Instruments Inc., USA) instrument was used in all experiments in the sequential injection mode according to figure 1. Solutions were driven by a 2.5 mL syringe pump and an eight-port rotary valve. The length of the holding coil was 300 cm with 0.5 mm i.d. The reaction coil was 200 cm long with an internal diameter of 0.5 mm. All other tubular paths were made of 0.5 mm i.d. polytetrafluoroethylene (PTFE) tubing. The system was controlled using a computer (Legend Cooperation, China), operating FIAlab software (FIAlab for Windows 5.0 Revision E). An USB2000-UV-VIS spectrophotometer (Ocean Optics, Inc., USA) equipped with a 10-mm light path-length fibre optic SMA Z-flow cell was used for absorbance measurements. The absorbance of the system was measured at 634 nm. A pH S-3C acidimeter (Shanghai Weiye Instrument Factory, China) was used for adjusting the pH.

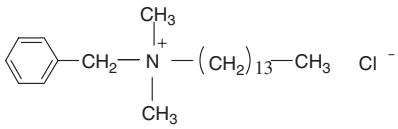
2.3 *Procedure*

The procedure for the determination of cationic surfactant was based upon the following steps: (1) aspiration of 300 μL of sample or standard solution; (2) aspiration of 140 μL of the mixed solution of Bromophenol Blue and Britton–Robinson buffer; and (3) propulsion of 1.4 mL of carrier through the reaction coil for measurement, waste and washing the line.

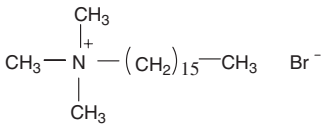
3. Results and discussion

The structures of Zeph, CTMAB and CPB are depicted in figure 2. Figure 3 shows the changes in absorption spectra of Bromophenol Blue with the addition of Zeph into

(1)



(2)



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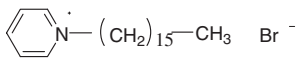

Figure 2. Structures of Zeph (1), CTMAB (2) and CPB (3).

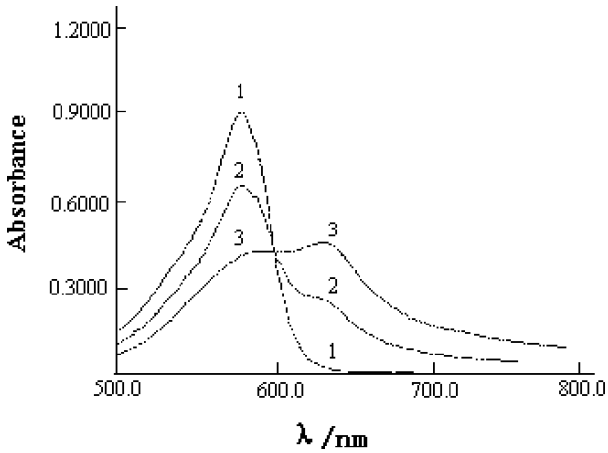

Figure 3. Absorption spectra of Bromophenol Blue with Zephiramine. BB, 1.2×10^{-5} mol/L; concentration of Zeph: 1, 0; 2, 5.08 μg mL^{-1}; 3, 10.2 μg mL^{-1}.

Bromophenol Blue solution. Bromophenol Blue had a maximum absorption at 585 nm. By increasing the Zeph concentration in the solution, the absorbance at 585 nm decreased gradually while the absorbance at 634 nm increased. This implies that cationic $Zeph^+$ may react with BB^- to form an ion-association complex $Zeph^+ \cdot BB^-$. Similar phenomena are also found for CTMAB and CPB. Furthermore, it is observed that there is a linear relationship between absorbance difference and the concentration of cationic surfactants at 585 nm and 634 nm, and that the standard deviations corresponding to five measurements for the blank at 634 nm and 585 nm were 0.001 and 0.072, respectively. Thus, the measurements were carried out at 634 nm.

3.1 *Method optimization*

In order to establish the optimum working conditions, various factors that influence the performance of the proposed method were optimized.

Several anionic dyes, such as Bromophenol Blue, Bromophenol Red and Eriochrome Black T were used as chromogenic reagents. The experimental results indicated that Bromophenol Red could almost react with Zeph and that the maximum change in absorbance was obtained when using Bromophenol Blue, as shown in table 1. Further, experiments were carried out using Bromophenol Blue.

The effect of flow rate on absorbance difference (ΔA) was evaluated between 5 and 40 μL/s. The flow rate plays an important role in the degree of zones dispersion and zones penetration. It can be seen from figure 4 that ΔA remained maximal and constant when the flow rate was in the range 15–35 μL/s. However, the best precision was obtained at a flow rate of 25 μL/s, and this was chosen as optimum for further studies.

Compared with a holding coil of 300 cm with an internal diameter of 0.7 mm, the holding coil of 300 cm with an internal diameter of 0.5 mm resulted in a higher sensitivity, so the latter was used. The length of the reaction coil has an effect on the sensitivity of the method. The effect of the length of the reaction coil on ΔA was shown in figure 5. It can be seen from figure 5 that the optimum length of the reaction coil is 200 cm, which was selected for further experiments.

The effect of pH on ΔA was examined in the range 3.47–7.18, and ΔA was found to be maximal and constant at a pH above 5.22. A pH of 5.80 was adopted for

Table 1. Comparison of Bromophenol Blue with Eriochrome Black T (EB)[a].

Chromogenic reagents	A_0	A	ΔA
BB, 1×10^{-4} mol/L	0.189	0.685	0.496
EB, 1.0×10^{-4} mol/L	0.114	0.168	0.054
EB, 2.0×10^{-4} mol/L	0.274	0.321	0.047

[a]Zeph, 25.4 μg/mL; other conditions are as described in section 2.3. A_0 and A denote the absorbance of the blank and sample solution, respectively.

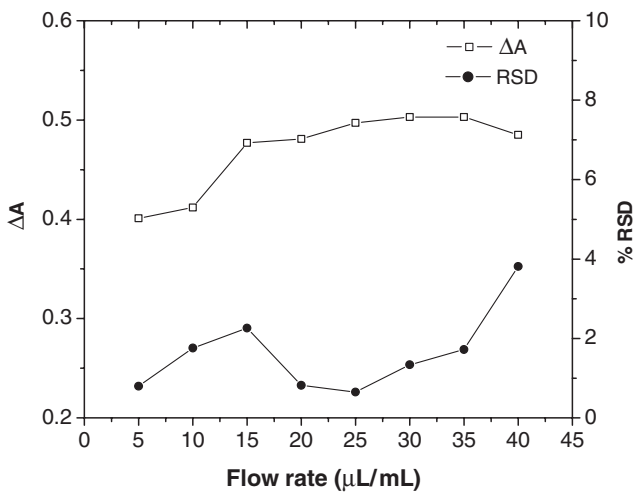

Figure 4. Influence of the flow rate on ΔA and precision of ΔA. Zeph, 25.4 μg/mL; BB, 1.0×10^{-4} mol/L; other conditions were as described in section 2.3.

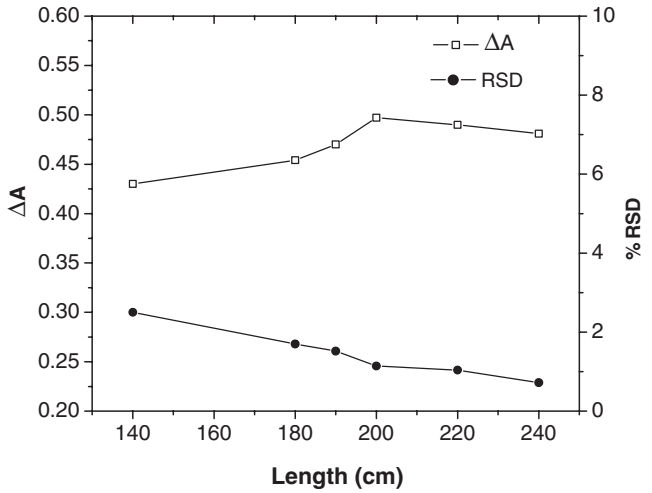

Figure 5. Influence of the reaction coil length on ΔA and precision of ΔA. Zeph, 25.4 μg/mL; BB, 1.0×10^{-4} mol/L; other conditions were as described in section 2.3.

further studies. The effects of several buffer solutions with pH 5.80 such as Britton–Robinson, NaOAc-HOAc, KH_2PO_4-NaOH, KH_2PO_4-Na_2HPO_4 on the sensitivity of the method were studied. When the concentration of Zeph was 20 μg/mL, the ΔA values were 0.386, 0.349, 0.343 and 0.356 ($n = 5$) for Britton–Robinson, NaOAc-HOAc, KH_2PO_4-NaOH and KH_2PO_4-Na_2HPO_4, respectively. The results indicated that Britton–Robinson offered a greater sensitivity, so Britton–Robinson solution was chosen for subsequent studies. The optimum amount of buffer solution was 1.0 mL in a final of 10 mL.

The volume of the sample was varied from 100 to 400 μL. Figure 6 shows that ΔA remained maximal and constant when sample volume was higher than 200 μL. However, the best precision was obtained at a sample volume of 300 μL, and this was regarded as the optimum volume. The effect of the volume of mixed solution on ΔA was studied, and the results are shown in figure 7 (140 μL of mixed solution was used).

3.2 *Analytical characteristics*

Under the optimum experimental conditions, absorbance increased linearly with increasing concentration of Zeph over the range 6.34–50.8 μg/mL. The relationship between ΔA and Zeph concentration was given by the equation $\Delta A = 0.0242 + 0.0182C$ ($n = 3$); $r = 0.9948$, where C is the concentration of Zeph in μg/mL. The relative standard deviation (RSD) was 1.2% for 11 determinations of 25.4 μg/mL Zeph. The calibration graphs were obtained in the range 7.29–32.8 μg/mL for CTMAB and 7.5–40.0 μg/mL for CPB, and the linear regression equations were $\Delta A = 0.0027 + 0.0143C$ (μg/mL) for CTMAB with a correlation coefficient of 0.9957 and $\Delta A = -0.1042 + 0.01612C$ (μg/mL) for CPB with a correlation coefficient of 0.9965. The RSD was 1.3% and 1.8% for 11 determinations of 21.9 μg/mL CTMAB and 25.0 μg/mL CPB, respectively. The detection limits, calculated according to $3s_0/S$, where s_0 is the standard deviation of the blank measurements ($n = 11$), and S,

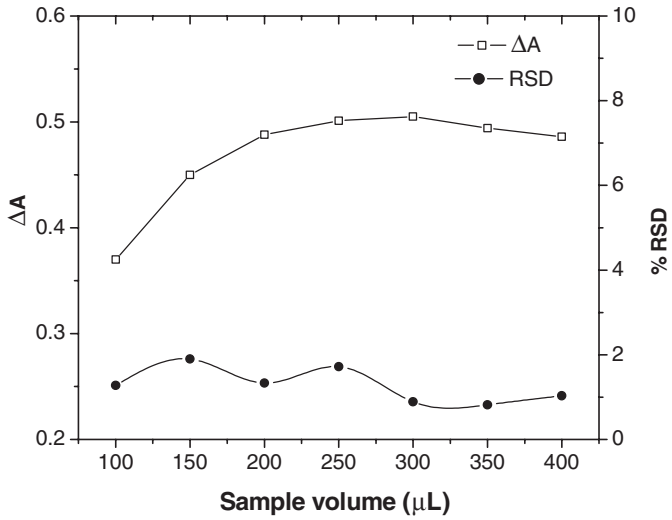

Figure 6. Influence of the sample volume on ΔA and percentage RSD of ΔA. Zeph, 25.4 μg/mL; BB, 1.0×10^{-4} mol/L; other conditions were as described in section 2.3.

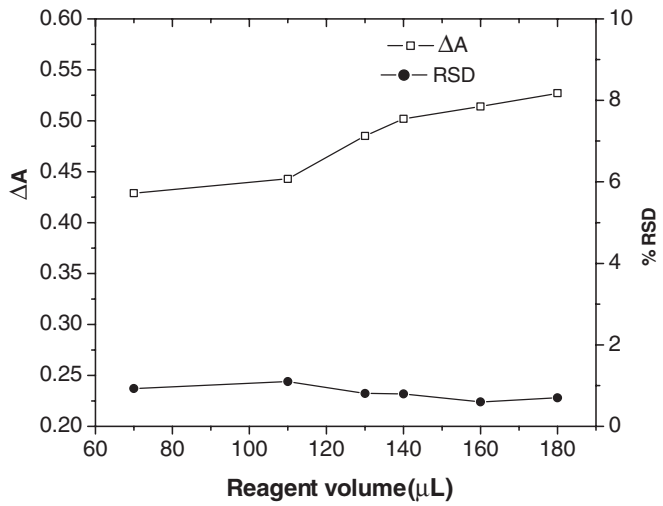

Figure 7. Influence of the reagent volume on ΔA and percentage RSD of ΔA. Zeph, 25.4 μg/mL; BB, 1.0×10^{-4} mol/L; other conditions were as described in section 2.3.

the slope of the calibration graph, is 0.22 μg/mL, 0.29 μg/mL and 0.25 μg/mL for Zeph, CTMAB and CPB, respectively. It took 123 s to complete one cycle, resulting in a sample frequency of 28 samples per hour.

3.3 *Interference study*

The effects of common ions and organic compounds on the determination of 12.7 μg/mL Zeph, 21.9 μg/mL CTMAB and 20.0 μg/mL CPB were investigated.

Table 2. Effects of foreign species or ions on the determination of 12.7 μg/mL of Zeph, 21.9 μg/mL CTMAB and 20.0 μg/mL CPB.

Compounds	Added as	Tolerable concentration (mg/mL)			Compounds	Added as	Tolerable concentration (mg/mL)		
		Zeph	CTMAB	CPB (μg/mL)			Zeph	CTMAB	CPB (μg/mL)
K^+	KCl	0.60	0.26	7.87	Mn^{2+}	$MnSO_4$	1.70	1.82	72.8
Na^+	$NaNO_2$	33.2	0.42	50.0	Cr^{3+}	$Cr_2(SO_4)_3$	0.34	7.84	0.056
NH_4^+	NH_4F	24.1	1.48	9.80	Fe^{3+}	$Fe(NO_3)_3$	0.14	1.04	1.39
Hg^+	$HgCl_2$	0.75	0.75	1.90	NO_2^-	$NaNO_2$	17.6	0.83	100
Ca^{2+}	$CaCl_2$	2.89	1.86	180	PO_4^{3-}	Na_3PO_4	0.03	0.03	0.35
Cd^{2+}	$CdCl_2$	0.31	6.13	31.0	DTAB		0.10	5.00[a]	2.5
Co^{2+}	$CoCl_2$	0.79	1.47	5.80	SDBS		1.70[a]	0.07[a]	1.4
Cu^{2+}	$CuSO_4$	0.04	3.58	1.20	SLS		2.50[a]	6.00[a]	8.0
Ni^{2+}	$NiSO_4$	0.04	1.86	250	Triton X-100		4.00[a]	20.0[a]	21.0
Mg^{2+}	$MgSO_4$	5.50	0.40	70.7	β-CD		0.10	40.0[a]	4.0

[a]μg/mL
DTAB, dodecyltrimethylammonium bromide; SDBS, docecylbenzene sulfonic acid sodium salt; SLS, sodium laurylsulfonate; β-CD, β-cyclodextrin.

Table 3. Determination of cationic surfactants in synthetic samples ($n = 5$).

Added (μg/mL)	Coexisting compounds (mg/mL)	Found (μg/mL)	RSD (%)	Recovery (%)
Zeph 12.7	$CoCl_2$ 0.12, $Cr_2(SO4)_3$ 0.004, $HgCl_2$ 0.051, Triton X-100 0.20	13.7	1.8	108
Zeph 12.0	$CoCl_2$ 0.12, $CaCl_2$ 0.01 $Fe(NO_3)_3$ 1.46×10^{-3}, CPB 0.02	12.7	2.4	106
Zeph 9.83	$NiSO_4$ 0.33, $MgSO_4$ 0.50, NH_4F 0.49, SLS 0.05	9.80	3.2	99.7
Zeph 12.7	β-CD 0.01, DTAB 0.50, SLS 0.02, CTMAB 1.8×10^{-4}	12.6	0.8	99.2
CTMAB 9.11	$MnSO_4$ 1.20, $CaCl_2$ 1.11, $Fe(NO_3)_3$ 8.6×10^{-3}, SLS 4.0×10^{-4}	8.81	3.1	96.7
CTMAB 7.65	$Fe(NO_3)_3$ 8.6×10^{-3}, Mg SO_4 0.75, NH_4F 1.48, DTAB 5.0×10^{-3}	8.49	4.1	111
CPB 20.0	$Cr_2(SO_4)_3$ 2.5×10^{-3}, $CdCl_2$ 0.25, $CaCl_2$ 0.25, β-CD 4.0×10^{-3}	19.4	3.5	97.0
CPB 11.0	$CuSO_4$ 0.006, $NiSO_4$ 0.24, $CoCl_2$ 0.39, $MgSO_4$ 0.25	10.9	2.8	99.1

Samples containing a fixed concentration of the foreign substance were injected. The tolerance limit was defined as the concentration of added species causing less than ±5% relative error. The results of this study were listed in table 2.

3.4 *Applications*

The proposed method was applied to the determination of cationic surfactants in synthetic sample and spiked tap water and well water. The results obtained, including recovery and precision, are shown in tables 3 and 4. The results demonstrate that the method can be applied satisfactorily to the determination of Zeph in tap water and well water.

Table 4. Determination of Zeph in tap and well water samples ($n = 5$).

Sample	Added (μg/mL)	Found (μg/mL)	RSD (%)	Recovery (%)
Tap water 1	25.4	24.4	1.0	96.1
Tap water 2	15.9	17.0	2.0	107
Well water 1	15.9	15.9	0.3	100
Well water 2	9.83	9.51	2.3	96.7

4. Conclusions

This paper presents an automated SIA system for the determination of trace levels of cationic surfactants in synthetic and spiked water. The main advantages of this system are the low analytical cost, fast sample-throughput rate, operation simplicity, and exclusion of any toxic organic solvents, although the sensitivity of the method is nearly the same as that of other methods [4, 8, 12, 19, 20] and is lower than that using the HPLC technique [9–11], which is routinely used for cationic surfactant analysis.

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