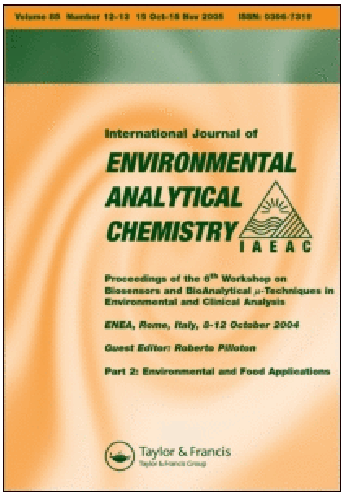

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Cloud point extraction of aluminum (III) in water samples and determination by electrothermal atomic absorption spectrometry, flame atomic absorption spectrometry and UV-visible spectrophotometry

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Cloud point extraction of aluminum (III) in water samples and determination by electrothermal atomic absorption spectrometry, flame atomic absorption spectrometry and UV-visible spectrophotometry

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Cloud point extraction was applied as a preconcentration step for the determination of trace level of Al(III) in water samples with electrothermal atomic absorption spectrometry (ETAAS), flame atomic absorption spectrometry (FAAS) and UV-visible spectrophotometry. The aluminum was extracted as aluminum-Eriochrome Cyanine R (ECR) complex, at pH 6 by micelles of the non-ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114). The investigations showed that the same CPE procedure can be used for different detection techniques. The results obtained from these techniques were evaluated. Under the optimal conditions, limit of detection obtained with ETAAS, FAAS and UV-visible spectrophotometry were $0.03\,\mathrm{ng\,mL^{-1}}$, $0.06\,\mathrm{\mu g\,mL^{-1}}$ and $0.01\,\mathrm{\mu g\,mL^{-1}}$, respectively. The accuracy of the procedure was tested by analysing certified reference material. The method was successfully applied to determination of aluminum in water samples and dialysis fluid.

Keywords: cloud point extraction; aluminum; electrothermal atomic absorption spectrometry; flame atomic absorption spectrometry; UV-visible spectrophotometry

1. Introduction

Aluminum naturally occurs in waters in very low concentrations. The concentration of aluminum in natural waters (e.g., lakes, streams) is generally below $0.1\,\mathrm{mg\,L^{-1}}$ unless the water is very acidic. Acid rain dissolves minerals in soils, and transports these to water sources. This markedly increases the aluminium content of rivers and lakes [1]. Dissolved Al(III) ions are toxic to plants because they decrease phosphate intake. The toxicity of Al(III) for humans usually results from inhibition of Mg(II)-dependent enzymes. Al(III) can replace Mg(II) in biological systems because of its much higher affinity for ligands [2]. Aluminum has long been known as a neurotoxic agent [3]. Several studies have been published relating aluminum exposure and neurological disorders, such as osteomalacia, encephalopathy, Alzheimer's disease and Parkinson's disease [4–7].

Aluminum salts are commonly used as coagulating agents. Aluminum sulphate is frequently employed in water treatment processes. However, if not used properly, aluminum levels in the treated water may increase because a small fraction of this salt is hydrolysed in water. Schintu *et al.* reported that a dissolved fraction of aluminum was

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present mostly as dissolved organic aluminum in raw water, and as dissolved inorganic aluminum in finished water [8]. Like tap water, aluminum may be found in some bottled waters because it occurs naturally at the source. Finally, the amount of free aluminum present in drinking water should be carefully monitored. EPA has recommended a Secondary Maximum Contaminant Level (SMCL) of 0.05–0.2 $\mathrm{mg\,L^{-1}}$ for aluminum in drinking water [9]. Also the World Health Organization (WHO) has proposed a guideline value of 0.2 $\mathrm{mg\,L^{-1}}$, not based on any assessment of risks to health, but as a compromise between the need to limit the use of aluminum salts in water treatment, and the effective discoloration of distributed water [1].

Instrumental techniques such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF-AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) are powerful tools for the determination of aluminum. However, separation and preconcentration steps are necessary, due to matrix effects and low concentration of aluminum in environmental samples. There are many methods of separation and/or preconcentration of aluminum, including solid phase extraction [10–13], electrochemical deposition [14, 15] and membrane extraction [16].

Cloud point extraction (CPE) has been used for the extraction and preconcentration of metal ions after the formation of hydrophobic complexes with suitable reagents. Hydrophobic species that are dissolved in the hydrophobic core of the micelles will separate and become concentrated in the small volume of the surfactant-rich phase [17–19]. The principle, advantages and applications of CPE have been well established and identified in recent years. From an analytical point of view, CPE has been successfully employed for the separation and preconcentration of trace elements from a variety of matrices, including environmental and biological samples [20–25].

To date, applications of CPE for preconcentration of aluminum prior to detection by spectrophotometry, spectrofluorimetry, ICP-AES and AAS have been published [26–29]. In the present work, CPE method has been developed and optimised as a preconcentration step for determination of trace level of Al(III) in water and dialysis fluid samples with three detection techniques. Electrothermal atomic absorption spectrometry (ETAAS), flame atomic absorption spectrometry (FAAS) and UV-visible spectrophotometry were investigated and evaluated for the determination of Al(III) after the same CPE procedure. In the preconcentration step, Eriochrome Cyanine R (ECR) and octylphenoxypolyethoxyethanol (Triton X-114) were used as the chelating agent and the non-ionic surfactant, respectively. This element was selected for evaluation of the procedure because aluminum is one of the principal metal ions for analytical interest due to its toxicity even at relatively low concentrations.

2. Experimental

2.1 *Instrumentation*

A PerkinElmer AAnalyst 800 Atomic Absorption Spectrometer (Shelton, CT, USA) equipped with a transversely heated graphite tube atomiser (THGA) with longitudinal Zeeman-effect background correction was used. A multi element hollow cathode lamp (PerkinElmer) was used as the radiation source at the 309.3 nm wavelength, which was operated at 35 mA, with a spectral bandwidth of 0.7 nm. A 20 µl volume of the standard or sample solutions and 5 µl volume of the matrix modifier were injected in the graphite furnace using an AS-800 autosampler. Pyrolytic graphite-coated electrographite tubes with

Table 1. Graphite furnace temperature program for the determination of Al in samples submitted to CPE.

Stage	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Ar flow rate (mL min^{-1})
Drying I	110	1	30	250
Drying II	130	15	30	250
Pyrolysis	1200	10	20	250
Atomisation	2350	–	5.0	0
Cleaning	2500	1	3.0	250

an integrated L'vov platform (PerkinElmer B3 000641) were used throughout. All measurements were performed using integrated absorbance (peak area). The graphite furnace temperature programme is given in Table 1. For FAAS measurements, PerkinElmer Model AAnalyst 800 Atomic Absorption Spectrophotometer equipped with deuterium background correction was used (wavelength of 309.3 nm, spectral bandwidth of 0.7 nm). The nitrous oxide-acetylene flow rate and the burner height were adjusted in order to obtain the maximum signal–noise ratios. Shimadzu UV–visible spectrophotometer (Model mini-1240, Kyoto, Japan) was used for spectrophotometric measurements (1.0 cm quartz cell) of the aluminum-ECR complex before and after CPE.

The pH values were measured with a Fisher Accument model 15 pH meter (Loughborough, England) supplied with a combined electrode. A Fisons variable speed vortex (Loughborough, England) was used for efficient mixing of surfactant added sample. A thermostated bath (Clifton-Nickel Electro, North Somerset, England) maintained at the desired temperature was used for cloud point preconcentration experiments. A Hettich EBA 21 (Tuttlingen, Germany) centrifuge was used to accelerate the phase separation process. All solutions were prepared with deionised water (18.1 MΩ cm) obtained from a Barnstead, Nanopure Diamond purification system (Iowa, USA).

2.2 *Reagent and solutions*

All the chemicals were of analytical grade from Merck (Darmstadt, Germany). The nonionic surfactant Triton X-114 was used without further purification from Sigma (St. Louis MO, USA). The stock standard solution of aluminum was prepared by direct dissolution of proper amounts of $Al(NO_3)_3 \cdot 9H_2O$ salt from BDH (Poole, England) in deionised water. Working standard solutions were obtained by appropriate dilution of the stock standard solution. The chelating reagent ECR was obtained from BDH (Poole, England). A 0.3 % (m/v) chemical modifier solution was prepared by diluting the appropriate amount of $Mg(NO_3)_2$. The following buffers were used to control the pH of the solutions: acetic acid-sodium acetate (pH 3–6) and ammonia-ammonium acetate (pH 7 and 8). Ethanol, methanol and acetonitrile were used to decrease the viscosity of surfactant-rich phase. The pipettes and vessels used for trace analysis were kept in 5% (v/v) nitric acid for at least 24 h and subsequently washed several times with deionised water. The following certified reference waters were used for method validation, TM-23.2 Fortified Water and SPS-SW1 Surface Water (LGC Promochem, Wesel, Germany).

2.3 *Cloud point preconcentration procedure*

For the CPE, aliquot of 10 mL of a solution containing the analyte, 0.10% (v/v) Triton X-114 and 0.10% (m/v) ECR buffered at a suitable pH, were kept for 15 min in the thermostatic bath at 70°C. Subsequently, separation of the phases was achieved by centrifugation for 5 min at 4000 rpm. The bulk aqueous phase was easily removed with a pipette. In order to reduce the viscosity of the surfactant-rich phase and facilitate sample handling prior to ETAAS analysis, the extract in the tube was made up to 200 µL by adding ethanol. A Twenty µL sample and 5 µL $Mg(NO_3)_2$ as matrix modifier were injected into the graphite furnace by the autosampler and submitted to the temperature programme shown in Table 1.

Preconcentrated aluminum was also determined by FAAS and UV-Visible spectrophotometry. The same CPE method was applied to standard and sample solutions and 1.5 mL of ethanol was added to the surfactant-rich phase in order to reduce its viscosity and facilitate sample handling. For UV-Visible spectrophotometric detection, the surfactant-rich phase was completely dissolved with ethanol and transferred into a quartz cell. The absorbance of the solution was measured at λ_{max} (535 nm).

For all three detection methods, a blank solution subjected to the same procedure described above was measured parallel to the standard solutions and samples.

3. Results and discussion

3.1 *Optimisation of experimental parameters for preconcentration of aluminum from aqueous solutions*

The preconcentration efficiency of the CPE method has been tested by following the procedure described in Section 2.3. An optimisation study was performed at the ng mL^{-1} and µg mL^{-1} levels of aluminum. Hence, the effect of pH and surfactant concentration was given according to ETAAS results and the optimisation of chelating agent concentration was given according to UV-Visible spectrophotometric measurements.

3.1.1 *Optimisation of the ETAAS conditions*

Direct measurement after the CPE procedure applied was carried out by ETAAS, and the atomic and background signals are given in Figure 1a. For the direct measurement of extract in ethanol, background signal was found to be very intense and the atomic signal was not a proper shape to obtain reproducible results. In ETAAS determination of trace aluminum, various chemical modifiers have been proposed in the literature. Nitrates of metals such as magnesium and calcium have commonly been used as chemical modifiers for the determination of aluminum [30–32]. Therefore, in this work, magnesium nitrate was used as chemical modifier.

Pyrolysis and atomisation curves were established using 0.25 ng mL^{-1} aluminum standard solution, submitted to the cloud point extraction procedure. Aliquots containing 20 µL of the final extract in ethanol and 5 µL of the modifier were co-injected into the graphite furnace using the auto-sampler. The pyrolysis and atomisation temperature were investigated in the range of 700–1500°C and 1700–2500°C, respectively (Figure 2). When the pyrolysis and atomisation temperatures were close to 1200°C and 2300°C, the maximum absorbance values were observed. Peak shapes and background absorption have also been considered when choosing the proper furnace conditions. Finally, 1200°C

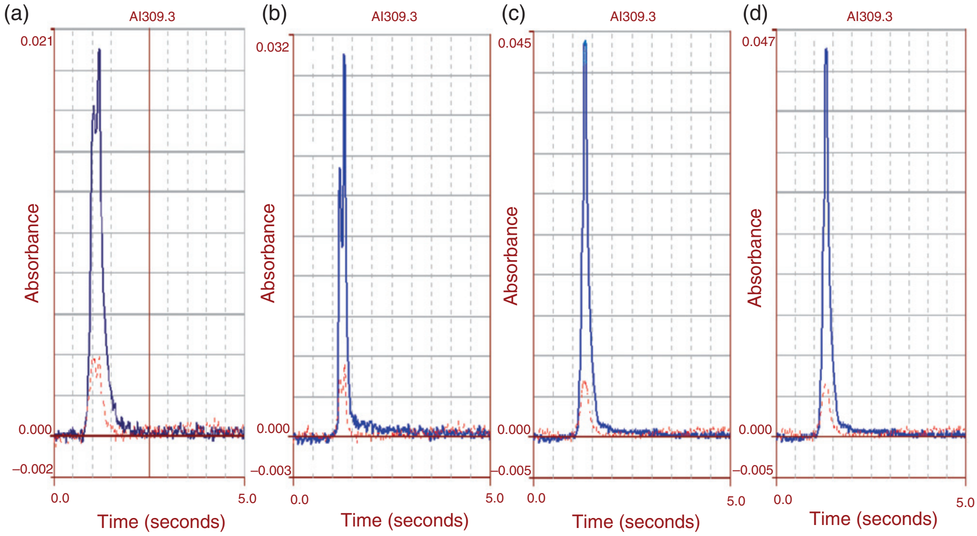

Figure 1. Atomisation profiles of Al(III) after the cloud point extraction; (a) without $Mg(NO_3)_2$; and with (b) 0.03% (w/v) $Mg(NO_3)_2$; (c) 0.3% (w/v) $Mg(NO_3)_2$; (d) 3.0% (w/v) $Mg(NO_3)_2$.

and 2350°C were selected as the optimised pyrolysis and atomisation temperature in the presence of the chemical modifier.

The effect of the concentration of the modifier on the absorption signal of aluminum was tested by using 0.03%, 0.30% and 3.0% (m/v) of magnesium nitrate solutions (Figures 1 and 2). When 0.3% and 3.0% (m/v) of magnesium nitrate was used, very intense atomic signals were obtained and there were background signals at low level (Figure 1c and 1d). Based on the experimental results, the concentration of magnesium nitrate was selected higher than 0.3%, the signals were not further improved and signal noise ratios are approximately the same for these two concentrations of modifier. Therefore, the concentration of magnesium nitrate was chosen as 0.3% (m/v).

3.1.2 *Effect of pH*

Because pH plays an important role on metal–chelate formation and subsequent extraction, the pH of the sample solution was the critical factor evaluated for its effect on the CPE of Al(III). It has been known that the optimal pH range of complex formation between Al(III) and ECR was pH 6–6.2 [33]. The pH of Al(III) standard solution ranged from 2.3 to 8.0. As shown in Figure 3, the aluminum signal increased markedly with the increase of sample pH from 4.0 to 6.2. The signal of the complex dropped rapidly at higher pH values. As can be seen in Figure 3, the maximum absorbance signal was obtained in the range of 5.7–6.2. Hence, pH 6.0 was chosen for CPE of aluminum.

3.1.3 *Effect of chelating agent concentration*

Optimisation of chelating agent concentration was carried out by UV-Visible spectrophotometric measurements. The effect of the concentration of ECR on the extraction of

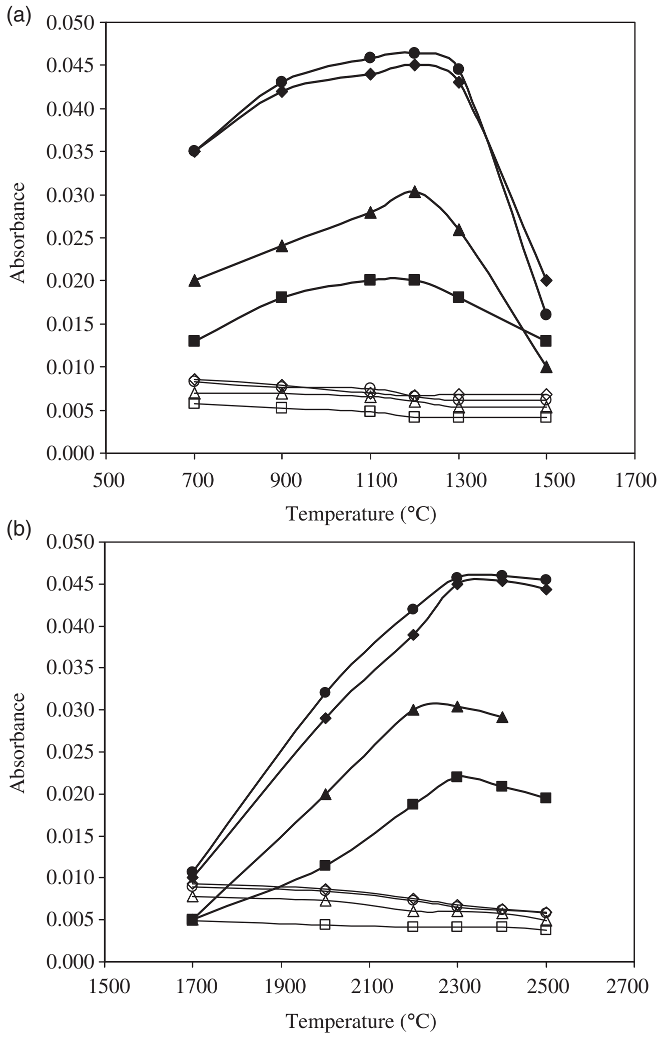

Figure 2. (a) Pyrolysis curve and (b) atomisation curve of Al(III) after CPE (■) No modifier and (□) background; (▲) 0.03% $Mg(NO_3)_2$ and (△) background; (◆) 0.3% $Mg(NO_3)_2$ and (◇) background; (•) 3.0% $Mg(NO_3)_2$, (o) background.

aluminum ($2\,\mu g\,mL^{-1}$) was investigated in the range of 0.01 to 0.25% (m/v). The analytical signal increased rapidly as the concentration of ECR increased from 0.01 to 0.10% (m/v) then almost kept constant with concentration of 0.25% (m/v) (Figure 4). According to the literature, aluminum gives three types of complex with ECR; $Al(ER)^{2+}$, $Al(ER)_2^+$ and $Al(ER)_3$. The uncharged complex is formed only when an excess of the ECR is present [34,35]. It is important to note that an uncharged complex is preferentially extracted to the surfactant-rich phase when non-ionic surfactant is used. At the lower ECR concentration, extraction recovery was low, probably charged complexes could have been formed. Thus, an ECR concentration of 0.10% (m/v) was chosen.

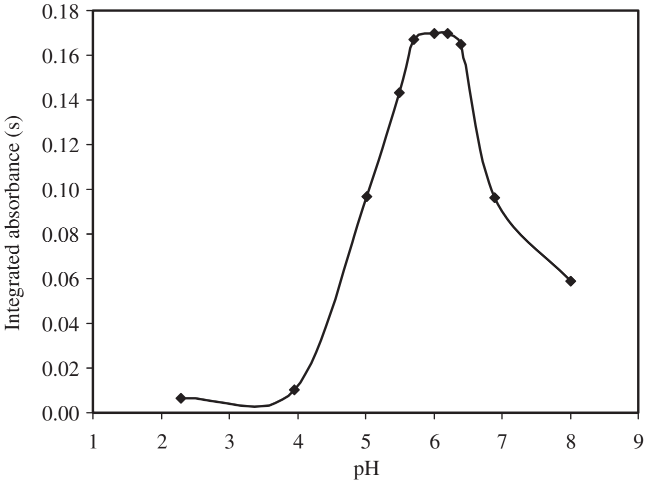

Figure 3. Effect of pH on the cloud point extraction of Al(III); 1 ng mL^{-1} Al(III), 0.1% (v/v) Triton X-114, 0.1% (m/v) ECR, incubation temperature 70°C.

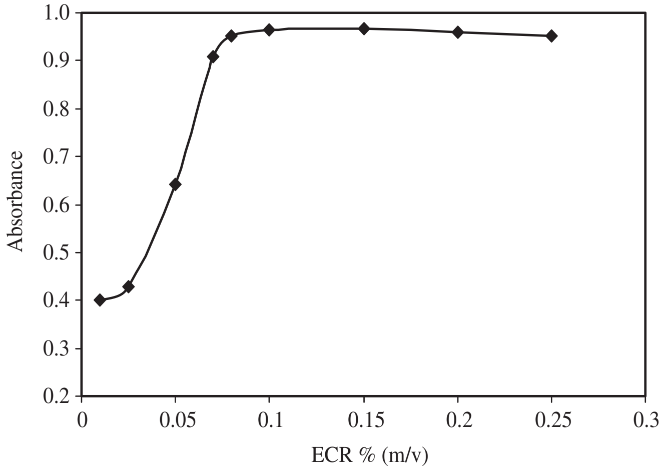

Figure 4. UV-Visible spectrophotometric results for effect of ECR concentration on the cloud point extraction of aluminum.

3.1.4 *Effect of surfactant concentration*

The variations in the analytical signal as a function of the concentration of Triton X-114 in the range of 0.01–0.40% (v/v) were investigated (Figure 5). Maximum absorbance signals were observed when the Triton X-114 concentration was above 0.10% (v/v). At lower concentrations (<0.10% v/v), the analytical signal was low, probably due to insufficient entrapment of hydrophobic complex quantitatively by micelles. Accordingly, a Triton X-114 concentration of 0.10% (v/v) was employed for further studies.

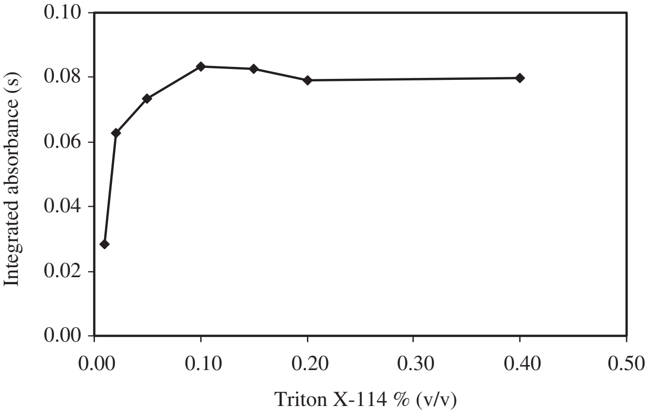

Figure 5. Effect of Triton X-114 concentration on the cloud point extraction of Al(III); 0.5 ng mL^{-1} Al(III), pH 6, 0.1% (m/v) ECR, incubation temperature 70°C.

3.1.5 *Selection of the diluting agent for surfactant-rich phase*

High viscosity of the surfactant-rich phase is effectively decreased using diluting agents. Diluting agent must dissolve the surfactant-rich phase completely. For that purpose, different solvents such as acetonitrile, methanol and ethanol were tried. In the presence of acetonitrile and methanol, surfactant rich phase could not be dissolved, completely. So the solution was turbid, on the other hand, in the presence of ethanol, surfactant-rich phase was clear (dissolved completely) and maximum absorbance values were obtained for three detection techniques. Therefore, ethanol was chosen as the diluting agent.

3.1.6 *Effects of other experimental factors*

In the CPE method, it is desirable to employ the shortest equilibration time and the lowest equilibration temperature for completion of the reaction and easy phase separation. The effect of the equilibration temperature and time were studied within a range of 20–80°C and 5–60 min, respectively. The results showed that an equilibration temperature of 70°C and an equilibration time of 15 min are adequate to obtain quantitative extraction of aluminum. The effect of the centrifugation time was also studied within the range of 5–15 min. The centrifugation time posed no significant alteration in the obtained signals of the recovery for aluminum therefore, 5 min at 4000 rpm was selected to separate the surfactant-rich phase from aqueous solution. The salt effect was studied by the addition of NaCl to the solution in the range of 0.005–0.1 mol L^{-1}. The results showed that the addition of the salt has no significant effect on the extraction efficiency. It is necessary to emphasise that different blank solutions were also evaluated and no significant signal was obtained. Thus, the ionic strength was fixed at 0.1 mol L^{-1} with NaCl.

3.2 *Interferences*

The interference is due to the competition of other heavy metal ions for the chelating agent and their subsequent co-extraction with the Al(III). ECR is known to be highly selective for aluminum at pH 6.0, but Fe (III) can be co-extracted with aluminum at this pH value. The interfering effect of Fe(III) can be eliminated by using ascorbic acid or thiogylcolic acid as masking agents since they form highly hydrophilic complexes [33] which do not interact with the miceller aggregates. Under the optimum experimental condition, the interfering effect of some ions were examined with 1 ng mL^{-1} Al(III) (for detection with ETAAS) and 0.5 μg mL^{-1} Al(III) (for detection with FAAS and UV-visible spectrophotometry) solutions. The tolerance limit is defined as the concentration of added ion that caused less than ±5% relative error. The tolerable concentration ratio of foreign species to 1 ng mL^{-1} Al(III) was over 400-fold for Pb(II), Bi(II), Co(II), Ni(II); 250-fold for Cu(II), Cd(II), Cr(III), Zn(II) and 10-fold for Fe(III). For 0.5 μg mL^{-1} Al(III), the tolerable concentration ratio of foreign ions was 500-fold for Pb(II), Bi(II), Co(II), Ni(II); 300-fold for Cu(II), Cd(II), Cr(III), Zn(II) and 10-fold for Fe(III). The interfering effect of Fe (III) up to 10 μg mL^{-1} was completely removed by addition of 0.5 mL of 0.1% (m/v) thiogylcolic acid solution to the water samples. The common ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cl^-, I^-, CO_3^{2-}, NO_3^-, SO_4^{2-} (20 mg L^{-1}) produce no interference with extraction of aluminum.

3.3 *Analytical performance*

A calibration curve was constructed by the preconcentration of 10 mL of standard solutions with Triton X-114. Table 2 summarises the analytical characteristics of the optimised method, including linear range, limit of detection, precision, regression equations and enhancement factor. The limit of detection (LOD), defined as three times the standard deviation of the blank signal (3σ). The enhancement factor (EF) was obtained from the slope ratio of the calibration graph with and without preconcentration. The regression equations without preconcentration were $A = 0.0035\,C$ (ng mL^{-1}) $- 0.0004$ ($R^2 = 0.9999$) for ETAAS (2.5–100 ng mL^{-1}); $A = 0.0013\,C$ (μg mL^{-1}) $+ 0.0003$ ($R^2 = 0.9997$) for FAAS (2–100 μg mL^{-1}) and $A = 0.0687\,C$ (μg mL^{-1}) $+ 0.0086$ ($R^2 = 0.999$) for UV-visible (0.2–6.0 μg mL^{-1}) detection. Consumptive index (CI) is another efficient way to evaluate the performance of the preconcentration method [36]. CI is expressed by volume of analyte solution (V, mL) and the EF ratio (CI = V / EF), thus indicating the necessary volume to obtain one unit of enrichment factor. It is important to emphasise that the consumptive index obtained for the CPE/ETAAS study was 0.2 mL, is lower than many procedures in the literature.

Table 2. Analytical characteristics of the method.

	ETAAS	FAAS	UV-Visible Spec.
Linear range	0.05–2.5^a	0.1–6.0^b	0.05–2.0^b
Regression equation	$A = 0.1799\ C^a + 0.0056$	$A = 0.0221C^b + 0.0014$	$A = 0.4828C^b - 0.0005$
Correlation coefficient	0.9977	0.9998	0.9999
Precision (RSD (%), $n = 7$	3.1^c	2.8^d	2.2^e
Limit of detection	0.03^a	0.06^b	0.01^b
Sample volume, Ml	10	10	10
Enhancement factor	51	17	7
Consumptive index, mL	0.2	0.59	1.43

Notes: ^{a}(ng mL^{-1}); ^{b}(μg mL^{-1}); ^{c} 0.25 ng mL^{-1}; ^{d} 0.5 μg mL^{-1}; ^{e} 0.2 μg mL^{-1}.

3.4 *Determination of aluminum in standard reference materials and spiked water samples*

The proposed method was applied to the preconcentration and determination of aluminum content standard reference materials (TM-23.2 – Fortified Water and SPS-SW1 – Surface Water). The results in Table 3 are based on the average of three replicates. Good agreement was obtained between the estimated contents and the certified values for FAAS and UV-visible detections. Since the concentration of Al(III) in the standard reference materials exceeded the linear range of the CPE/ETAAS method, the proposed CPE/ETAAS method was not applied to these standard reference materials.

CPE procedure was also applied to the tap water, bottled drinking water, bottled mineral water and acidic dialysis concentrate. For FAAS and UV-visible measurements, a different amount of Al(III) was added to 10 mL of water samples. As shown in Table 4, obtained results were in good agreement with those determined by independent ETAAS measurements.

Table 3. Determination of aluminum in certified reference materials ($n = 3$).

Sample	Certified value (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
		FAAS	
TM-23.2	96	93.4 ± 0.5	97
		UV-Vis	
TM-23.2	96	94.6 ± 1.1	98
SPS-SW1	50	48.6 ± 0.3	97

Table 4. Results from the analysis of acidic dialysis concentrate and spiked water samples ($n = 3$).

Sample	CPE Added (ng mL^{-1})	CPE Found (ng mL^{-1})	Direct determination by ET-AAS (ng mL^{-1})	Recovery(%)
		FAAS		
Tap water	–	109.7 ± 2.1	114.6 ± 1.7	96
	200	316.5 ± 1.3		102
	500	618.4 ± 0.9		103
		UV-Visible		
Tap water	–	112.3 ± 2.7	114.6 ± 1.7	98
	200	317.7 ± 2.1		103
	500	617.3 ± 1.8		102
Mineral water	–	57.0 ± 0.4	56.2 ± 0.6	101
	200	255.1 ± 2.6		98
	500	557.6 ± 2.1		102
		ET-AAS		
Acidic dialysis concentrate		11.6 ± 1.2		–

Table 5. Comparison of enhancement factor (EF), consumptive index (CI) and limit of detection (LOD) of proposed method with other CPE procedures for Al(III).

Reagent	Surfactant	EF	Sample volume (mL)	CI (mL)	LOD (ng mL^{-1})	Detection	Ref.
CAS[a]	PONPE 7.5	50	10	0.20	3.02	FI-spectr.[g]	[37]
–	PONPE 7.5	200	50	0.25	0.25	FI-ICP-OES	[28]
HQ[b]	TX-100	9.4	–	–	–	ICP-AES	[38]
CAS[a]	CTAB[c] / TX-114	40.3	10	0.25	0.52	Spectr.[g]	[26]
8-HQ[d]	TX-114	10	25	0.40	0.79	Spectrf.[h]	[27]
PMBP[e]	TX-114	37	10	0.27	0.09	GF-AAS	[29]
ECR[f]	TX-114	51	10	0.19	0.03	GF-AAS	This work
		17		0.59	60	FAAS	
		7		1.43	10	UV-Visible	

Notes: [a]Chrome Azurol S; [b]8-quinolinol; [c]Cetyltrimethylammonium bromide; [d]8-hydroxyquinoline; [e]1-phenyl-3-methyl-4-benzoyl-5-pyrazolone; [f]Eriochrome Cyanine R; [g]Spectrophotometry; [h]Spectrofluorometry.

Aluminum was analysed in acidic dialysis concentrate routinely employed by haemodialysis centres. In the haemodialysis practice, 1 L of acidic concentrate is mixed with 1.225 L of basic concentrate and 32.775 L of distilled water. The acidic dialysis concentrate was diluted 35 times with the distilled water, then the CPE/ETAAS method was applied. The results are shown in Table 4.

3.5 *Comparison to other methods*

A comparison of the proposed method with other reported cloud point extraction procedures is given in Table 5. As can be seen from the table, analytical characteristics obtained for CPE/ETAAS method are comparable to those presented by many methods in the table. The consumptive index for the CPE/ETAAS system is lower than that of the most procedures in the literature. For the CPE/FAAS and CPE/UV-visible method, enrichment factor can be improved by using larger sample volumes.

4. Conclusion

The investigations showed that the same CPE procedure can be used for different detection techniques. The detection limit of the CPE/ETAAS method for the determination of Al(III) was 0.03 ng mL^{-1} and is lower than many published works [26–29,37,38]. For the FAAS and UV-visible method the detection limits and the precision were found to be at the same order of magnitude. The correlation coefficient obtained for the calibration graph in the case of UV-visible spectrophotometry is also high when compared with the FAAS technique. The UV-visible spectrophotometric detection has been found to be more suitable for this analysis when compared with FAAS. UV-visible detection of course is less sensitive than the atomic spectrometry methods but ECR is a sensitive reagent for spectrophotometric determination of Al(III), because molar absorptivity of the complex is very high [33]. For the real samples the analysis results showed that the CPE procedure consisting of the three detection methods is very useful for the determination of Al(III) in water and samples.

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