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Green technology for monitoring the quality of water: determination of toxic trace analyte concentrations using multielemental mixed micelle cloud point extraction

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ABSTRACT

A simple multielemental mixed micelle cloud point extraction procedure has been developed for the simultaneous separation and preconcentration of toxic trace analytes from natural and wastewater samples prior to their determination by electrothermal atomic absorption spectrometry. The analytes Cr, Be, Pb, Cd, Tl, and Hg were converted simultaneously, as hydrophilic anionic iodide species formed with KI in the presence of HCl. The method is based on the formation of extractable ion associates of anionic iodide species with solubilizing cationic and hydrophobic sites of mixed micelles. The mixed micelles are formed by cationic, Aliquat-336 (*N*-methyl-*N*,*N*,*N*-trioctylammonium chloride) and nonionic, Triton X-114. The ion associates formed are preconcentrated from bulk aqueous phase into a small mixed micelle-rich phase, avoiding the addition of an external chelating agent. The parameters affecting the process are evaluated and optimized. The recoveries of anaytes are in the range of 86–102% at 0.1–10 μg L^{-1}. The accuracy of the procedure has been verified by using certified reference materials, such as National Institute of Standards and Technology (NIST) 1640a natural water, Community Bureau of Reference (BCR)-713 final effluent, and BCR-715 industrial effluent and being applied to industrial wastewater.

Keywords: Cloud point extraction; Surfactants; Mixed-micelles; Toxic analytes; Wastewater samples

1. Introduction

Providing safe drinking water for human consumption is the top priority for all concerned agencies worldwide because its quality causes direct impact on human health [1]. However, due to rapid industrialization and urbanization, and uncontrolled disposal of wastes in natural water bodies, the water available from natural sources is being contaminated to alarming levels [2]. Many studies have been reported in this area using conventional procedures. But they involve toxic chemicals and generate higher amounts of toxic waste [3–5]. Therefore, there is a need to develop technology, which do not contaminate the environment and these can be termed as green technology.

One such environmentally friendly technique is cloud point extraction (CPE). It uses dilute nonionic

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surfactants that are nonhazardous, nonflammable, nonvolatile and generates very little waste [6,7]. But these do have some limitations like poor extraction efficiency for hydrophilic ionic species [8]. Nowadays, a combination of ionic and nonionic surfactants have been introduced in CPE, which enhances extraction efficiencies of hydrophilic ionic analytes along with metal chelates by utilizing the reactive solubilising sites of formed mixed aggregates and also avoids the use of chelating agent [9,10].

The mixed micelle CPE has been used for the extraction of inorganic analytes after forming metal chelates, which use reactive hydrophobic solubilizing sites of mixed aggregates. Beiraghi et al. used cetyl pyridinium chloride and Triton X-114 mixed micelles for the extraction of Be with 1,8-dihydroxyanthrone as chelating agent [11]. The sodium dodecyl sulfate and Triton X-114 mixed micelles have been used for the extraction of Cr and various other toxic analytes using diphenyl carbazide and ammonium pyrrolidine dithiocarbamate, respectively [12,13]. The mixture of alkylphenol ethoxylate NP-7 and NP-9 surfactants have been used for the extraction of Pb and Cd using ammonium pyrrolidine dithiocarbamate [14]. A mixed micelle mediated extraction procedure for the separation of Ti(IV) was elaborated using alizarin red S as a complexing agent and CTAB at pH 3 followed by extraction with Triton X-114 in the presence of Na_2SO_4 [15]. Triton-X114 and benzyldimethylhexadecyl–ammonium chloride were used as mixed micellar medium for the extraction of Pb(II) after the formation of a complex with chelating agent PAR in acidic media [16]. Only a limited publications have appeared on the applicability of head group solubilizing sites of mixed micelles [17,18]. There is a dearth of information regarding the utility of ionic head group solubilizing sites of mixed micelles in the multielemental extraction of hydrophilic inorganic ions, without using chelating agents.

In this work, we describe a simple multielemental mixed micelle CPE procedure for the simultaneous separation and preconcentration of various toxic trace analytes from natural and wastewater samples. The principle of the method is that Cr, Be, Pb, Cd, Tl, and Hg forms hydrophilic iodide species in presence of HCl and KI. These anionic species have been reacted simultaneously with cationic head group solubilizing sites of Aliquat-336/Triton X-114 mixed surfactant by forming neutral hydrophobic ion-associates. These ion associates have been preconcentrated simultaneously from the bulk aqueous phase into a small mixed micelles-rich phase. The factors affecting the extraction efficiencies are evaluated meticulously using electrothermal atomic absorption spectrometry (ETAAS). The accuracy of the procedure is validated by analysing certified reference materials such as the NIST 1640a natural water, BCE-713 final effluent and BCR-715 industrial effluent.

2. Methodology

2.1. Instrumentation

The concentrations of Cr, Be, Pb, Cd, Tl, and Hg in the mixed micelles-rich phases were determined by using continuum source ETAAS (Contra AA 700, Analytik Jena AG, Jena, Germany). A transversely heated graphite tube, MPE 60 auto sampler and xenon short arc lamp in hot-spot mode operated at 300 W as the continuum radiation source were used. The analytical lines 357.6687, 234.8605, 283.3060, 228.8018, 276.7870, and 253.6519 nm, were used, respectively for measuring the Cr, Be, Pb, Cd, Tl, and Hg integrated absorbance's. The optimized temperature program used is given in Table 1.

2.2. Reagents and standard solutions

Ultra pure water obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to prepare all the solutions. Sub-boiled HNO_3 and HCl (Merck, Darmstadt, Germany) was prepared in our laboratory using quartz stills placed inside the clean bench. Stock multielemental standard solution (Merck, Darmstadt, Germany) was used for the preparation of working standards daily by subsequent dilution. The solutions of 10% m/v Aliquat-336 and Triton X-114 (Sigma-Aldrich, Steinheim, Germany) were prepared in methanol and water, respectively. The solution of 10% m/v KI (Merck, Mumbai, India) solution was prepared in water. A solution of 10% m/v Ir (Merck, Darmstadt, Germany) was used for coating the graphite tube. All the polypropylene containers were soaked in mixture of 10% HNO_3 and 10% HCl for 6 h and cleaned with Milli-Q water before use. The interference studies were carried out by using varying amounts of single elemental stock standard solutions of ($1\ mg\ mL^{-1}$) of Na^+, Mg^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, SO_4^{2-} and F^-. All the sample preparations were carried out in class 10 clean bench located in the class 100 clean laboratory. Wastewater sample was collected from local domestic wastewater treatment plant, Hyderabad, India. These samples were filtered through a 0.45-μm membrane filter and kept in a refrigerator at 4°C until use.

2.3. Mixed micelle cloud point extraction procedure

Aliquots of 1–5 mL water and wastewater samples were taken in precleaned polypropylene containers and 2% v/v HCl was added. To this solutions, 0.2 mL

Table 1
Optimized temperature program used for the determination of Cr, Be, Pb, Cd, Tl, and Hg in the surfactant rich phase using Ir-coated tube in continuum source ETAAS

Steps	Temperature (℃)	Ramp (℃ s^{-1})	Hold (s)	Ar flow (mL min^{-1})
Drying-1	80	6	20	250
Drying-2	110	5	20	250
Pyrolysis	1,200 (Cr), 800 (Be), 600 (Pb), 500 (Cd), 800 (Tl), and 600 (Hg)	300	10	250
Atomisation	2,300 (Cr and Be), 1,400 (Pb and Cd), 2,200 (Tl), and 1,100 (Hg)	500	5	0
Cleaning	2,400	300	3	250

of 10% m/v KI, 0.3 mL of 10% m/v Aliquat-336 and 1 mL of 10% m/v Triton X-114 were added and made up to 10 mL using Milli-Q water. The solution was heated at 50℃ for 10 min, which led to gravitational phase separation. Then, the tubes were kept in the refrigerator for 10 min to increase the viscosity of the mixed micelle rich phase so that the aqueous phase was easily removed by decantation. The formed 0.5 mL mixed micelles-rich phase was dissolved in 0.3 mL methanol to decrease the viscosity. The final volume was made up to 1 mL with deionized water. Metal concentration of final solution was determined by ETAAS. Process blanks were also prepared in similar manner.

3. Results

The parameters affecting the simultaneous separation and preconcentration of Cr, Be, Pb, Cd, Tl, and Hg by the reactive solubilizing sites of the cationic mixed micelles were studied by spiking these analytes in the range 0.1–10 μg L^{-1} to wastewaters.

The concentration of KI plays important role in the formation of extractable anionic iodide species and their interaction with extracting cationic surfactant aggregates. Hence, the effect of KI in the range of 0–1% m/v on the recovery of Cr, Be, Pb, Cd, Tl, and Hg were studied. Results are shown in Fig. 1. As can be seen in Fig. 1, in the absence of KI, the recoveries of these analytes were in the range of 5–20% only. However, these recoveries increased with increase in the concentration of KI from 0.05 to 0.2% and reached the quantitative recoveries between 90 and 98%. Hence, a concentration of 0.2% m/v KI was selected.

The effect of HCl concentration on the recovery of Cr, Be, Pb, Cd, Tl, and Hg was studied in the range of 0–10% v/v in the presence of 0.2% m/v KI, 0.3% m/v Aliquat-336 and 1% m/v Triton X-114. In the absence of HCl, the recoveries of these analytes were in the range of 10–35% only. It indicates that iodide alone could not be able to extract these anaytes quantitatively. However, these recoveries increased with increase in the concentration of HCl from 0.5 to 1.5% and then reached the quantitative recoveries of 92–100% between the 2–10% HCl concentrations. It may be due to formation of iodide or tri-iodide. Hence, a concentration of 2% v/v HCl was selected for further studies.

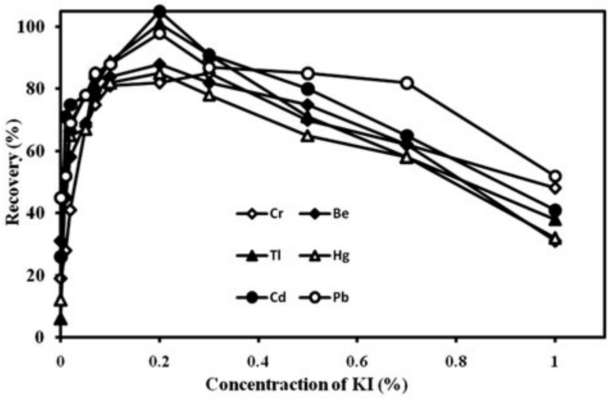

Fig. 1. Effect of concentration of KI on the recovery of Cr, Be, Pb, Cd, Tl, and Hg in presence of 2% v/v HCl, 0.3% m/v Aliquat-336 and 1% m/v Triton X-114.

In order to develop a successful mixed micelle CPE procedure, it is necessary to optimize concentrations of cationic and nonionic surfactants. Hence, the effect of cationic surfactant, Aliquat-336 concentration on percentage recovery of Cr, Be, Pb, Cd, Tl, and Hg was studied in the range 0–2% m/v, by keeping Triton X-114 concentration at 1% m/v. The results showed that without Aliquat-336, the recoveries of Cr, Be, Pb, Cd, Tl, and Hg were 10, 20, 85, 76, 65, and 55%, respectively. These recoveries increased gradually with increase in the concentration of Aliquat-336 and near quantitative recoveries of 90–95% were obtained at 0.3% v/v Aliquat-336. Hence, a concentration of 0.3% m/v Aliquat-336 was selected. Then, the effect of nonionic surfactant, Triton X-114 concentration on percentage recovery of Cr, Be, Pb, Cd, Tl, and Hg were studied in the range 0–2% m/v, by keeping Aliquat-336 concentration at 0.3% m/v. The results showed that without Triton X-114, no phase separation was observed. Clear phase separation was observed at 0.1% Triton X-114, under these conditions, the recoveries were 60, 50, 90, 95, 90, and 85%, respectively. These recoveries were increased with increase in the concentration of Triton X-114 up to 0.8% and then reached a plateau with near quantitative recoveries in the range 90–98%. Hence, a concentration of 1% m/v Triton X-114 was selected.

Optimization of incubation temperature and time is necessary to study the ion-associated kinetics of analytes with mixed micelles and their effective transfer into the micelles aggregates. Therefore, the effects of incubation temperature on recovery of analytes were studied in the range 25–60˚C using 20 min incubation time. The clouding temperature of the solution under optimized conditions was found to be 25˚C, whereas maximum extraction efficiencies (86–102%) were achieved after 45˚C. Therefore, a 50˚C incubation temperature was selected. The optimization of incubation time was carried out between 5 and 30 min. The extractions of these ion associates were fast and efficient after 10 min of incubation time. Therefore, 10-min incubation time was selected.

The recovery studies were performed by spiking the wastewater sample with Cr, Be, Pb, Cd, Tl, and Hg species individually in the range of 0.1–10 μg L^{-1}. The values obtained are given in Table 2. As shown in Table 2, the recoveries were in between 86 and 102% for all studied analytes. Therefore, this procedure was used for the determination of these analytes in natural and wastewater samples.

Under the optimized conditions the pre-concentration factors, i.e. the ratio of the analyte concentration in the final surfactant-rich phase to that of the initial aqueous phase was evaluated and found to be 10 for all the studied analytes.

3.1. Interference studies

In order to evaluate the performance of the present optimized procedure, the highest tolerability of various common interfering ions was studied. These include the anionic species that may react with cationic solubilizing sites and metal ions that may react with iodide ions, which subsequently interacted with cationic mixed micelles. The tolerance limits of these foreign ions were studied in wastewater sample spiked with 0.5–10 μg L^{-1} of studied analytes by keeping the relative error between ±5%. It was found that 500 mg L^{-1} of Na^+; 100 mg L^{-1} of Mg^{2+}; 50 mg L^{-1} of Ca^{2+}; 20 mg L^{-1} of Ni^{2+}; 10 mg L^{-1} of Zn^{2+} and 5 mg L^{-1} of Cu^{2+}; 1 mg L^{-1} SO_4^{2-} and F^- showed no interferences. Therefore, this method can be applied to water and wastewater samples.

Table 2
Spiked recoveries of trace analytes from wastewater samples using mixed micelle cloud point extraction procedure ($n = 4$)

Analytes	Spiked (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Cr	–	0.33 ± 0.01	–
	0.5	0.78 ± 0.01	90 ± 2
Be	–	<0.01	86 ± 1
	0.1	0.086 ± 0.001	
Pb	–	0.40 ± 0.02	–
	1.0	1.35 ± 0.03	95 ± 3
Cd	–	0.050 ± 0.002	102 ± 3
	0.1	0.152 ± 0.003	
Tl	–	0.16 ± 0.01	94 ± 1
	1.0	1.10 ± 0.01	
Hg	–	<0.3	94 ± 3
	10	9.4 ± 0.3	

3.2. Analytical figures of merit

Under the optimized conditions, the calibration curves were obtained by preconcentrating the successively spiked standards of Cr, Be, Pb, Cd, Tl, and Hg in the range of 0.2–10, 0.1–5, 0.5–15, 0.1–5, 0.5–20, and 5–25 μg L^{-1}, respectively. The correlation coefficients were between 0.9925 and 0.9998. Quantifications were performed by external calibration using aqueous standards. The limits of detection calculated based on three times the standard deviation of ten measurements of procedural blanks were 0.05, 0.01, 0.06, 0.01, 0.02, and 0.3 μg L^{-1}, respectively, for Cr, Be, Pb, Cd, Tl, and Hg. A comparison of the proposed procedure with the recently published CPE procedures is given in Table 3 [11–16,19]. As indicated in Table 3, the present procedure shows better detection limits for Pb and Cd and comparable detection limits for other elements compared to other reported procedures. However, the reported procedure has the advantage of simultaneous multi-elemental separation and preconcentration by effectively utilizing the reactive solubilising sites of the mixed micelles, which avoid the use of chelating agents.

3.3. Validation of the procedure

The accuracy of the proposed procedure developed for the simultaneous CPE and analysis of Cr, Be, Pb, Cd, Tl, and Hg was verified by analysis of certified reference materials such as NIST 1640a natural water, BCR-713 final effluent and BCR-715 industrial effluent. The results are given in Table 4. The values obtained are in good agreement with certified values. The Student's *t*-test was applied at the 95% confidence level, which showed that the measured values of analytes in these matrices provided better confidence limits compared with the certi-

Table 3
Comparison of analytical figures of merit of proposed multielemental mixed micelle cloud point extraction procedure with other reported procedures

Chelating agent	Surfactants/Aggregates	Detection system	DL (μg L^{-1})	Refs.
Hydroxyquinoline	Triton X-114/Micelles	ICP-OES	Cd (2), Pb (2.2), Cu (3.2), Ni (0.23), Co (2.2), and Zn (1.9)[a]	[19]
Dihydroxyanthrone	CPC[b] and Triton X-114/MM	ICP-OES	Be (0.001)	[11]
Diphenyl carbazide	SDS[c] and Triton X-114/MM	ETAAS	Cr (0.001)	[12]
APDC[d]	SDS and Triton X-114/MM	ETAAS	Cd (0.005), Pb (0.08), Cu (0.03), Ni (0.05), and Mn (0.01)	[13]
APDC	Alkylphenol ethoxylate NP-7 and NP-9/MM	FAAS	0.5 (Pb) and 0.28(Cd)	[14]
–	CTAB[e] and Triton X-114/MM	ICP-MS	Tl (0.02)[f]	[15]
–	TOAC[g] and Triton X-114/MM	CV-AAS[h]	–	[16]
–	Aliquat-336 and Triton X-114/MM	ETAAS	Be (0.01), Cd (0.01), Cr (0.05), Hg (0.3), Pb (0.06), and Tl (0.02)	Present work

[a] Limits of quantifications.
[b] Cetyl pyridinium chloride.
[c] Sodium dodecyl sulfate.
[d] Ammonium pyrrolidine dithio carbamate.
[e] Cetyl trimethyl ammonium bromide.
[f] Values are in ng L^{-1}.
[g] Tri octyl ammonium chloride.
[h] Cold vapor atomic absorption spectrometry.

Table 4
The determined values of Cr, Be, Pb, Cd, Tl, and Hg in various certified reference using proposed mixed micelle cloud point extraction

	Concentrations (μg L^{-1}) (mean ± $t.s\ (n)^{-1/2}$)[a]					
	BCR 713		BCR 715		NIST 1640a	
Elements	Certified	Measured	Certified	Measured	Certified	Measured
Cd	5.1 ± 0.6	5.4 ± 0.6	40 ± 5	39 ± 4	3.992 ± 0.072	3.98 ± 0.07
Pb	47 ± 4	46.8 ± 2.5	0.49 ± 0.04	0.48 ± 0.03	12.005 ± 0.050	11.9 ± 0.3
Cr	21.9 ± 2.4	22.5 ± 1.5	–	–	40.54 ± 0.30	40.35 ± 0.45
Tl	–	–	–	–	1.619 ± 0.016	1.62 ± 0.01
Be	–	–	–	–	3.002 ± 0.028	3.01 ± 0.02

[a] $t_{0.95} = 3.18$; $n = 4$; s = standard deviation.

fied values. As the concentration of Hg is not certified, the accuracy of the Hg was validated by spike recovery studies only. It indicates the applicability of the present procedures to industrial wastewater samples.

4. Conclusions

A simple environmental friendly multielemental mixed micelle CPE procedure has been reported for separation and pre-concentration of Cr, Be, Pb, Cd, Tl, and Hg from natural and wastewater samples. In this procedure, the head group-reactive solubilizing sites of mixed micelles have been utilized effectively for simultaneous extraction of hydrophilic iodide species of studied inorganic analytes. It avoids the use of chelating agents. This method can be applied to industrial effluents, influents and natural water samples. This fast and green chemical procedure is more useful to regularly monitor drinking water by concerned agencies.

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