

# A Novel Synergetic Salt- and Acid-induced Ligandless Mixed Micelle Cloud Point Extraction of Ultratrace Levels of Cd, Hg, Bi, and Tl From Petrochemical Effluents Followed by ETAAS Determination

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## ABSTRACT

A new synergetic salt- and acid-induced ligandless mixed micelle cloud point extraction procedure was developed for the simultaneous separation and pre-concentration of Cd, Hg, Bi, and Tl from petrochemical effluents and groundwater samples. The cationic mixed micelles are formed by the micelle-micelle interaction of cationic cetylpyridinium ammonium bromide (CPAB) and nonionic Triton<sup>®</sup> X-114 micelles, which act as an ion pair and extracting agent. Due to the synergetic effect of potassium iodide and sulfuric acid, the hydrophilic anionic Cd, Hg, Bi, and Tl iodide species are formed. These also induce the clouding phenomenon in cationic mixed micelles. The strong electrostatic interaction between the mixed micelles head groups and the anionic iodide species form the hydrophobic ion pairs which are separated from the bulk aqueous phase into a small mixed

micelle-rich phase, thus avoiding the addition of an external chelating agent. Under the optimized conditions, a pre-concentration factor of nearly 20 times was obtained for all of the elements. The limits of detection obtained were 0.0005, 0.2, 0.04, and 0.05 ng mL<sup>-1</sup> for Cd, Hg, Bi, and Tl, respectively. The recoveries were in the range of 93–102% at 0.1 to 10 ng mL<sup>-1</sup> with a relative standard deviation of 2–10%. The accuracy of the method was validated by analysis of certified reference materials BCR 714 Initial Influent, BCR 715 Industrial Effluent, BCR 610 Groundwater, and NIST 1643e, 1643f, and 1642b Trace Elements in Water. The method was also applied to real samples of petrochemical effluents and groundwater collected locally. A continuum source electrothermal atomic absorption spectrometer (CS-ETAAS) was used for the determination of the elements.

ber of reactive ionic head group solubilizing sites in the mixed micelles needs to be increased. This can be achieved by addition of the ionic surfactant above its critical micelles concentration along with non-ionic micelles. However, it is expected that the clouding temperature of the system will increase due to the repulsions within and between the head groups of the mixed micelles which causes difficulty in achieving the clouding and phase separations (8, 10). These limitations prevent the analytical applicability of the synergetic properties of mixed micelles formed between the interactions of ionic micelles with non-ionic micelles. Hence, it is necessary to overcome this limitation in order to effectively utilize the increased reactive ionic head groups of the mixed micelles for the extraction of the hydrophilic inorganic metal ions through electrostatic interaction.

Clouding and phase separation in mixed micelles has been achieved by reducing the hydrophilic character of limited ionic head groups by the addition of dehydrating agents. Recently, Kenawy (11), Jalbani (12), and Hassanien (13) have utilized the salt-induced clouding concept in cationic mixed micelles formed by interaction with cationic CTAB and benzyl dimethylhexadecyl ammonium chloride monomers with Triton<sup>®</sup> X-114 micelles for the extraction of Ti and rare earth elements and Pb with alizarin red S and pyridylazo resorcinol chelating agents, respectively (11–13). Ezodidin (14) reported the acid-induced

## INTRODUCTION

Over the last several decades, special interest has been focused on the development of environmentally friendly microextraction procedures using the reactive solubilizing properties of self-assembled surfactant molecules (1–3). The use of mixed micelle cloud point extraction (MM-CPE) has become more popular (4–6) due to the existence of both hydrophobic and hydro-

philic reactive solubilizing sites in mixed micelles as compared to single hydrophobic sites of micelles. Most of the mixed micelles have been formed by the interaction of ionic monomers with non-ionic micelles and are used for the selective extraction of bulky metal ions and hydrophobic metal chelates (7–9). One of the limitations of MM-CPE is the low extraction efficiency of hydrophilic metal ions and polar organic compounds due to the lack of sufficient hydrophilic head group reactive sites. In order to overcome this limitation, the num-

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clouding concept in anionic mixed micelles formed by interaction of the SDS monomer with Triton X-114 micelles for the extraction of Cr with the diphenylcarbazide chelating agent. The authors of the present work reported the formation of cationic CTAB/Triton X-100 and Aliquat-336/Triton X-114 mixed micelle from the micelle-micelle interaction of ionic and non-ionic micelles for the extraction of trace metals and Pt, respectively, with and without using a chelating agent (15, 16). However, little information is available with regard to the clouding and synergistic properties of various mixed micelle solubilizing sites for the determination of hydrophilic metal ions without using chelating agents.

Electrothermal atomic absorption spectrometry (ETAAS) is a very suitable technique for the analysis of small volumes of a surfactant-rich phase obtained in the microextraction process and also has a high tolerance towards organics. Its performance can be further improved by using Ir as the permanent chemical modifier.

In this work, a new synergetic salt- and acid-induced ligandless mixed micelle CPE procedure is described for the separation and pre-concentration of Cd, Bi, Hg, and Tl from petrochemical effluents and groundwater samples. The mixed micelles are formed by the interaction of cationic cetylpyridinium ammonium bromide (CPAB) micelles with nonionic Triton X-114 micelles. To the best of our knowledge, no literature has been published on the clouding and phase separation induced by the synergetic effect of potassium iodide and sulfuric acid. The hydrophilic anionic iodide species of Cd, Hg, Bi, and Tl simultaneously react with the positively charged head groups of CPAB/Triton X-114 mixed micelles and form the ion pairs without a chelating agent.

These are subsequently pre-concentrated into a small mixed micelle-rich phase. The accuracy of the proposed procedure is verified by analyzing certified reference materials BCR 714 Initial Influent, BCR 715 Industrial Effluents, and BCR 610 Groundwater (Institute for Reference Materials and Measurements Geel, Belgium) and NIST 1643e, 1643f, and 1642b Trace Elements in Water (National Institute of Standards and Technology, Gaithersburg, MD, USA) using ETAAS.

## EXPERIMENTAL

### Instrumentation

The concentrations of Cd, Bi, Hg, and Tl in dissolved mixed micelle-rich phases were determined by using continuum source ETAAS (Contra AA 700, Analytik Jena AG, Jena, Germany). Also used were a transversely heated graphite tube, MPE 60 auto-sampler and a Xenon short arc lamp in hot spot mode operated at 300W as the continuum

radiation source. A high resolution double monochromator consisting of a prism and an Echelle grating monochromator with a spectral bandwidth per pixel of ca. 2 pm at 200 nm was used. A linear charge coupled device (CCD) array detector was used for measuring the integrated absorbance of Cd, Bi, Hg, and Tl at the 228.8018, 223.1608, 253.6519, and 276.7860 nm lines, respectively. Argon with a purity of 99.99% was used as the purge gas. The optimized temperature program and the operating instrumental parameters for the determination of Cd, Hg, Bi, and Tl in the mixed micelle-rich phase are listed in Table I.

### Reagents and Standard Solutions

Ultrapure water obtained from a Milli-Q® water purification system (Millipore Corporation, Bedford, MA, USA) was used to prepare all solutions. Sub-boiled HNO<sub>3</sub> and HCl (Merck, Darmstadt, Germany) were

**TABLE I**  
**Optimized Temperature Program and Operating Instrumental Parameters Used for the Determination of Cd, Hg, Bi, and Tl in the Mixed Micelle-rich Phase After Mixed Micelle Cloud Point Extraction Using CS-ETAAS With Ir as Permanent Chemical Modifier**

Elements	Wavelength (nm)	Lamp Current (A)	Power (W)	
Cd	228.8018	15	300	
Hg	253.6519	13	300	
Bi	223.1608	15	300	
Tl	276.7860	13	300	
Steps	Temperature (°C)	Ramp (°C s <sup>-1</sup> )	Hold (s)	Ar flow (mL min <sup>-1</sup> )
Drying-1	80	6	20	250
Drying-2	90	3	20	250
Drying-3	110	5	10	250
Pyrolysis	400 (Hg), 800 (Tl&Cd) and 1000 (Bi)	300	10	250
Gas Adaption	400 (Hg), 800 (Tl&Cd) and 1000 (Bi)	0	5	250
Atomization	1000 (Hg), 2000 (Tl& Cd) and 2200 (Bi)	1000	3	0 (read)
Cleaning	2300	500	3	250

prepared using quartz stills kept inside the clean bench. Analytical grade sulfuric acid (Merck, Darmstadt, Germany) was used without any further purification. Stock standard solutions of Cd, Hg, Bi, and Tl at 1 mg mL<sup>-1</sup> were prepared by dissolving 99.9% pure metals in the appropriate acids. Working standards were prepared daily by subsequent dilutions. The non-ionic surfactant Triton<sup>®</sup> X-114 (0.011% CMC, Fluka, Switzerland) and cationic surfactant CPAB (0.026% CMC, Sigma-Aldrich, Steinheim, Germany) were used to prepare the 10% (w/v) solution in ultrapure water. Potassium iodide, 10% (w/v) solution, was prepared by dissolving the appropriate amount in ultrapure water. Iridium solution of 0.1 mg mL<sup>-1</sup> was prepared by dissolving the appropriate amount of ammonium hexachloroiridate in 10 mL of 10% (v/v) HCl. The analytes used for the interference study such as Na, Ca, Mg, Cu, Ni, Pb, Cd, F, and phosphate at 1 mg mL<sup>-1</sup> were prepared by dissolving the appropriate amounts of their respective salts in ultrapure water. Groundwater and petrochemical industrial effluents were collected locally in pre-cleaned polypropylene containers with screw caps, then filtered through a 0.45- $\mu$ m filter, and used without further sample preparation. All containers, vials, and micropipette tips (Tarson, Mumbai, India) were cleaned by soaking in 10% (v/v) sub-boiled nitric acid for 24 hours at 60 °C, then washed with ultrapure water, and the procedure repeated using 10% (v/v) HCl. All sample preparations were carried out in a class 10 clean bench located in a class 100 clean laboratory.

### Iridium Coating

The Ir permanent coating (20  $\mu$ g) on the integrated platform of a transversely heated graphite tube was performed by injecting 50  $\mu$ L

of 0.1 mg mL<sup>-1</sup> Ir solution four times while the tube was heated stepwise to higher temperatures (1000 °C) for conversion of the iridium oxides to metal.

### Mixed Micelle Cloud Point Extraction Procedure

Aliquots of 1–5 mL of sample solutions and certified reference materials were transferred into pre-cleaned 15-mL polypropylene centrifuge tubes. To these solutions, 0.5 mL sulfuric acid, 0.5 mL of 10% (w/v) CPAB, 0.4 mL of 10% (w/v) KI, and 2 mL of 10% (w/v) Triton X-114 were added. These solutions were diluted to 10 mL using ultrapure water and then heated at 90 °C for 20 minutes. Gravitational phase separation was observed during heating and completed by cooling the solution for 10 minutes in an ice bath, then the supernatant phases were decanted. The viscosity of the 0.3-mL mixed micelle-rich phases was reduced by dissolving in 0.2 mL of methanol containing 5% (v/v) nitric acid and analysis of Cd, Hg, Bi, and Tl by ETAAS. Procedural blanks were also prepared in a similar manner.

## RESULTS AND DISCUSSION

### Clouding Phenomenon in CPAB/Triton X-114 Micelle-Micelle Interacting System

Clouding and phase separation will not be observed normally in cationic micelles and mixed micelles formed by micelle-micelle interaction of cationic and non-ionic micelles on heating due to strong electrostatic repulsions between the charged head groups. Therefore, the cloud point temperature (CPT) of the cationic mixed surfactant CPAB/Triton X-114 was studied by varying the CPAB and acid (HCl and H<sub>2</sub>SO<sub>4</sub>) concentration in the range of 0–0.6% (w/v) and 0–5% (v/v), respectively, with and without KI (0.4% w/v) in the presence of 2% (w/v) Triton X-114. The results are shown in Figure 1. Without any additives, the CPT of CPAB increased with an increase in the CPAB concentration. This increment was slow up to the critical micelle concentration (CMC, 0.026 w/v %) of CPAB and a steeper rise was observed immediately above the CMC, and reached 95 °C at 0.1% CPAB (not shown in the figure). Below the CMC, the cationic monomers formed mixed micelles with the Triton X-114 micelles and have

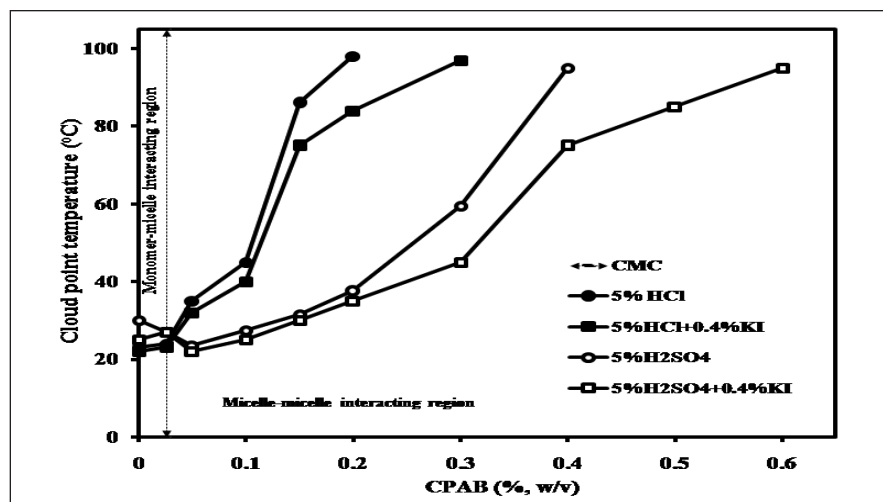


Fig. 1. The effect of HCl and H<sub>2</sub>SO<sub>4</sub> on the cloud point temperature of CPAB in the presence of 2% Triton X-100.



weak electrostatic repulsions, but above the CMC, the cationic micelles formed mixed micelles and showed strong electrostatic repulsions between and within the mixed micelles, which caused a steeper rise in the CPT of CPAB. Therefore, it is difficult to achieve clouding and phase separation above 0.1% CPAB. As shown in this figure, the presence of acid additives such as HCl and H<sub>2</sub>SO<sub>4</sub> creates an anionic micro environment by the Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> groups around the cationic head group of micelles and mixed micelles. Depending on the extent of neutralization of the head group charge by these anions, clouding and phase separation even above 0.1% CPAB is possible. Hence, the CPT at 98 and 95 °C was achieved for HCl and H<sub>2</sub>SO<sub>4</sub> at 0.2% and 0.4% CPAB concentration, respectively. Clouding and phase separation was observed at CPT 95 °C by using high concentrations of CPAB (0.6%) in combination with these acids and 0.2–0.4% (w/v) KI, and in the presence of 2% Triton X-114 which formed micelle-micelle based mixed micelles. These enhanced cationic head group reactive sites were used for the extraction of the anionic inorganic species.

#### Optimization of Cationic Mixed Micelle Cloud Point Extraction Parameters

Based on the hard and soft acids and bases (HSAB) concept, soft metals form stable anionic species with soft halide ions. This property is used in the present procedure for the simultaneous extraction of the anionic Cd, Hg, Bi, and Tl iodide species formed in the presence of sulfuric acid and potassium iodide and using the enhanced cationic head group reactive sites of mixed micelles obtained from the micelle-micelle interaction of CPAB and Triton X-114. Therefore, the parameters affecting the extraction process were studied and opti-

mized by using 0.02, 10, 2, and 1 ng mL<sup>-1</sup> of Cd, Hg, Bi, and Tl spiked simultaneously to petrochemical effluents and groundwater samples.

#### Effect of Acids

Sulfuric acid plays a very crucial role in the formation of a clouding and phase separation in CPAB/Triton X-114 mixed micelles in the presence of KI. As discussed above (Figure 1), for HCl with 0.4% (w/v) KI no phase separation was observed in the presence of 0.4% (w/v) CPAB. Hence, the effect of sulfuric acid on the recoveries of Cd, Hg, Bi, and Tl were studied in the range of 0–10% (v/v) in the presence of 0.5% (w/v) CPAB and 2% (w/v) Triton X-114 with and without 0.4% (m/v) KI in groundwater. The results in Figure 2 show that without KI, the recoveries were within the range of 50–60% even at 10% H<sub>2</sub>SO<sub>4</sub>. It indicates that H<sub>2</sub>SO<sub>4</sub> alone is insufficient to extract Cd, Hg, Bi, and Tl quantitatively. With KI, the recoveries were increased by increasing the acid concentration of H<sub>2</sub>SO<sub>4</sub> up to 4%, and then reached the plateau region with 94–102% up to the studied concentration of H<sub>2</sub>SO<sub>4</sub>. Therefore, 5% (v/v) H<sub>2</sub>SO<sub>4</sub> was selected for further studied.

Optimization of the KI concentration is required for the formation and simultaneous extraction of the Cd, Hg, Bi, and Tl iodide species into the cationic mixed micelles surfactant-rich phase, especially for real samples. Therefore, the effects of KI concentrations on the recovery of Cd, Hg, Bi, and Tl from groundwater and effluent samples were evaluated carefully in the range of 0–0.5% (m/v). The recoveries were near quantitative (92–100%) in the petroleum effluent and groundwater samples with 0.4% and 0.2% KI concentration, respectively. These different behaviors may be due to the differences in the metal ion competition for KI. Further increases in the concentra-

tion of KI did not affect the recoveries. Hence, to ensure quantitative recovery in petroleum effluent and groundwater samples, an optimum concentration of 0.4% (w/v) KI was selected for further work

#### Effect of Surfactants

In this extraction, the cationic head group solubilizing site of mixed micelles plays an important role; hence, the recovery of Cd, Hg, Bi, and Tl was studied in the concentration range of 0–0.6% (w/v) CPAB in the presence of 5% (v/v) H<sub>2</sub>SO<sub>4</sub>, 0.4% (w/v) KI, and 2% (w/v) Triton X-114. The results in Figure 3 indicate that without CPAB only non-ionic micelles are responsible for the extraction of the hydrophilic anionic species of Cd, Hg, Bi, and Tl with qualitative recoveries between 20–40% (no chelating agents). With the addition of CPAB up to the critical micelles concentration (CMC 0.025%), the monomers responsible for the formation of monomer-micelle mixed micelles showed a reduction in recoveries of 10–30%. Above the CMC, the recoveries increased with an increase in the concentration of CPAB to above 0.4% and reached plateau with 95–102% recoveries. The lower recoveries at 0% CPAB are mainly due to the lack of any electrostatic interacting sites in the extracting non-ionic Triton X-114 micelles. Below CMC, lower recoveries may be due to an increase in the hydrophilic character of the metal iodide species in the presence of cationic monomers. Quantitative recoveries were obtained only with mixed micelles formed by the interaction of cationic CPAB micelles with non-ionic Triton X-114 micelles. Hence, a concentration of 0.5% (w/v) CPAB in the plateau region was selected for further studies.

The variations in the Cd, Hg, Bi, and Tl recoveries with Triton X-114 in the 0–3% (w/v) range at 0.5% (w/v) CPAB were also studied. Without Triton X-114, only cationic

micelles were present in the solution, which shows no clouding and phase separation because of the strong electrostatic repulsion between the charged head groups. For achieving clear cloud point phase separation, a minimum of 1.5% Triton X-114 was required in the presence of 0.5% CPAB. At 2% Triton X-114, Cd, Hg, Bi, and Tl showed recoveries at 98, 96, 99, and 100%. These recoveries were stable up to the studied concentration of 3% Triton X-114. Hence, 2% (w/v) Triton X-114 was selected.

### Effect of Extraction Temperature and Time

Optimization of extraction temperature and time is necessary to study the reactivity of KI with metal ions and its stability, and their effective simultaneous transfer and pre-concentration into the mixed micelle-rich phase. The selected extraction temperature must be higher than the cloud point temperature of the clouding solution. The clouding temperature of the solution under optimized conditions was found to be 85 °C (Figure 1). Hence, the effect of

extraction temperature on the recovery of Cd, Hg, Bi, and Tl was studied in the range of 75–95 °C using a 20-minute extraction time. The results showed that the recoveries of Cd, Hg, Bi, and Tl were between 95–102% in the temperature range between 90–95 °C. Hence, a temperature of 90 °C was selected for further studies.

The optimization of extraction time was carried out in the range of 20 to 60 minutes. These results showed that quantitative recoveries of the studied analytes were in the range between 96–101%. Therefore, a 20-minute extraction time was selected. The amount of surfactants, incubation temperature, and time decides the pre-concentration factor (PCF) and phase volume ratio (PVR). The PCF is the ratio of the analyte concentration in the micelle-rich phase to that of the initial aqueous phase, and PVR is the ratio of the final volume of the micelle-rich phase to that of the aqueous phase. Under these conditions, the PCF and PVR were found to be 20 and 0.05, respectively.

### Interference Studies

In order to evaluate the performance of this procedure for various natural environmental matrices, the highest tolerability of common interfering ions was studied. These include the anionic species that may interact with cationic solubilizing sites and cationic species that may react with iodide species. The highest tolerance limits were studied in the effluent by keeping the relative error between  $\pm 5\%$  and were found to be 2 g L<sup>-1</sup> of Na<sup>+</sup>; 800 mg L<sup>-1</sup> of Ca<sup>2+</sup> and Mg<sup>2+</sup>; 200 mg L<sup>-1</sup> of Cu<sup>2+</sup> and Ni<sup>2+</sup>; 10 mg L<sup>-1</sup> of Pb<sup>2+</sup> and Cd<sup>2+</sup>; and 2 mg L<sup>-1</sup> of F<sup>-</sup>; and 1 mg L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup>. These results demonstrate the selectivity of the procedure.

### Optimization of Furnace Temperature Program

The effect of pyrolysis temperature on the integrated absorbance signals of Cd, Hg, Bi, and Tl was studied using Ir (20 µg) coated and pyrocoated standard tubes. The results indicated that the Ir-coated tubes stabilize Cd, Hg, Bi, and Tl up to 800, 400, 1000, and 800 °C,

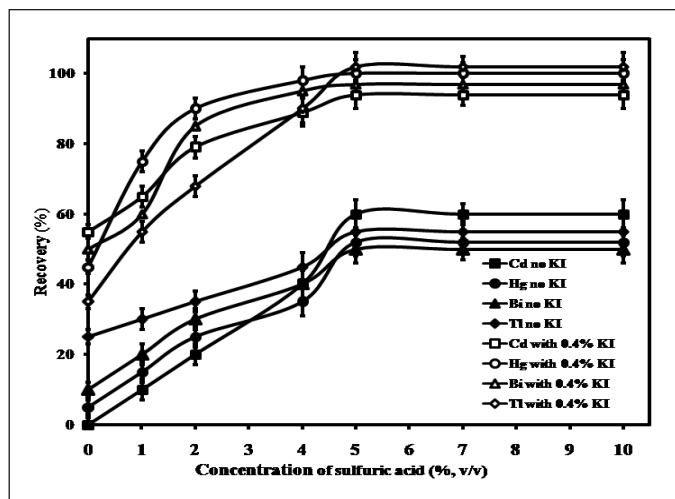


Fig. 2. Effect sulfuric acid on the recovery of Cd, Hg, Bi and Tl using cationic mixed micelle CPE in presence of 0.5% w/v CPAB and 2% w/v Triton X-114 with and without KI (0.4% w/v). The error bars indicate the standard deviation at each measurement (n=4).

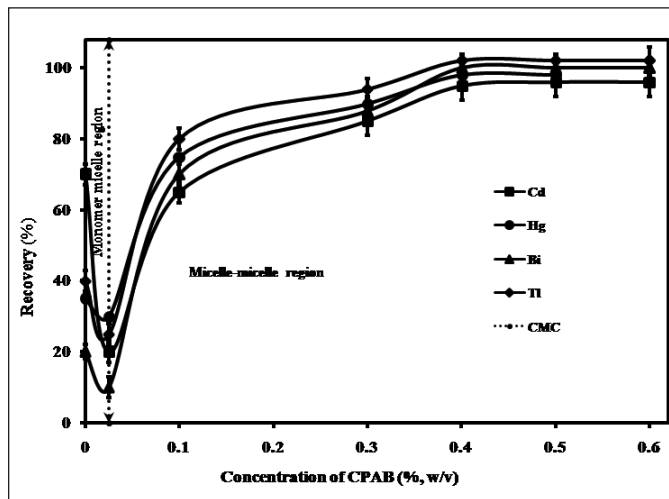


Fig. 3. Effect of CPAB concentration on the recoveries of Cd, Hg, Bi and Tl in presence of 5% (v/v) H<sub>2</sub>SO<sub>4</sub>, 0.4% (w/v) KI and 2% (w/v) Triton X-114, and heated at 90 °C. The error bars indicate the standard deviation at each measurements (n=4).

respectively, in the surfactant-rich phase. These temperatures are 200 to 300 °C higher than for pyro-coated tubes. The use of a high pyrolysis temperature lowers the background absorbance signals and increases the sensitivities by 20–30%. Therefore, Ir-coated tubes were used throughout this study.

### Analytical Figures of Merit

Under the optimized conditions, the linear dynamic ranges of the calibration curves were obtained by pre-concentrating the successively spiked four aqueous standards of Cd, Hg, Bi, and Tl in the range of 0.01–0.3, 1–20, 1–15, and 0.2–4 ng mL<sup>-1</sup>, respectively. The correlating coefficients were in between 0.9954 to 0.9975. Quantification was performed using aqueous standards prepared in 0.2% HNO<sub>3</sub>. The limits of detection (LODs), calculated based on three times the standard deviation of 10 measurements of the procedural blanks of Cd, Hg, Bi, and Tl, were 0.0005, 0.2, 0.04, and 0.05 ng mL<sup>-1</sup>, respectively. A comparison

of the proposed procedure with the recently published micelle and mixed micelles cloud point extraction procedures is given in Table II. In the present procedure, the enhanced head group solubilizing sites of the mixed micelles formed by micelle-micelle interaction of CPAB and Triton X-114 for the quantitative extraction of Cd, Hg, Bi, and Tl resulted in better LODs compared to the reported procedures. The synergetic effect of potassium iodide and sulfuric acid along with the dehydration step provides the clouding and phase separation in the micelle-micelle interacting system and avoids the addition of chelating agents.

### Validation of the Procedure and Analysis of Real Samples

Recovery studies of Cd, Hg, Bi, and Tl were performed by spiking the analytes in the range of 0.1 to 10 ng mL<sup>-1</sup> into petroleum effluent, domestic effluent, and groundwater samples. The recoveries listed in Table III were between 93 and

102% in all studied matrices, with a relative standard deviation between 2 and 10%. These results indicate that the studied matrices have no significant effect on the proposed extraction procedure.

The accuracy of the proposed procedure was validated by analyzing the certified reference materials BCR 714 Initial Influent, BCR 715 Industrial Effluent, BCR 610 Groundwater and NIST 1643e, 1643f and 1642b Trac Elements in Water. The results in Table IV show good agreement with the certified values based on the Student's *t*-test at the 95% confidence level. The values obtained by the present procedure in the certified reference materials were also compared with the results obtained by a reported conventional cloud point extraction procedure using chelating agents (17–20). This result also shows that there is good agreement for both procedures. The proposed procedure was also applied to real petrochemical effluents and groundwater samples. The values of Hg and Tl in

**TABLE II**  
**Comparison of Proposed Ligandless Mixed Micelle Cloud Point Extraction With Other Reported Cloud Point Extraction Procedures**

Preconcentration/ Analytical Method	Chelating Agent/ Surfactant Aggregates	Clouding Concept	LOD (ng mL <sup>-1</sup> )	Ref.
CPE-HG-ICP-OES	<sup>a</sup> DDTP+KI / Triton X-114 micelles	Heating	As (0.055), Bi( 0.057), Cd (0.047), Pb (0.28)	(17)
CPE-FAAS	<sup>b</sup> MG + KI/Triton X-114 micelles	Heating	Cd (0.9)	(18)
MM-CPE-ICP-OES	Alizarin red S / CTAB + Triton X-114 monomer-micelle	Salt+Heating	Ti (0.1)	(11)
MM-CPE-FAAS	Pyridylazo resorcinol / <sup>c</sup> BDMHDAC + Triton X-114 monomer-micelle	Salt+Heating	Pb (1.15)	(12)
MM-CPE-ICP-OES	Alizarin red S / CTAB + Triton X-114 monomer-micelle	Salt+Heating	<sup>d</sup> REE	(13)
MM-CPE-ETAAS	Diphenyle carbazid + HCl / <sup>e</sup> SDS + Triton X-114 monomers-micelles	Acid+Heating	Cr(VI) <sup>f</sup>	(14)
MM-CPE-ETAAS	No chelating agent / CPAB + Triton X-114 micelles-micelles	Salt+ Acid+ Heating	Cd( 0.0005) Hg (0.2), Bi (0.04), Tl (0.05)	Present Method

<sup>a</sup> = Diethyldithiophosphate, <sup>b</sup> = Methyl green, <sup>c</sup> = Benzyltrimethylhexadecylammonium chloride, <sup>d</sup> = Rare earth elements, <sup>e</sup> = Sodium dodecyl sulfate, <sup>f</sup> = Speciation.

**TABLE III**  
**Recovery of Cd, Hg, Bi, and Tl in Various Real Petrochemical Effluents and Groundwater Samples**  
**Using the Proposed Procedure**

Matrices	Spiked (ng mL <sup>-1</sup> )				Found <sup>a</sup> (ng mL <sup>-1</sup> ) (Recovery %) <sup>b</sup>			
	Cd	Hg	Bi	Tl	Cd	Hg	Bi	Tl
Petrochemical Effluent-1	-	-	-	-	0.556±0.002	4.0±0.2	2.2±0.1	4.6±0.1
	0.1	5	2	3	0.095±0.006 (95±6)	5.1±0.3 (102±6)	1.9±0.2 (95±10)	2.8±0.2 (93±7)
Petrochemical Effluent-2	-	-	-	-	0.325±0.005	7.5±0.4	2.4±0.2	4.5±0.2
	0.1	10	4	6	0.099±0.004 (99±4)	9.7±0.3 (97±3)	3.8±0.3 (95±8)	5.9±0.3 (98±5)
Petrochemical Effluent-3	-	-	-	-	0.123±0.003	4.5±0.2	4.2±0.2	1.2±0.1
	0.2	5	4	3	0.205±0.004 (102±2)	4.8±0.4 (96±8)	3.9±0.3 (98±8)	2.9±0.2 (97±7)
Groundwater	-	-	-	-	0.085±0.004	2.6±0.2	0.6±0.1	1.5±0.1
	0.1	2	2	3	0.093±0.006 (93±6)	1.9±0.1 (95±5)	1.9±0.1 (95±5)	3.0±0.2 (100±7)

<sup>a</sup> = Mean of four determinations ± standard deviation.

<sup>b</sup> = Parentheses indicate the recovery.

**TABLE IV**  
**Analytical Results for the Determination of Cd, Hg, Bi and Tl in Certified Reference Materials**  
**Using the Proposed Procedure**

CRMs	Analytes	Measured Values/ng mL <sup>-1</sup> (mean ± <sup>a</sup> ts(n) <sup>-1/2</sup> )		
		Proposed MM-CPE	Reported CPE <sup>b</sup>	Certified Values (ng mL <sup>-1</sup> )
BCR 714 Initial Influent	Cd	20.5 ± 0.8	21.2 ± 0.9	19.9 ± 1.6
BCR 715 Industrial Effluent	Cd	41.8 ± 1.2	42.5 ± 1.4	40 ± 5
BCR 610 Groundwater	Cd	3.0 ± 0.1	3.0 ± 0.2	2.94 ± 0.16
NIST 1643e Water	Bi	14.1 ± 0.1	14.2 ± 0.2	14.09 ± 0.15
	Tl	7.4 ± 0.1	7.5 ± 0.2	7.444 ± 0.096
NIST 1643f Water	Cd	6.0 ± 0.1	6.0 ± 0.2	5.89 ± 0.13
	Bi	12.6 ± 0.1	12.7 ± 0.2	12.62 ± 0.11
	Tl	6.8 ± 0.1	6.9 ± 0.2	6.892 ± 0.035
NIST 1642b Water	Hg	1.5 ± 0.1	1.5 ± 0.2	1.49 ± 0.06

<sup>a</sup> =  $t_{0.95} = 3.18$ ,  $n = 4$ ,  $s$ =Standard deviation.

<sup>b</sup> = Values are obtained from cloud point extraction method ref. (17-20).

these samples are above the U.S. EPA and IS10500 specifications, which indicates anthropogenic contamination of nearby groundwater with petrochemical effluents (21, 22).

#### CONCLUSION

A simple new salt- and acid-induced ligandless mixed micelle cloud point extraction procedure is described for the simultaneous pre-

concentration of hydrophilic Cd, Hg, Bi, and Tl species from petrochemical effluents and groundwater samples. In this study, the synergetic properties of additives and mixed micelles formed by



micelle-micelle interactions of ionic and nonionic surfactants for the pre-concentration of toxic trace analytes were used. It was found that potassium iodide and sulfuric acid not only converts the analytes into their corresponding iodides, but they also act as salting out agents, reduce the cloud point temperature, and provide phase separation. The mixed micelles acts as an extracting agent and avoid the addition of an external chelating agent which otherwise is routinely used in conventional cloud point extraction. The developed procedure will be useful in monitoring these species in petrochemical effluents and groundwater samples on a regular basis.

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