Talanta 104 (2013) 180–186

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Microwave assisted aqua regia extraction of thallium from sediment and coal fly ash samples and interference free determination by continuum source ETAAS after cloud point extraction

Noorbasha N. Meeravali, K. Madhavi, Sunil Jai Kumar*

National Center for Compositional Characterization of Materials, Bhabha Atomic Research Centre, ECIL Post, Hyderabad 500 062, India

ARTICLE INFO

Article history:
Received 4 September 2012
Received in revised form
31 October 2012
Accepted 1 November 2012
Available online 10 November 2012

Keywords:
Thallium
Aqua regia extracts
Marine sediments and coal fly ash
Cloud point extraction
CS-ETAAS

ABSTRACT

A simple cloud point extraction method is described for the separation and pre-concentration of thallium from the microwave assisted aqua regia extracts of sediment and coal fly ash samples. The method is based on the formation of extractable species of thallium and its interaction with hydrophobic solubilizing sites of Triton X-114 micelles in the presence of aqua regia and electrolyte NaCl. These interactions of micelles are used for extraction of thallium from a bulk aqueous phase into a small micelles-rich phase. The potential chloride interferences are eliminated effectively, which enabled interference free determination of thallium from aqua regia extracts using continuum source ETAAS. The parameters affecting the extraction process are optimized. Under the optimized conditions, pre-concentration factor and limit of detection are 40 and 0.2 ng g^{-1}, respectively. The recoveries are in the range of 95–102%. A characteristic mass, 13 pg was obtained. The accuracy of the method is verified by analyzing certified reference materials such as NIST 1633b coal fly ash, NIST 1944 marine sediment and GBW 07312 stream sediments. The results obtained are in good agreement with the certified values and method is also applied to real samples.

1. Introduction

Thallium is attracting more attention recently due to their intoxication to living organisms that affect the central nervous system [1,2]. Its toxicity to mammals is higher than that of Hg, Cd and Pb and is named as poisoners' poison [3]. The natural levels of thallium in lake sediment, marine sediment and coal fly ash samples are in the range of 2.1–23.1, 0.08–5 and 1–2 μg g^{-1}, respectively [4–6]. But, these levels are increasing in the environment due to anthropogenic activities such as production of cement, mining of sulfide ores and burning of coal, which is a major concern. Owing to its high toxicity and elevation of its levels in the environment, periodic monitoring of thallium is very important.

Accurate determination of thallium in chloride rich marine matrices is a difficult task, even after using a versatile technique like ETAAS [7–9]. This is mainly due to low levels of thallium and high levels of interfering species present in these matrices. Major problems in determination of thallium by ETAAS are the spectral interferences due to iron and sulfate and also the non-spectral interferences due to high levels of chloride present in the marine matrices [8–15]. In the presence of chloride, thallium forms volatile and thermally stable TlCl (g) with a high dissociation energy of 88 kcal mol^{-1}, which is lost from the furnace before atomization. For reducing this non-spectral interference, various modifiers such as reduced palladium and lithium, and combination of palladium or ruthenium permanent chemical modifier with ammonium nitrate have been used [9]. But, all these modifiers are unable to remove this interference completely, especially chloride rich matrices [14,16]. Therefore, there is a need to develop a method that is free from spectral as well as non spectral interferences for accurate determination of thallium, especially in aqua regia extracts of geological matrices. Though the use of continuum source ETAAS (CS-ETAAS) can eliminate the spectral interferences effectively, but it is unable to reduce the non-spectral interferences [17] for which, matrix separation methods like liquid–liquid and solid phase extractions have been applied to various water samples [18,19]. These methods use chelating agents which form hydrophobic complexes with thallium that works mostly in the pH range, hence, cannot be applied to aqua regia extracts.

Cloud point extraction (CPE) is an efficient and environmental friendly separation and pre-concentration technique [20,21]. It extracts the species based on the hydrophobicity of both the extracting species and surfactants used in the process. But, these do have some limitations like poor extraction efficiency for

---

* Corresponding author. Fax: +91 40 27125463.
E-mail address: suniljaikumar@rediffmail.com (S.J. Kumar).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.11.002

hydrophilic ionic species [21]. Over the last three decades, only few CPE methods are reported for thallium. Xiao et al. [22] and Jiang et al. [23,24] used micelles and also mixed-micelles for the extraction of thallium from different types of waters under basic and acidic conditions, respectively. To the best of our knowledge, there are no reports on extraction of thallium from aqua regia extracts of marine sediment and coal fly ash matrices using cloud point extraction and elimination of the interferences on thallium in the ETAAS determination.

In the present paper, we describe a simple cloud point extraction method for the determination of thallium in sediment and coal fly ash matrices. This method enables simultaneous separation and pre-concentration of thallium from the aqua regia extracts in one step. The principle of the method is that thallium forms extractable chloro nitro species in presence of aqua regia. The Triton X-114 micelles have been used to pre-concentrate thallium species from the bulk aqueous phase into a small micelles-rich phase in the presence of an electrolyte NaCl. The factors affecting the extraction efficiencies are evaluated meticulously. The tolerances limits of interfering ions are also studied carefully using CS-ETAAS. The accuracy is verified by analyzing certified reference materials such as NIST 1633b coal fly ash, NIST 1944 marine sediment and GBW CRM 07312 stream sediments.

2. Experimental

2.1. Instrumentation

Thallium concentrations in the dissolved micelles-rich phases were determined by using CS-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 a continuum radiation source were used. A high resolution double monochromator consisting of a prism and an echelle grating monochromator, providing a spectral bandwidth per pixel of ca. 2 pm at 200 nm was used. A linear charge coupled device array detector of total 588 pixels, of which 200 pixels were used for the determination of dispersed radiation. The thallium absorption was measured using the central pixel (CP) ± 1 pixels i.e., over a spectral interval of approximately 6 pm. Argon with a purity of 99.99% was used as the purge gas in all stages, except during atomization step. A spectral line at 276.7870 nm was used. The optimized temperature program used for the determination of thallium is given in Table 1. All samples were digested using a MARS (CEM, Matthews, NC, USA) microwave oven and PTFE vessels.

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 HCl and HNO_3 (Merck, Darmstadt, Germany) were prepared in our laboratory using quartz stills, and HF (Merck, Darmstadt, Germany) was used. The solutions of 10 m/v% Triton X-114 (Sigma–Aldrich, Steinheim, Germany) and 30 m/v% NaCl were prepared by dissolving appropriate amounts in Milli-Q water. Thallium calibration solutions in the range of 0.5–5 ng mL^{-1} were prepared from its stock standard of 1 mg mL^{-1} (Merck, Darmstadt, Germany). The 1 mg mL^{-1} Pd solution in 2 v/v% HNO_3 prepared from the 10 mg mL^{-1} stock (Sigma–Aldrich, Steinheim, Germany) was used as a modifier. Methanol was used for dissolving micelles-rich phases. Stock solutions (1 mg mL^{-1}) of Mg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, F^-, PO_4^{3-} and SO_4^{2-} were used for interference study. All the sample preparations were carried out in a class 10 clean bench located in the class 100 clean laboratory. The lake sediment and coal fly ash samples were collected from Hyderabad Hussain sager lake and Vijayawada thermal power plant.

Table 1
Optimized temperature program used for the determination of thallium in the micelles-rich phase after cloud point extraction using CS-ETAAS.

Step	Temperature/°C	Ramp/°C s^{-1}	Hold/s	Ar flow/mL min^{-1}
Drying-1	80	6	20	250
Drying-2	90	3	20	250
Drying-3	110	5	10	250
Pyrolysis	800	300	10	250
Gas adaption	800	0	5	250
Atomization	2000	1000	4	0 (read)
Cleaning	2200	500	3	250

2.3. Microwave assisted aqua regia extraction of thallium

Samples and reference materials were accurately weighted in the range 200–300 mg and transferred into high pressure vessels of microwave digestion system. To this 4 mL aqua regia (1 mL HNO_3 and 3 mL HCl) was added. These vessels were closed and heated in the microwave cavity using three step optimized microwave program: 100, 150 and 200 °C for 5, 6 and 10 min, respectively, at 600 W power and 800 psi pressure. All these vessels were cooled to room temperature and opened carefully inside the fume hood. The digests were made up to 5 mL using Milli-Q water. Procedural blanks were prepared in a similar manner.

2.4. Cloud point extraction method

Aliquots of 0.1–1 mL extracts were taken in poly propylene centrifuge tubes and appropriately diluted by Milli-Q water so that the concentration of aqua regia was around 20 v/v%. To these solutions, 1 mL of 30 m/v% NaCl and 1 mL of 10 m/v% Triton X-114 were added and made up to 10 mL using Milli-Q water and heated to 90°C for 20 min after which gravitational phase separation was obtained. The ~0.1 mL micelles-rich phase was separated by decanting the bulk aqueous phase, after cooling the solution in a refrigerator for 10 min. The viscosity of the micelles-rich phase was reduced by dissolving in 0.15 mL methanol containing 0.05 mL HNO_3. It was then analyzed for thallium using CS-ETAAS by using aliquots of 15 μL along with 5 μL of palladium modifier. Process blank was also prepared and analyzed in a similar manner.

3. Results and discussion

3.1. Selection of the microwave assisted extraction procedure

Thallium forms volatile $TlCl_3$ (37 °C MP and 100 °C BP) and $Tl(NO_3)_3$ (100 °C MP and 83 °C BP), respectively, with HCl and HNO_3. Hence, selection of an efficient sample decomposition procedure is necessary to prevent the loss of thallium. Two extraction procedures one using nitric acid and hydrofluoric acid and other aqua regia were used in a closed microwave digestion system. An evaporation step was necessary to remove excess HF as well as aqua regia. But this resulted in recovery of only 35–50% indicating loss of Tl. Therefore, sample extracts of aqua regia was diluted to avoid evaporation step and a recovery of 94% was obtained. However, HF being hazardous even after dilution, it cannot be used. So microwave assisted aqua regia extraction procedure was selected for this work and NIST 1633b coal fly ash was used for these studies.

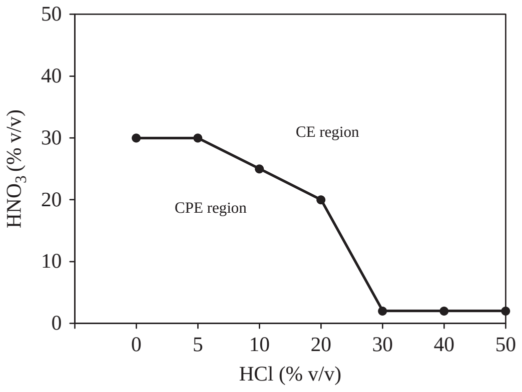

Fig. 1. Phase separation behavior of 1 m/v% Triton X-114, in the presence of 3 m/v% NaCl, with HCl and HNO_3 additives at 80 °C for 1 h.

3.2. *Effect of additives on the clouding temperature and phase behavior of Triton X-114*

The properties of surfactants can be varied by using additives such as electrolytes and acids [25]. Hence, the phase separation behavior and clouding temperature of Triton X-114 were studied with various additives, such as HCl, HNO_3 and NaCl and their mixtures. Fig. 1 shows the phase separation behavior of 1 m/v% Triton X-114 using HCl and HNO_3 with concentrations varied independently and in combination in the range of 0–50 v/v%, in the presence of 3 m/v% NaCl. As shown in Fig. 1, two different regions were observed with a clear phase boundary. They are formed by ionic species induced coacervate extraction (CE) and cloud point extraction (CPE) regions, which indicates the characteristic behavior of ionic and non-ionic surfactants, respectively. The area of each region depends on the concentration of additives. The area of CPE region was in the range of 0–30% HCl and 0–30% HNO_3. Beyond 30% of either of the acids, the CPE region decreased with simultaneous increase of the CE region. When mixed acids were used (in the range 5 and 20% either acids) the CPE region was found to reduce as shown in Fig. 1. This behavior is mainly due to the increase in the ionic characteristics due to additives (Cl^- and NO_3^-) around the polar head group of non-ionic micelles [26]. With increase in concentration of acids, this characteristic behavior increases, which prevent the micelles aggregation. The CPE region was wide enough for analytical purpose, used in this study.

The clouding temperature (CT) of surfactants varies with the additives [27]. Hence, the variation of CT of 1 m/v% Triton X-114 was studied by varying the HCl and HNO_3 concentration in the range of 0–50 v/v% in the presence of 3 m/v% NaCl. The results are shown in Fig. 2(a). As shown in Fig. 2(a), using HCl alone, the CT of Triton X-114 increased with increase in the concentration of HCl from 1 to 50% and reached a maximum of 100 °C at 50% HCl concentration. In the case of only HNO_3, this trend is quite different; CT of Triton X-114 was approximately constant with increase in the HNO_3 concentration up to 20% and then decreased with further increase in the HNO_3 up to 50% and reached a minimum of 3 °C at 50% HNO_3. This trend is possibly due the difference in the behavior of chloride and nitrate ions in the microenvironment around the micelles head groups.

The combined effect of the mixed acids such as aqua regia and NaCl on the CT of Triton X-114 was also studied by varying their concentrations in the range of 1–50 v/v% and 0–10 m/v%, respectively, and results are shown in Fig. 2(b). As shown in Fig. 2(b), without NaCl, the CT of Triton X-114, increased linearly from 23 to 48 °C with increase in the aqua regia concentration from 1 to 30%. Further increase in the concentration of aqua regia even up to 50% did not result any change in the CT. The addition of NaCl was found to decrease the CT gradually in the studied range from 23 to 10 °C and 48 to 21 °C, respectively, for 1–50% aqua regia concentrations.

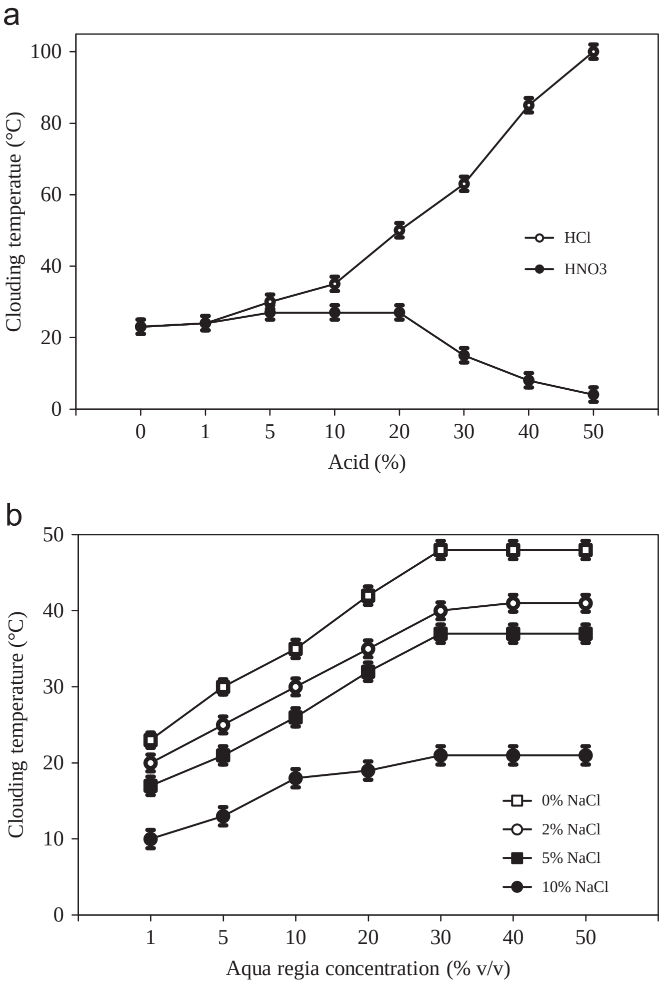

Fig. 2. Variation of clouding temperature (CT) of 1 m/v% Triton X-114 with (a) acids (HCl and HNO_3) in the presence of 3 m/v% NaCl and (b) aqua regia with NaCl.

3.3. *Optimization of cloud point extraction parameters*

It is well documented that the determination of thallium by ETAAS was significantly influenced by the concentration of chloride present in the matrices as well as in digested acid mixture [11]. The determination of thallium in dilute aqua regia extracts of NIST-1633b CFA was carried out using modifier in CS-ETAAS and results are shown in Fig. 3(a). These results showed that the signals corresponding to thallium at 276.7860 nm and secondary line of iron which is 34 pm away from this are well resolved and there is no signal corresponding to thallium due to loss of thallium as chloride. It indicated that it is possible to overcome the spectral interferences of iron using CS-ETAAS and impossible even to alleviate the non-spectral chloride interferences even in dilute aqua regia. To overcome this interference, preliminary experiments were carried out by using cloud point extraction method and results are shown in Fig. 3(b). From this figure it is seen that the signal of iron is completely absent as it was not extracted and a prominent thallium absorption profile could be seen due to pre-concentration and removal of chloride based interference. Therefore, in this study, we have optimized

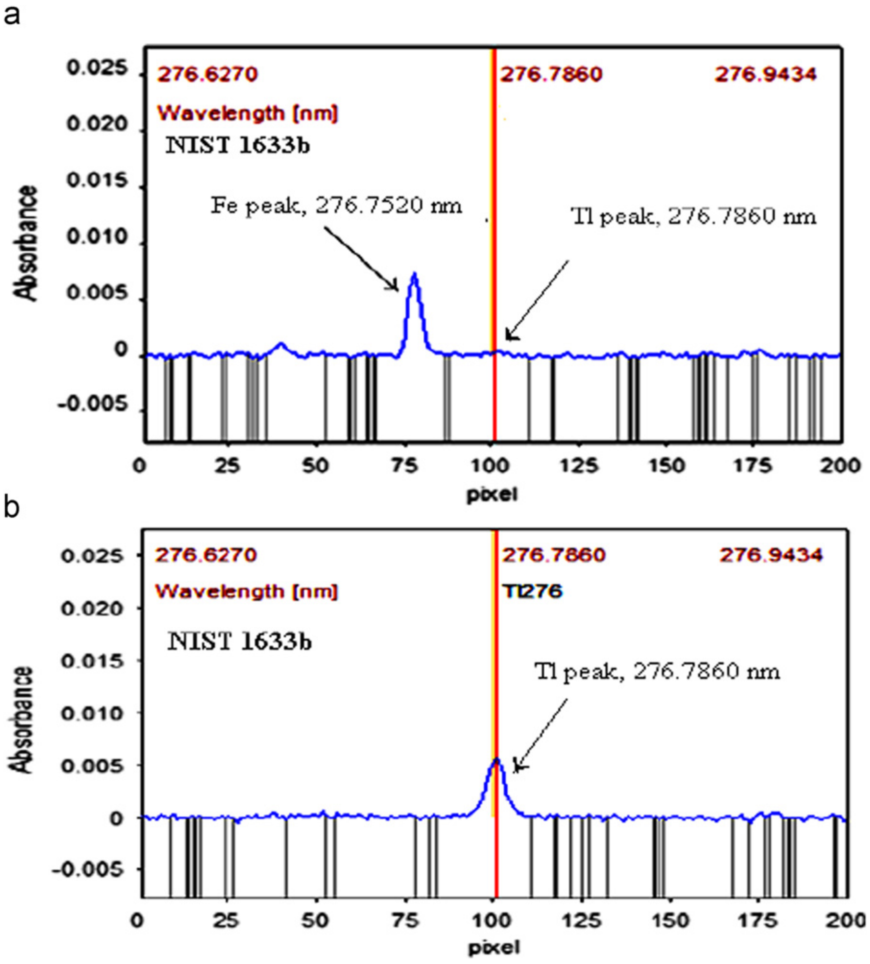

Fig. 3. Atomic absorption peaks measured simultaneously over the wavelength range of 276.6270 nm (0 pixel) to 276.9434 nm (200 pixel) using CS-ETAAS after injecting the 2 mg mL^{-1} NIST 1633b coal fly ash aqua regia extract consisting of 24 ng mL^{-1} thallium (276.7860 nm) and 311 µg g^{-1} iron (276.7520 nm) using Pd modifier. (a) Direct injection and (b) Injection of micelles-rich phase after cloud point extraction.

the cloud point extraction parameters for pre-concentration of thallium and efficient separation of interfering ions. The effect of each variable parameter in the cloud point extraction has been studied by spiking 1 ng mL^{-1} thallium to aqueous and NIST 1633b coal fly ash aqua regia extract.

3.3.1. *Effect of acids concentration*

The type of acid used and its concentration play an important role not only for clouding and phase separation in the Triton X-114 micelles (as discussed above) but also in the dissolution of sample matrices as well as the formation of stable and selective extractable thallium species. Hence, the effect of HCl and HNO_3 separately as well as their mixtures on the recovery of thallium was studied in the range of 0–30 v/v%. The results are shown in Fig. 4. From this figure it is seen that, without any acids, only 35% recovery of thallium was observed. With HCl and HNO_3, the maximum recovery was 75% and 80%. However, when different combinations of both acid mixtures were used in the range of 5–30% HCl and 5–10% HNO_3, quantitative recoveries (97–100%) of thallium was obtained. It may be due to formation of mixed chloro nitro anionic species $(TlCl_x^-(NO_3^-)_y)^{(x+y)-3}$. Therefore, a mixture of 15% HCl and 5% HNO_3 equal to 20 v/v% aqua regia was selected.

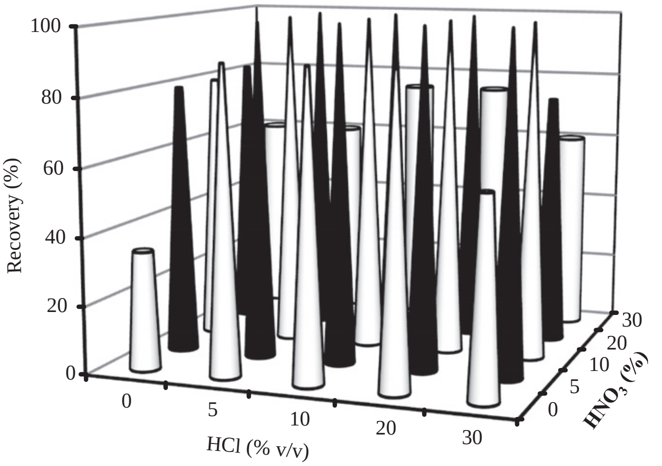

Fig. 4. Effect of concentrations of HCl and HNO_3 on the recovery (%) of thallium from 1 ng mL^{-1} spiked water in the presence of 3 m/v% NaCl and 1 m/v% Triton X-114. The relative standard deviations were in between 1 and 2%.

3.3.2. *Effect of Triton x-114*

The success of non-ionic surfactant based cloud point extraction depends mainly on the hydrophobicity of the extracting species and the kinetics of their transfer into the micelle aggregates during their micelles-rich phase separation especially in real samples. The preliminary results showed that the concentration of Triton X-114 required for the quantitative recovery of thallium species from aqueous Milli-Q water and NIST 1633b coal fly ash (CFA) extracts were different. Therefore, the effect of the

Table 2
Effect of Triton X-114 concentration on the recovery of 1 ng mL^{-1} thallium spiked to Milli-Q water and NIST 1633b extract in the presence of 20 v/v% aqua regia and 3 m/v% NaCl and determination using CS-ETAAS.

Concentration of Triton X-114	Recovery[a] (%)	
	Milli-Q water	NIST 1633b
0.25	98 ± 3	50 ± 3
0.50	99 ± 2	70 ± 4
0.75	99 ± 3	85 ± 3
1.00	100 ± 3	98 ± 3
1.50	101 ± 2	98 ± 3
2.00	100 ± 3	98 ± 3

[a] Mean of four determinations ± relative standard deviation.

Table 3
Effect of NaCl concentration on the recovery of 1 ng mL^{-1} thallium spiked to Milli-Q water and NIST 1633b extract in the presence of 20 v/v% aqua regia and 1 m/v% Triton X-114 and determination using CS-ETAAS.

Concentration of NaCl	Recovery[a] (%)	
	Milli-Q water	NIST 1633b
0	25 ± 5	65 ± 4
1.0	55 ± 4	95 ± 3
2.0	85 ± 3	95 ± 2
3.0	98 ± 2	96 ± 2
4.0	99 ± 3	96 ± 3
5.0	85 ± 3	75 ± 5

[a] Mean of four determinations ± relative standard deviation.

Table 4
Recovery of thallium from various water and real samples using proposed cloud point extraction method ($n=6$).

Matrices	Spiked/ng mL^{-1}	Found/ng mL^{-1} (mean ± SD)[a]	Recovery (%)
Tap water	1	0.99 ± 0.04	99 ± 4
	2	1.92 ± 0.06	96 ± 3
Ground water	1	1.02 ± 0.03	102 ± 3
	3	2.94 ± 0.06	98 ± 2
Coal fly ash	3	2.91 ± 0.03	97 ± 1
	5	4.95 ± 0.10	99 ± 2
Lake sediment	2	1.90 ± 0.08	95 ± 4
	4	388 ± 0.12	97 ± 3

[a] Mean of six determinations ± standard deviation.

concentration of Triton X-114 on the recovery of thallium spiked in Milli-Q water and NIST 1633b CFA extracts were evaluated in the range between 0.25 and 2 m/v% Triton X-114 and results are shown in Table 2. These results indicate that the recovery was nearly quantitative with 0.25% and 1 m/v% Triton X-114, respectively, for Milli-Q water and CFA. Therefore, an optimum value of 1 m/v% Triton X-114 was selected.

3.3.3. *Effect of NaCl*

The role of an electrolyte is crucial in achieving low clouding temperature and efficient phase separation in non-ionic Triton X-114 micelle based cloud point extraction in the presence of aqua regia as shown in Fig. 2(b). The natural concentration of the electrolytes present in the samples may vary with the type and quantity of the matrix used for extraction. The preliminary results showed that the concentration of NaCl required for the quantitative recovery of thallium from aqueous solutions was quite different compared to NIST 1633b CFA extract. Hence, the effect of the concentration of NaCl on the recovery of thallium in spiked Milli-Q water and NIST 1633b CFA extracts were studied in the range of 0–5 m/v% by keeping other parameters constant. The results are shown in Table 3. These results indicated that when NaCl was not used, the recovery of thallium was 25% and 65%, respectively, in Milli-Q water and CFA. These recoveries were increased by increasing the concentration of NaCl and reached a quantitative recovery between 3 and 5% NaCl for both CFA and Milli-Q water samples. Therefore, an optimum value of 3 m/v% NaCl was selected.

3.3.4. *Effect of extraction temperature and time*

The effect of extraction temperature on micelles-rich phase volumes and recovery of thallium were studied in the range of 30–90 °C using a 20 min extraction time. These results indicate that the recovery of thallium increased from 40 to 95% with increase in the extraction temperature from 30 to 80 °C and then reached a plateau (95–100%) when the temperature was further increased to 90 °C. Improvement in recoveries at higher temperatures indicates efficient stabilization of the thallium species in micelles medium compared to mixed micelles reported earlier [24]. Hence, a 90 °C extraction temperature was selected. Optimization of extraction time was carried out in the range of 10–40 min. These results showed that the recovery of thallium between 95 and 101% at all the studied time intervals. Therefore, a 20 min extraction time was selected. Under these conditions, the phase volume ratio and pre-concentration factor were found to be 0.025 and 40, respectively.

3.3.5. *Interference and recovery studied*

In order to evaluate the performance of the present optimized method, the main interfering iron and sulfate were spiked separately in the range of 0.01–0.1% and 0.03–0.15%, respectively, to 4 ng mL^{-1} thallium solutions and analyzed by CS-ETAAS. These results showed no significant effect of these ions on the recovery of thallium (95 ± 5%), indicating the effective removal of these interferences in the studied concentration range. However, beyond this range the recovery of thallium was found in the range of 80–90%, this lower recovery is mainly due to the change of clouding behavior of Triton X-114 from CPE to CE phase. The studied concentrations of iron and sulfur were far higher than their concentrations in the digested aliquots used in this study. Therefore, these studies indicate effective elimination of the potential interfering species on thallium determination. The tolerance limits of various other common interfering species were also studied. It was found that 2 g L^{-1} of Mg^{2+}, 0.5 g L^{-1} of Cd^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+}, 2 mg L^{-1} of F^- and PO_4^{3-} showed no interferences. These results demonstrated the high selectivity of the proposed method for the extraction of thallium.

The recovery studies were performed by spiking the thallium to tap water, ground water and extracts of coal fly ash and sediment samples, in the range of 1–5 ng mL^{-1}. The recoveries obtained are given in Table 4. The recoveries were in between 95 and 102%, which indicated that the studied matrices have no significant effect on the recoveries of thallium. The relative standard deviations of the measurements were between 1 and 4%.

3.4. *Optimization of furnace temperature program*

The effect of pyrolysis and atomization temperatures on the absorbance signal of 25 ng mL^{-1} of thallium in 0.2% HNO_3 with Pd modifier and micelles-rich phase with and without palladium modifier were studied. The results are shown in Fig. 5. From this figure it is observed that after initial increase in absorbance between 400 and 700 °C, thallium is stable up to a pyrolysis temperature of 1000 °C, beyond which there is a loss. The plateau region between 800 and 1000 °C pyrolysis temperature has signal of 0.025, 0.10 and 0.12 absorbance, for aqueous standard with Pd

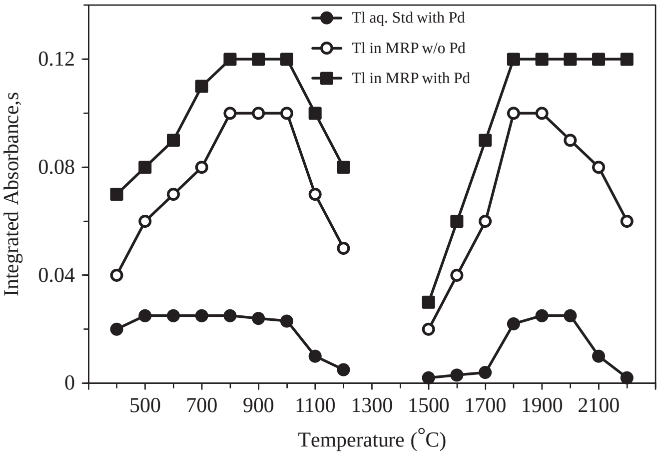

Fig. 5. Effect of pyrolysis and atomization temperature on the absorbance of 25 ng mL^{-1} of thallium in 0.2% HNO$_3$ with Pd modifier and in micelles-rich phase (MRP) with and without Pd modifier.

modifier and micelles-rich phase without and with Pd modifier, respectively. These results indicate that the Triton X-114 in the micelles-rich phase can also act as a chemical modifier. Hence, a pyrolysis temperature of 800 °C was selected. The optimizations of atomization temperature were carried out in the range of 1500–2200°C. The absorbance signal increased with increase in the atomization temperature from 1500 to 1700 °C and stabilizes around 1800–1900 °C in all cases. However, with 0.2% nitric acid and Pd modifier and only micelles-rich phase, the loss was seen when atomization temperature was increased beyond 2000 °C, and 1900 °C, respectively. With Pd modifier and micelles-rich phase, no loss was observed even beyond 2200 °C. Hence, a 2000 °C atomization temperature was selected.

3.5. Analytical figures of merit

Under the optimized experimental conditions, the calibration curve was obtained by pre-concentrating the successively spiked standards of thallium in the range of 0.5–5 ng mL^{-1}. The correlation coefficient was 0.9994. Quantifications of thallium have been performed by using standard addition calibration graph. The limit of detection calculated based on three times the standard deviation of ten measurements of procedural blanks was 2 pg mL^{-1} for water and 0.2 ng g^{-1} for sediment samples, which is better than that of the recently published non-ionic surfactant based CPE method applied to surface waters [22]. The analytical capability of hydrophobic solubilizing sites of Triton X-114 micelles has been used effectively for quantitative extraction of thallium directly from the aqua regia extracts of coal fly ash and sediments samples. A characteristic mass (m_o), 13 pg was obtained by measuring the integrated absorbance with central pixel ±1.

3.6. Analysis of certified reference materials and samples

The accuracy of the proposed method was evaluated by analyzing certified reference materials such as NIST 1633b coal fly ash, NIST 1944 marine sediment, GBW 07312 stream sediments after aqua regia extraction using microwave energy. The values obtained were in good agreement with certified value in case of NIST 1944 marine sediment and informative values in case of NIST 1633b and GBW 07312 based on student *t* test at 95% confidence level. This method has also been applied to non-certified IAEA 433 marine sediment and IAEA 394 coal fly ash and real lake sediment and coal fly ash samples and the results are given in Table 5. The thallium concentrations obtained by the present method in real, non-certified and certified reference materials were also compared with the results obtained by a reported mixed-micelle CPE method [24]. These results show that there is a good agreement in the real, non-certified as well as in certified reference material by both the methods. The levels of thallium in coal fly ash and lake sediments samples collected locally were within the natural range in these matrices [4–6].

Table 5
Analytical results for the determination of thallium in certified reference materials and real samples using the proposed CPE method.

Matrices	Measured values/μg g^{-1} (mean ± $^{a}ts(n)^{-1/2}$)		
	Proposed CPE	MM-CPE[b]	Certified values
GBW 07312 stream sediment	1.79 ± 0.12	1.82 ± 0.18	1.76[c]
NIST 1633b coal fly ash	5.95 ± 0.09	5.88 ± 0.12	5.9[c]
NIST 1944 marine sediment	0.60 ± 0.06	0.58 ± 0.13	0.59 ± 0.1
IAEA 433 marine sediment	0.33 ± 0.06	0.32 ± 0.09	–
IAEA 394 coal fly ash	3.52 ± 0.10	3.45 ± 0.12	–
Real samples			
Coal fly ash	1.05 ± 0.12	0.98 ± 0.13	–
Lake sediment	0.52 ± 0.09	0.49 ± 0.15	–

[a] $t_{0.95}$=3.18, n=4, s=standard deviation.
[b] Values are obtained from mixed-micelle cloud point extraction method Ref. [24].
[c] Information values.

4. Conclusions

A simple and efficient cloud point extraction method has been described for the pre-concentration of thallium from aqua regia extracts of sediment and coal fly ash samples. This process provided the interference free determination of thallium using CS-ETAAS. The micelles acted as extracting agent and avoid the addition of an external chelating agent commonly used in the non-ionic surfactant based cloud point extraction and also act as a modifier to stabilize thallium in the CS-ETAAS. This method is more eco-friendly and uses non-toxic non-ionic surfactant and agrees with the green chemistry principles to clean-up the thallium contamination in environmental samples. The efficient removal of interfering elements in the present method is more useful for accurate quantification of thallium even by using conventional ETAAS with poor resolution instruments

References

[1] A.K. Das, M. Dutta, M.L. Cervera, M. de la Guardia, Microchem. J. 86 (2007) 2.
[2] 〈http://emedicine.medscape.com/article/821465-overview〉.
[3] M.K.W. Barber, K. Lyall, R.W. Ferenbaugh, J. Environ. Sci. Health A20 (1985) 689.
[4] M. Rehkamper, S.G. Nielsen, Mar. Chem. 85 (2004) 125.
[5] B.J. Mathis, N.R. Kevern, Hydrobiologia 42 (1975) 133.
[6] A.D. Matthews, J.P. Riley, Chem. Geol. 6 (1970) 149.
[7] R. Dobrowolski, Anal. Bioanal. Chem. 374 (2002) 1294.
[8] M.R.G. Vale, M.M. Silva, B. Welz, R. Nowka, J. Anal. At. Spectrom. 17 (2002) 38.
[9] M.R.G. Vale, B. Welz, Spectrochim. Acta, Part B 57 (2002) 1821.
[10] K. Matsusaki, T. Oishi, Anal. Sci. 9 (1993) 381.
[11] D. Zendelovska, T. Stafilov, Anal. Sci. 17 (2001) 425.
[12] B. Welz, G. Bozsai, M. Sperling, B. Radziuk, J. Anal. At. Spectrom. 7 (1992) 505.
[13] B.V. L'vov, Spectrochim. Acta Part B 33 (1978) 153.
[14] B. Welz, G. Schlemmer, J.R. Mudakavi, Anal. Chem. 60 (1988) 2567.
[15] D.C. Manning, W. Slavin, Spectrochim. Acta, Part B 43 (1988) 1157.
[16] L.M. Voth-Beach, D.E. Shrader, J. Anal. At. Spectrom. 2 (1987) 45.
[17] B. Welz, M.G.R. Vale, M.M. Silva, H. Becker-Ross, H. Mao-dong, S. Florek, U Heitmann, Spectrochim. Acta, Part B 57 (2002) 1043.
[18] L.B. Escudero, P. Berton, E.M. Martinis, R.A. Olsina, R.G. Wuilloud, Talanta 88 (2012) 277.
[19] R. Horiguchi, I. Nukatsuka, Y. Shimizu, S. Sekikawa, K. Ohzeki, Bunseki Kagaku 51, (2002)675.
[20] N.N. Meeravali, S.J. Jiang, Talanta 80 (2009) 173.

[21] R.P. Frankewich, W.L. Hinze, Anal. Chem. 66 (1994) 944.
[22] Y. Xiao, B. Zheng, K.R. Zhang, Chinese J. Anal. Chem. 35 (2007) 1654.
[23] N.N. Meeravali, S.J. Jiang, J. Anal. At. Spectrom. 23 (2008) 555.
[24] N.N. Meeravali, S.J. Jiang, J. Anal. At. Spectrom. 23 (2008) 1365.
[25] C.B. Ojeda, F.S. Rojas, Anal. Bioanal. Chem. 394 (2009) 759.
[26] H. Schott, J. Colloid Interface Sci. 169 (1997) 117.
[27] W.N. Maclay, J. Colloid Sci. 11 (1956) 272.