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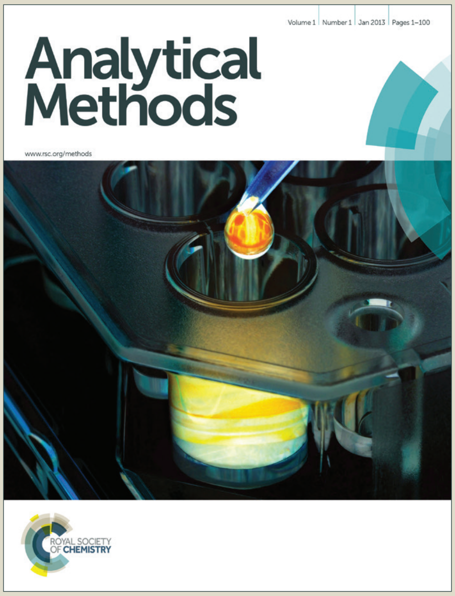

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A Cloud point extraction procedure for gallium, indium and thallium determination in liquid crystal display and sediment samples

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Abstract

A simple, sensitive and rapid cloud point extraction (CPE) methodology has been developed for the selective separation and preconcentration of gallium, indium and thallium, after complexation with gallic acid in the presence of Triton X-114 as a non ionic surfactant. Quantitative extraction of gallium, indium and thallium was performed at pH 2.5, 0.04 mmol L^{-1} gallic acid, 0.05% (w/v) Triton X-114 and at 40 ^{o}C. Dilution of the surfactant-rich phase with acidified methanol was performed after phase separation, and the metal ions were determined by flame atomic absorption spectrometry. Under the optimum experimental conditions, the calibration curve is linear over the concentration range 6-150 ng mL^{-1} for gallium, 2-150 ng mL^{-1} for indium, and 2-100 ng mL^{-1} for thallium. The limits of detection, based on three times of standard deviation of blank signal by seven replicate measurements were 3.50, 1.25 and 0.92 ng mL^{-1}, respectively. The relative standard deviations of this method were 1.55, 1.40 and 1.82% for gallium, indium and thallium, respectively (C=50 ng mL^{-1}, n=7). The results showed the developed method was not susceptible to interference effects, providing good recoveries. The developed method was successfully applied to gallium, indium and thallium determination in sediments and mobile phone liquid crystal display samples with satisfactory results.

Key words

Cloud point extraction; gallium; indium; thallium; gallic acid; flame atomic absorption spectrometry

Introduction

Gallium, indium and thallium occur in rare quantities in the Earth's crust. Gallium can be found as a trace in a variety of ores, including bauxite and sphalerite. [1] It is produced as a by-product of the aluminium industry. Gallium compounds are used in the production of low-melting alloys, such as intermetallic compounds used in the electronic industry for manufacturing of semiconductors, lasers, special optical glasses and thermometers.[2] Citrate and nitrate salts of gallium are used in medicine as tumor-scanning and antitumoral agents, respectively.[3] Indium and thallium are found in low abundance in the sulphide ores of metals such as zinc, iron and copper. Indium compounds have numerous industrial applications and they are currently used in the manufacture of liquid crystal displays (LCDs), semiconductors, low-temperature solders and infrared photodetectors. Thallium compounds are used in photocells, infrared detectors, low temperature switches and low-melting glasses.[1]

Electronic waste is classified as hazardous material therefore should be managed properly. However, the presence of valuable metals in electronic waste such as Ga, In and Tl makes it attractive for recycling. Various analytical procedures have been used for mutual separation and recovery of Ga, In and Tl from different matrices, such as solid phase extraction,[4-6] liquid–liquid extraction,[7,8] co-precipitation,[9] and ion exchange.[10] These procedures either are time-consuming and/or generate large amounts of hazardous waste.

Nowadays, cloud point extraction (CPE) using a non-ionic surfactant has attracted considerable attention as an alternative to the conventional extraction techniques for separation and preconcentration.[11] It is based on the non-ionic surfactant properties in aqueous media that induce formation of micelles and cause the samples to become turbid upon heating to the cloud point temperature. With exposure to a temperature higher than the cloud point temperature, the micellar solution separates into two phases: a surfactant-rich phase with a small volume and an aqueous phase. CPE based on surfactant-mediated phase separation has been recognized as an alternative to the conventional extraction because of its high efficiency, low cost and low toxicity. Only a few CPE methods are reported for gallium, indium and/or thallium.[12-15]

In the present paper, we describe a simple and rapid CPE method for the selective separation of Ga(III), In(III) and Tl(III) prior to their determination by flame atomic absorption spectrometry (FAAS). This method enables simultaneous separation and pre-concentration of these metal ions from real samples at trace levels. In the developed system gallic acid [3,4,5-trihydroxybenzoic acid, GA] was used as the chelating agent and Triton X-114 as a non ionic surfactant. The experimental parameters affecting the CPE efficiency were investigated and optimized. The analytical figures of merit and interfering ions tolerance are presented.

Experimental

Apparatus

A Perkin Elmer® atomic absorption spectrophotometer (Model AAnalyst™ 800) with an air–acetylene flame was used for determination of the metal ions. The wavelengths used for monitoring Tl, In and Ga were 276.8, 303.9, and 294.4 nm, respectively, at a spectral band pass of 0.2 nm. The system is equipped with win Lab 32 software. The solution pH was adjusted using Hanna instrument model 8519 digital pH meter. A centrifuge model of CH90-2 (Hinotek Technology Co. Ltd., China) was used to accelerate the phase separation process. A thermostated water-bath (Model Kottermann 3006, Hänigsen, Germany) was employed for temperature control. Digestion of the samples was carried out in a CEM MDS 2000 microwave digestion system (Matthews, NC, USA).

Reagents and solutions

All aqueous solutions were prepared with ultrapure water obtained by Milli-Q water purification system (Millipore, Billerica, MA, USA). Reagents used were of analytical grade from Sigma–Aldrich (St. Louis, MO, USA), Fluka (Buches, Switzerland) or Merck (Darmstadt, Germany). The laboratory glassware was kept overnight in 10% v/v HNO_3 solution. washed with deionized water and dried in a dust free environment. Stock solutions of Ga(III) and In(III) were prepared by dissolving the pure metal in HCl 1:4. They were standardized by titration with EDTA. [16] Tl(III) stock solution (1000 mg L^{-1}) was prepared by dissolving 0.293 g of TlCl in 25 ml of deionized water. Two drops of bromine water was added to oxidize Tl(I) to Tl(III); the mixture was warmed to remove excess bromine, cooled and diluted to 1 L. Working solutions were freshly prepared from the stock solution by dilutions with deionized water. One mmol L^{-1} solution of GA was prepared by dissolving appropriate amounts of the reagent in 100 mL of 50% ethanol.

Procedures

The recommended CPE system

An aliquot of 25 ml of a solution containing Ga(III), In(III) or Tl(III), pH 2.5, Triton X-114 (0.05% w/v) and 4×10^{-5} mol L^{-1} of GA were kept for 10 min in a thermostatic bath at 40 ^{o}C. The surfactant-rich phase typically settles through the aqueous phase. The phase separation was accelerated by centrifuging at 4000 rpm for 10 min. The mixture was cooled down in an ice bath in order to increase the viscosity of the surfactant rich phase. The aqueous phase was discarded by inverting the tube. The surfactant rich phase in the tube was dried at 80^{o}C in a water bath, and the residue was made up to 0.5 ml by adding mixture of methanol/conc. HNO_3 (5:1). This final solution was introduced into the flame by conventional aspiration.

Preparation of Real Samples

The sediment samples were collected from different locations along the River Nile at Mansoura city, Egypt. The samples were dried at 90 ^{o}C for 2 h, ground and homogenized. 5 mL of concentrated HNO_3, 2 mL of concentrated HF and 3 mL of deionized water were added to accurately weighted sample (0.3-0.5 g) in a 125 ml pressure-resistant PTFE bottle and digested in the microwave oven by applying the heating program shown in Table 1. Finally, 20 mL of 5% w/v boric acid was added to neutralize excess HF and the solution was filtered and brought to a final volume of 25 mL with deionized water.

Fragmented LCD glasses of mobile phones were collected from maintenance communication centers located at Mansoura city. Each sample was cut into 2–3 mm pieces using stainless steel knife. About 200 mg of sample was accurately weighed into a Teflon™ vessel. Aqua regia (6 ml) was added to the beaker, and the mixture was digested as described above for sediment samples. The resulted solution was filtered and the volume was completed to 25 mL volumetric flask. Aliquots of 5 mL of the digested samples were analyzed according to the recommended CPE procedure.

Result and discussion

Preliminary studies

Initially, GA was used as the ligand in the present work because it is a multi-dentate chelating agent which react with some metal ions through carboxylic or hydroxo groups and has been used for the preconcentration and separation of various metal ions.[17-20] The stability constants of the complex formed between GA with the metal ions were calculated spectrophotometry according to the method of Harvey and Manning. [21] It was found to be 2.6×10^5, 3.1×10^5 and 3.2×10^5 L mol^{-1} for Ga(III), In(III) and Tl(III), respectively, which indicates good stability of the complex. By means of the Mole Ratio Method and the Job Method of Continuous Variation a metal:ligand ratio of 1:3 was estimated through UV-Vis spectrophotometry.

Optimization

The aim of this work was to develop a selective procedure for Ga(III), In(III) and Tl(III) determination using CPE and flame atomic absorption spectrometry. In this regard, the influence of various effective parameters including, pH, GA and surfactant concentrations, incubation time and temperature, centrifuge time and rate, as well as the effect of ionic strength on extraction recovery, were optimized. GA is an acidic reagent (pKa, 4.2) [22] and its dissociation equilibrium depends on the pK value as well as pH of the solution. Hence, its complex formation and extraction behavior is also pH dependent. Thus, the effect of the pH on metal ion extraction was assessed by varying the pH from 0.5 to 10 with HNO_3 and NaOH. As can be seen from Fig. 1, the optimal extraction efficiency was observed for pH values ranges from 2.0 to 3.0, which is lower than the precipitation of the hydroxide of most transition metals.[23] At lower pH (< 2), the extraction is not quantitative which may be attributed to the incomplete formation of the metal complexes, while at higher pH, the recovery is reduced due to the competition between complex formation and hydrolysis of the metal ion (K_{sp} for $Ga(OH)_3$, $In(OH)_3$ and $Tl(OH)_3$ are 7.28×10^{-36}, 6.3×10^{-34}, 1.68×10^{-44}, respectively). [24] Consequently, pH 2.5 was selected for the subsequent studies.

The effect of GA concentration in the range of 1-100 μmol L^{-1} on the recovery of the extracted metal ions was investigated, while the other experimental parameters remained constant. The results (Fig. 2) show that the recoveries of the metal ions were enhanced by increasing the concentration of GA up to 4×10^{-5} mol L^{-1} and reaches the plateau afterwards due to 56, 92 and

163 molar fold excess of GA in relation to Ga(III), In(III) and Tl(III), respectively. Thus, GA concentration of 4 × 10^{-5} mol L^{-1} was employed throughout the work.

The type and concentration of surfactant are also important factors that affect CPE. Triton X-114 was chosen because of its physicochemical characteristics, low cloud point temperature (23–26 ^{o}C), commercial availability, relatively low price, low toxicity, high density in the surfactant-rich phase, which facilitates phase separation.[12] For these reasons, most CPE systems developed for metal ions are designed around this non-ionic surfactant. The effect of surfactants concentration in the range of 0.01-0.1% (w/v) on the extraction efficiency was examined. According to the results in Fig. 3, the optimum extraction recovery of Ga(III), In(III) and Tl(III) was maximum at Triton X-114 concentration of 0.05 % (w/v). At lower Triton X-114 concentrations, the extraction recovery of the complex is low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively. The lowest concentration of Triton X-114 possible was chosen in this experiment to minimize the volume of the surfactant rich phase, which should positively affect the preconcentration factor. Hence, a concentration of 0.05 % (w/v) was chosen for further studies.

The extraction efficiency is strongly affected by the temperature and incubation time. It was desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which compromise completion of the reaction and efficient separation of the phases.[25]

As Ga(III), In(III) and Tl(III) form stable complexes with GA at the desired pH. These hydrophobic complexes which are present in the solution and bound to the micelles are extracted to the surfactant-rich phase when the solution is heated over a cloud extraction temperature. [25] As the cloud point temperature of Triton X-114 is ranging from 23-26 ^{o}C. Therefore, the relationship between the extraction of the metal ions and the equilibrium temperature and time was investigated between 20-80 ^{o}C and 5–30 min, respectively. The results showed that holding the sample solutions for 10 min at temperature range of 40-60°C was found to be satisfactory to achieve quantitative extraction. Above this temperature, reduction of extraction efficiency was noted, probably due to the decomposition of metal complexes. At lower temperature, the extraction of the metal ions is not quantitative which may be owing to the incomplete formation of metal complexes. So, sample incubation at 40^{o}C for 10 min was selected as optimum for further experiments.

Preconcentrating trace amounts of Ga(III), In(III) and Tl(III) with maximum efficiency in a short time is required. Therefore, the dependence of extraction efficiency upon centrifugation rate and time was studied with a range of 2000–4000 rpm and 5–20 min, respectively. The results showed that centrifugation for 10 min at 4000 rpm lead to the maximum recoveries. No appreciable improvements were observed for longer centrifugation times and rates. At lower ones, the enrichment phase did not separate completely.

The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency. Therefore, to investigate the influence of ionic strength on extraction efficiency, various experiments were performed by adding different amounts of $NaNO_3$ (0-1 mol L^{-1}) and the rest of the experimental conditions were kept constant. Based on the obtained results, the addition of $NaNO_3$ within the interval of 0-0.5 mol L^{-1} had no significant effect on the CPE efficiency. The analytical signal decreased considerably by increasing $NaNO_3$ concentrations (>0.5 mol L^{-1}). This effect might be explained by the additional surface charge when the $NaNO_3$ concentration is very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process.[26]

In the phase separation step, the surfactant-rich phase with high viscosity was settled. The addition of a diluent reduces the surfactant phase viscosity and facilitates its transfer into the the nebulizer of FAAS. An organic solvent should have characteristics such as low viscosity, low surface tension and combustible for use in atomic absorption. Different solvents (DMF, DMSO, ethanol and acetonitrile and methanol/HNO_3 mixture 5:1) for the surfactant-rich phase were tested so as to select the one producing the optimal results regarding sensitivity. The best solvent was methanol/HNO_3 mixture and the signals of the three metals were diminished in the presence of the other organic solvents. Better recovery was observed when 0.5 mL of acidified methanol was employed.

Effect of concomitants

In order to investigate the selectivity of the method, 25 mL of the sample solution containing 50 ng mL^{-1} of Ga(III), In(III) or Tl(III) was extracted under the selected experimental conditions in the presence of high concentration of various cations and anions usually present in real samples. An ion was considered to be interfering when it caused a variation greater than ± 5% in the recovery. As shown in Table 2, large amounts of commonly occurring cations and anions as well as some chelating agents did not affect the determinations. The tolerable ratio of Fe(III) was increased from 50 to 800 by adding 5 ml of 10% L-ascorbic acid. The removal of Fe(III) interference by reducing it to Fe(II) is due to the effect of pH on the complexation of GA with Fe(II) and Fe(III). Fe(II) forms stable complex with GA at pH >7, while Fe(III) requires more acidic solution (pH<3.5). Moreover, formation of iron(II) complex with GA requires complete exclusion of oxygen which makes the formation of Fe(II)-GA complex difficult under the optimum condition of the present procedure. [27] Al^{3+} also showed strong interference which overcome by addition of 0.1 % fluoride ion as a masking agent. Thus the method is highly selective and may safely be applied for the determination of Ga(III), In(III) and Tl(III) in various real samples.

Analytical features

The calibration solutions were submitted to the same treatment given to the samples with respect to CPE. The results indicated that, the calibration curve was linear over the concentration range 6–150, 2-150 and 2-100 ng mL^{-1} for Ga(III), In(II) and Tl(III) with a correlation coefficients of 0.999. The limits of detection (LODs), defined as the analyte concentration giving a signal equal to three times the standard deviation of the blank signal (n=7), were 3.50, 1.25, 0.92 ng mL^{-1} for Ga(III), In(III) and Tl(III), respectively. Furthermore, for 25 ml of the working standard solutions the preconcentration factor was 50, and the enrichment factor defined as the ratio of the slope of the calibration curve after and before the preconcentration procedure was found to be 54, 48 and 52 for Ga(III), In(III) and Tl(III), respectively. The relative standard deviations (RSDs), obtained for seven determinations of Ga(III), In(III) and Tl(III) were 1.55, 1.40 and 1.82%, respectively.

Recovery tests and application

To test the accuracy of the method, the determination of Ga(III), In(III) and Tl(III) was carried out in spiked samples. Recovery experiments were carried out by spiking the samples with different amounts of the metal ion before any pretreatment. Table 3 shows the obtained results. As it can be seen, the results of five analyses of each sample show that, in all cases, the ions recoveries is almost quantitative with a low RSD. The suitability of the developed method was also examined by applying it to the separation and determination of Ga(III), In(III) and Tl(III) in a variety of synthetic mixtures, which are frequently in association. A solution containing 50 µg of Ga(III), In(III) or Tl(III) was taken and known amounts of other metals were added (Table 4). The extraction of Ga(III), In(III) and Tl(III) was performed using the method developed herein. The results obtained were in good agreement with the amount added.

A comparison between the characteristics of the developed CPE procedure and other reported preconcentration procedures [4,5,12-15,28-33] recently used for simultaneous determination of Ga(III), In(III) and Tl(III) is summarized in Table 5. The detections limit of the proposed method was lower than other FAAS.[4,5,29] Although the LODs of Ga(III), In(III) and Tl(III) in our study were higher than those reported by ICP and GFAAS techniques, the availability of FAAS in most analytical chemistry laboratories as well as the low cost of GA may support our method. From toxicological point of view, the presented work is environmentally friendly procedure as it consumes small volumes of reagents and generates negligible hazard waste.

Conclusion

CPE using Triton X-114 and GA has shown to be an efficient and easy separation and preconcentration of Ga(III), In(III) and Tl(III) in liquid crystal display and sediment samples. Our proposed procedure resulted in low detection limits. The method works in acidic (pH 2.5) conditions, avoiding the interferences caused by the precipitation of transition metal hydroxides. Additionally, use of toxic organic extractant solvents (i.e., chloroform, toluene, carbon tetrachloride, etc.) has been replaced with Triton X-114 as a green alternative. Coexistent ions in different samples did not interfere in the determination and were found to be tolerable. The developed method is proposed as a suitable alternative to more expensive instruments for Ga(III), In(III) and Tl(III) determination at trace levels. Simple operation procedure makes the sample preparation very easy and rapid, only a few minutes are needed before instrumental analysis. Thus, the proposed method could be of great interest for Ga(III), In(III) and Tl(III) determination in routine analytical laboratories.

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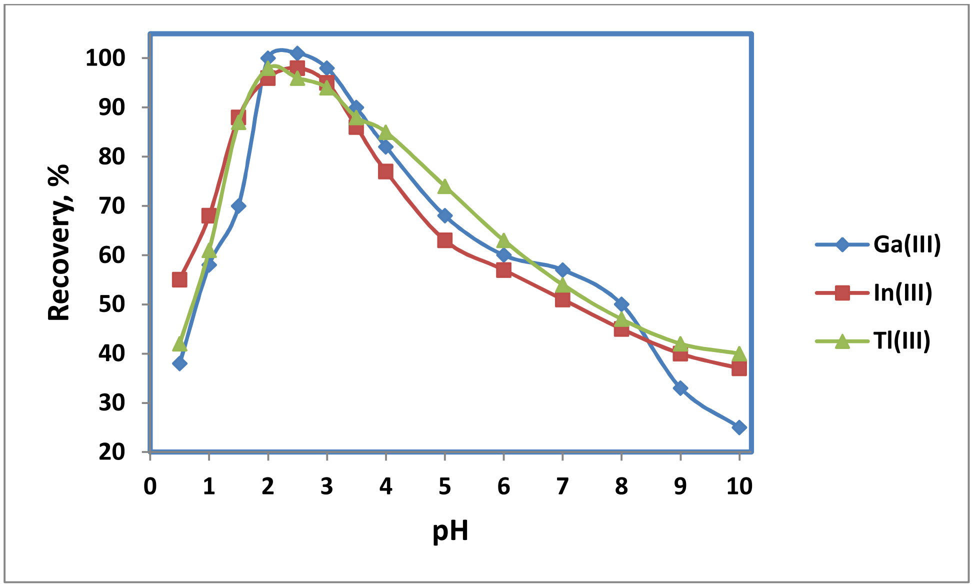


Fig. 1 Influence of the pH on the extraction recovery of Ga(III), In(III) and Tl(III). Conditions: 50 ng mL^{-1} metal ion; 0.05% w/v Triton X-114; 4x10^{-5} mol L^{-1} GA. Other experimental conditions are described in the experimental section.

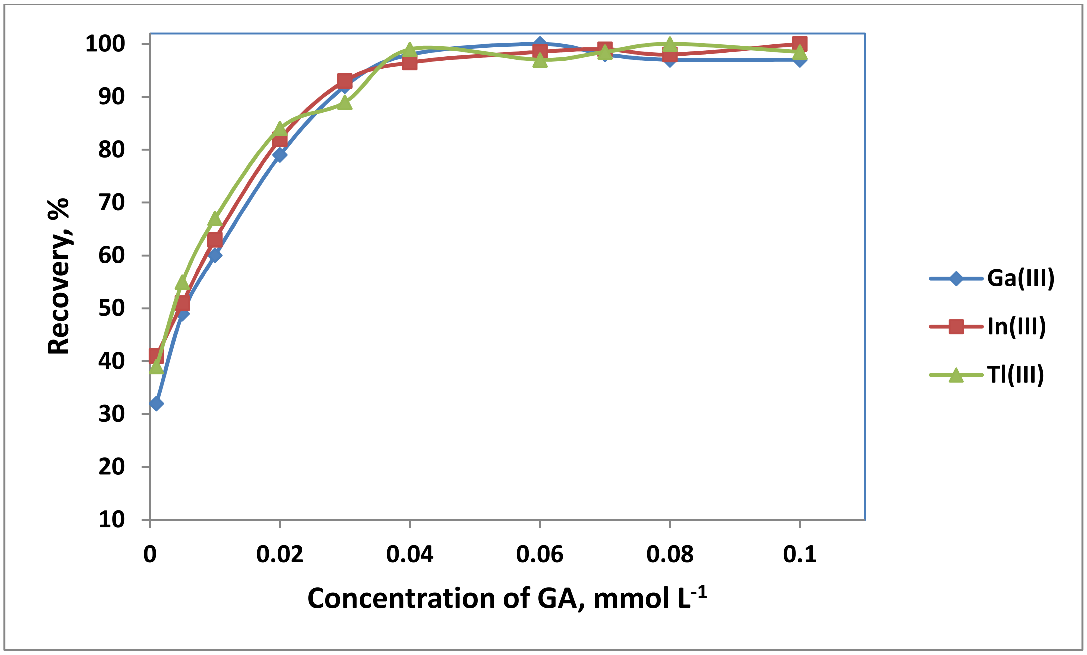


Fig. 2 Effect of the GA concentration on the extraction recovery of Ga(III), In(III) and Tl(III). Conditions: 50 ng mL^{-1} metal ion; pH 2.5; 0.05% w/v Triton X-114. Other experimental conditions are described in the experimental section.

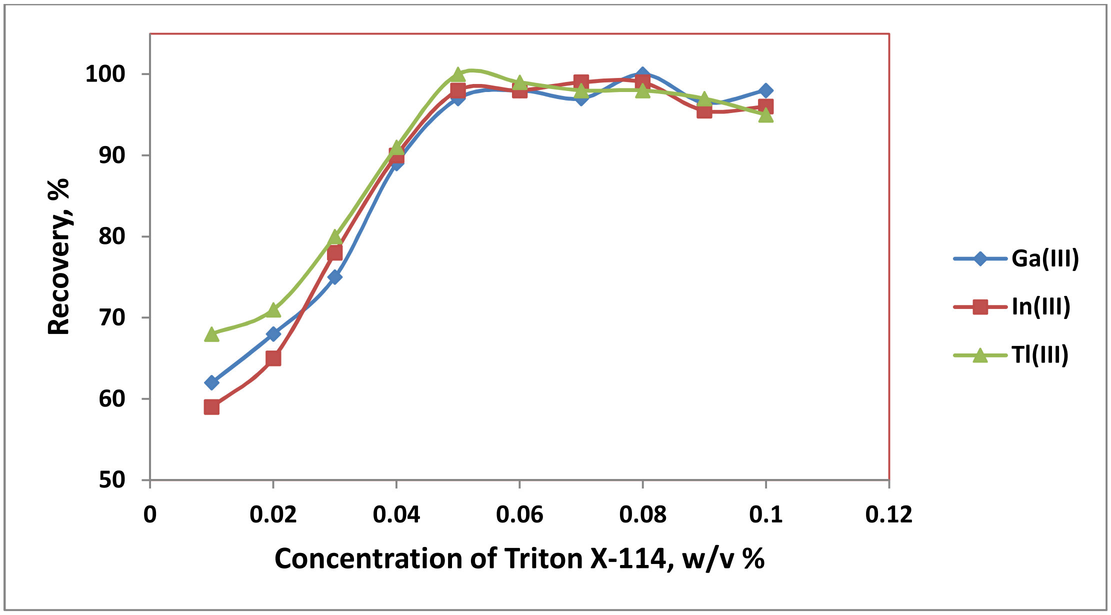


Fig. 3 Influence of the Triton X-114 concentration on the extraction recovery of Ga(III), In(III) and Tl(III). Conditions: 50 ng mL^{-1} metal ion; pH 2.5; $4x10^{-5}$ mol L^{-1} GA. Other experimental conditions are described in the experimental section.

Table 1. Microwave digestion program for the digestion of the geological samples

Step	1	2	3	4
Power (%)	60	60	60	60
Pressure (psi)	100	130	160	170
T1[*] (min)	30	30	30	30
T2[*] (min)	15	10	5	5

[*] T1: maximum time needed to reach the required pressure; T2: time the sample remains at the required pressure.

Table 2 Tolerance limits of potentially interfering ions

Ion	Added as	Tolerance ratio	Recovery			Ion	Added as	Tolerance ratio	Recovery		
			Ga(III)	In(III)	Tl(III)				Ga(III)	In(III)	Tl(III)
Na^+	$NaNO_3$	2000	95.8	98.2	98.4	Fe^{3+}	$Fe(NO_3)_3$	50	95.2	96.2	96.5
								800[a]	98.5	99.4	96.9
K^+	KNO_3	2000	97.0	95.8	97.5	Al^{3+}	$Al(NO_3)_3$	50	99.8	95.80	97.0
								500 [b]	96.5	100.6	99.6
Li^+	LiCl	2000	98.6	100.0	99.5	Ti^{4+}	$Ti(SO_4)_2$	250	99.8	102.1	95.2
Ca^{2+}	$Ca(NO_3)_2$	500	96.9	98.6	95.9	Zr^{4+}	$ZrOCl_2$	250	100.2	101.3	95.0
Mg^{2+}	$MgCl_2$	500	99.0	97.2	95.6	Cr^{6+}	$K_2Cr_2O_7$	200	101.2	102.2	100.8
Sr^{2+}	$Sr(NO_3)_2$	500	102.1	95.8	98.7	Cr^{3+}	$CrK(SO_4)_2$	200	101.1	97.9	95.6
Ba^{2+}	$BaCl_2$	500	97.5	95.5	97.2	Cl^-	NaCl	2000	99.1	97.8	95.5
Cu^{2+}	$Cu(NO_3)_2$	500	98.0	97.2	102.1	NO_3^-	$NaNO_3$	2000	101.3	96.0	97.2
Pb^{2+}	$Pb(NO_3)_2$	250	98.2	98.0	95.8	NO_2^-	$NaNO_2$	2000	99.6	100.1	98.8
Hg^{2+}	$HgCl_2$	250	100.4	103.0	96.5	HCO_3^-	$NaHCO_3$	2000	95.2	99.8	100.0
Zn^{2+}	$ZnCl_2$	500	95.7	98.7	104.0	CH_3COO^-	CH_3COONa	2000	95.0	99.6	96.4
Ni^{2+}	$Ni(NO_3)_2$	500	97.6	100.6	98.6	CO_3^{-2}	Na_2CO_3	2000	100.8	97.4	97.5
Cd^{2+}	$Cd(NO_3)_2$	500	99.7	102.4	96.5	SO_4^{-2}	Na_2SO_4	1000	95.6	95.7	95.2
Co^{2+}	$CoCl_2$	500	97.3	96.6	98.0	PO_4^{-3}	KH_2PO_4	400	95.5	98.6	101.2
Mn^{2+}	$MnSO_4$	500	96.5	98.4	96.5	Thiourea	Thiourea	200	97.2	99.7	103.0
Ag^+	$AgNO_3$	250	99.0	97.3	100.5	EDTA	Disodium-EDTA	50	98.8	97.4	99.6
Pd^{2+}	$PdCl_2$	250	98.4	99.2	95.7	Oxalate	Sodium oxalate	100	99.0	95.8	98.4
Fe^{2+}	$FeSO_4$	800	99.3	101.5	98.2	Citrate	Trisodium citrate	500	96.5	100.8	100.1

[a] In the presence of 5 mL of 10% L-ascorbic acid

[b] In the presence of F^- as masking agent

Table 3. Analysis of Ga, In and Tl ions in real samples by the proposed method

Sample	Element	Added ($\mu g\ g^{-1}$)	Found * ($\mu g\ g^{-1}$)	Recovery (%)	RSD (%)
Sediments	Ga	-	12.90	-	1.8
		2.0	14.80	95.0	1.5
		5.0	17.62	94.4	3.2
	In	-	7.84	-	2.1
		2.0	9.86	102.0	1.8
		5.0	12.74	95.0	2.1
	Tl	-	10.40	-	1.4
		2.0	12.35	97.5	2.6
		5.0	15.22	96.4	2.9
Mobile phone LCDs	Ga	-	6.41	-	2.1
		2.0	8.32	96.0	1.9
		5.0	11.32	98.4	3.1
	In	-	28.50	-	2.5
		2.0	30.50	100.0	1.4
		5.0	33.45	99.0	2.3
	Tl	-	4.65	-	1.7
		2.0	6.67	101	1.5
		5.0	9.55	98.0	2.7

* Mean value of five determinations

Table 4 Determination of Ga(III), In(III) and Tl(III) in synthetic mixtures

Composition of Synthesized mixture, mg	Ga(III)			In(III)			Tl(III)		
	Found	R, %	RSD	Found	R, %	RSD	Found	R, %	RSD
0.5 Hg(II), 0.8 Cd (II), 1.5 Zn (II)	47.6	95.2	0.87	49.5	99.0	0.60	49.0	98.0	0.80
2.5 Cu (II),1.2 Co(II), 0.8 Ni(II)	48.5	97.0	0.63	47.5	95.0	0.75	49.5	99.0	0.53
1.25 Cu(II), 1.5 Pb(II), 1.6 Ni(II)	49.0	98.0	1.20	51.0	102.0	1.60	48.6	97.2	1.40
1.5 Mg(II), 0.8 Sr(II), 0.5 Ba(II)	48.8	97.6	0.77	48.0	96.0	0.35	50.2	100.4	0.80
0.5 Al(III), 0.5 Fe(III)	48.2	96.4	1.16	47.8	95.6	0.55	48.0	96.0	0.44

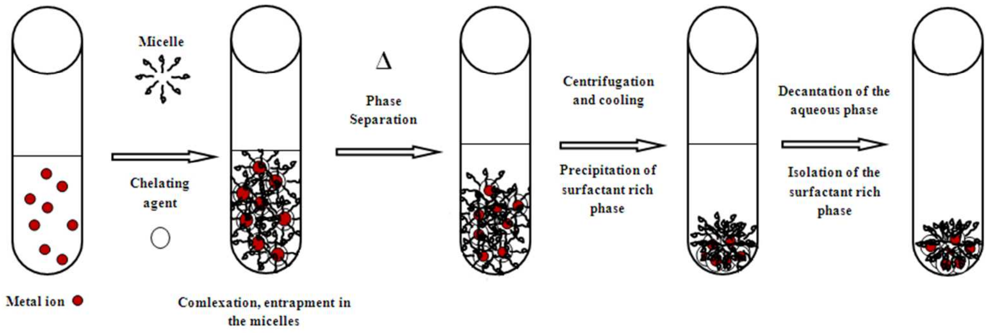
50 µg of Ga(III), In(III) or Tl(III)

Results of three determinations of each sample.

Table 5. Comparison from some separation methods recently applied for simultaneous determination of Ga(III), In(III) and Tl(III)

Sample	Analyte	Separation method	Detection technique	LOD	Linearity	RSD (%)	Ref.
water samples, zinc granules and lead sheet.	Ga, In, Tl	Sorption on amino silica gel modified by gallic acid	FAAS	5.80, 1.82, 1.11 ng mL^{-1}	7.5-150, 3.0-100, 2.5-50 ng mL^{-1}	1.6, 2.1, 1.9	[4]
Synthetic mixtures	Ga, In, Tl	Solid phase extraction using DAPCH loaded on Duolite C20 as a sorbent	FAAS	30, 13, 20 ng mL^{-1}	-	< 5	[5]
Urine and tap water	Ga, In	CPE using 5-Br-PADAP as chelating agent and Triton X-100 as surfactant	ICP-OES	0.72, 0.28 ng mL^{-1}	6–200, 2–200 ng mL^{-1}	0.3-1.6	[12]
Water samples	Tl	CPE of Tl(III) using DTPA as complexing agent and SDS and Triton X-114 as mixed surfactant system	ICP-MS	0.02 pg $mL^{-1\,*}$	2-500 pg mL^{-1}	1–3	[13]
Aqua regia extracts of sediment and coal fly ash samples.	Tl	CPE of chloro nitro Tl species from the bulk aqueous phase into a small micelles-rich phase in the presence of an electrolyte NaCl.	Continuum source ETAAS	2 pg mL^{-1}	-	-	[14]
Water samples	Tl	Microwave assisted CPE of $TlCl_3^{2-}$ using mixed surfactant (CTAB and Triton X-114)	ICP-MS	0.02 pg mL^{-1}	10-500 pg mL^{-1}	0.8–1.8	[15]
Alloy, leaves, SRM	Ga, In	With 5-Br-PADAP in cationic micellar medium	derivative spectrophotometry	0.012, 0.035 ng mL^{-1}	0.023-0.700, 0.076-1.52 µg mL^{-1}	< 1.54	[24]
Geological certified reference materials and natural water	Ga, In	A modified nanometer-sized alumina packed micro-column	FI-ICP-OES	0.19, 0.54 ng mL^{-1}	-	1.6, 1.9	[25]
Synthetic seawater, natural waters wastewater human blood, serum.	Ga, In	Affinity binding by Amberlite XAD-7 resin impregnated with a hexadentates naphthol derivative Schiff base	FAAS	2.82, 0.74 ng mL^{-1}	-	< 2.50	[26]
Water samples and human blood serum	Ga, In	adsorption on Amberlite XAD-4 resin loaded with HMPN	FAAS	3.4, 0.92 ng mL^{-1}	-	< 3.0	[27]
Water, coal, river sediment, soil and zinc samples	In	Solid phase extraction using Chromosorb 108 resin.	GFAAS	0.012 ng mL^{-1}	-	< 5.0	[28]
aluminum alloys, natural waters and urine	Ga	on-line preconcentration using a polyurethane foam mini-column	FAAS	6 ng mL^{-1}	0.02-3.00 µg mL^{-1}	3.3	[29]
Water, urine, sediment and mobile phone LCD samples	Ga, In, Tl	CPE using GA as chelating agent and Triton X-144 as surfactant	FAAS	3.50, 1.25, 0.92 ng mL^{-1}	6-150, 2-150, 2-100 ng mL^{-1}	1.4, 1.55, 1.82	Our method

5-Br-PADAP = 2-(5-bromo-2- pyridylazo)-5-diethylaminophenol, CTAB = cetyltrimethylammonium bromide, DTPA = diethylenetriaminepentaacetic acid, SDS = sodium dodecyl sulfate, DAPCH = 1-(3,4-dihydroxybenzaldehyde)-2-acetylpyridiniumchloride hydrazone, HMPN = 1-{[(6-{[(E)-1-(2-hydroxy-1-naphthyl)methylidene]amino}-2-pyridyl)imino]methyl}-2-naphthol.


Micelle
Δ
Phase Separation
Centrifugation and cooling
Decantation of the aqueous phase
Chelating agent
Precipitation of surfactant rich phase
Isolation of the surfactant rich phase
Metal ion
Comlexation, entrapment in the micelles