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Separation and Preconcentration of Trace Gallium and Indium by Amberlite XAD-7 Resin Impregnated with a New Hexadentates Naphthol-Derivative Schiff Base

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Abstract: A new chelating polymeric sorbent has been developed using impregnation of Amberlite XAD-7 resin with a newly-synthesized hexadentates naphthol-derivative Schiff base 1-[(1E,9E)-10-(2-hydroxy-1-naphthyl)-4,7-dioxa-2,9-diaza-1,9-decadienyl]-2-naphth (EHND). The impregnated resin showed high binding affinity for Ga(III) and In(III) ions and was used for their preconcentration prior to determination by flame AAS. The optimum pH values for the quantitative sorption of Ga(III) and In(III) are 4.0–6.0 and 4.5–8.0, respectively, and their desorptions can be achieved by using 5 mL of 1 M HNO_3. The sorption capacities of the resin for gallium and indium were 1.1 and 1.3 mg g^{-1}, respectively. The enrichment factor for preconcentration of gallium and indium was found to be 200. The precision of the method, evaluated as the relative standard deviation obtained by analyzing a series of ten replicates, was below 2.5% for both elements. The practical applicability of the polymer was tested with synthetic seawater, natural waters, wastewater and human blood serum.

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Keywords: Amberlite XAD-7, gallium(III), indium(III), Schiff base, solid phase extraction

INTRODUCTION

Gallium and indium have emerged as important strategic metals as they are vital for the electronic industry. Gallium and its compounds are used in the production of low-melting alloys and intermetallic compounds used in the electronic industry for manufacturing of semiconductors, lasers, special optical glasses, and thermometers (1). It is a low-order toxic element and its citrate and nitrate salts are used in medicine as tumor-scanning and antitumoral agents, respectively. The role of gallium in pharmacokinetics and its toxicity have been investigated thoroughly (2,3).

Indium is an important element in the semiconductor industry, in nuclear studies, and in the production of high purity materials (4,5). Indium and its compounds have numerous industrial applications including the manufacture of liquid crystal displays (LCD), semiconductors, low-temperature solders, and infrared photodetectors (5). Indium salts play important roles in alkaline batteries. Indium is however widely distributed in the earth's crust at low concentrations. Indium compounds damage the heart, kidney, and liver. Due to the above applications, the world production of gallium and indium is increasing and the levels of these metal ions in the environment are beginning to rise, mainly around industrial areas (6).

Thus, there is a need for specific and precise determination of gallium and indium traces in environmental and biological samples. Inductively coupled plasma mass spectrometry (7) and electrothermal atomic absorption spectrometry (8) are very capable for ultra trace analysis; however, these techniques are expensive, time consuming, and require high operator's skill. On the other hand, flame atomic absorption spectrometry (FAAS) technique (9), which is among the most common methods employed for the determination of metals in solutions, suffers from a poor sensitivity in the determination of heavy elements in real samples. This drawback can be overcome by the combination of a suitable preconcentration technique with subsequent FAAS determination. The most common preconcentration methods used for real samples are solvent extraction (10), coprecipitation (11), ion exchange resins (12) and cloud point extraction (13). These preconcentration methods provide low detection limits and also help to avoid matrix interferences in the analysis of real samples.

Solid-phase extraction (SPE) for the analysis of trace concentrations of metal ions in various samples has received much attention in recent years. This technique reduces solvent usage and exposure, disposal costs, and extraction time. Various adsorbents, such as octadecyl functional groups bonded on silica gel, C_{18} (14), glycerol–silica gel (15), chelating adsorbents (16), Amberlite XAD resins (17), Chromosorb resins (18), and other sorbents (19,20) have been used for the adsorption of metal chelates in the preconcentration and separation of metal ions.

Amberlite XAD resins have physically or chemically been loaded with the various ligands to prepare new chelating resins and explored extensively for metal enrichment. Their attractive features are easy regeneration for multiple sorption-desorption cycles, good mechanical stability, and reproducible sorption characteristics. The impregnation of polymer matrices with common chelating ligands is an easy way to design chelating collectors. Amberlite XAD-2 (21), Amberlite XAD-4 (22), Amberlite XAD-7 (23), Amberlite XAD-16 (24), and Amberlite IRC-718 (25) have been used as a support for such preparations.

Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base in 1864. The Schiff base ligands are able to coordinate metal ions through imine nitrogen and other groups usually linked to the aldehyde (26). When two equivalents of salicylaldehyde are combined with one equivalent diamine, a particular chelating Schiff base is produced, which is also called a Salen ligand. Salens are very much like porphyrins, but they are easier to prepare and as polydentate ligands are known to form very stable complexes with some metal ions (27,28). Almost all metal ions form 1:1 metal complexes with Schiff bases. The feature of Schiff bases results in geometric and cavity control of host–guest complexation and modulation of its lipophilicity, and produces remarkable selectivity, sensitivity, and stability for a specific ion. In recent years, the Salen ligands have been employed as ion carriers in a variety of analytical applications, including liquid-liquid and solid phase extractions (29,30), liquid membrane transport (31), and ion selective PVC membrane electrodes (32,33).

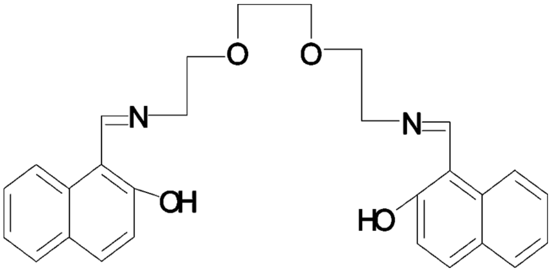

Figure 1. Structure of EHND.

In this paper we introduce a procedure for the separation and preconcentration of trace amounts of gallium(III) and indium(III) ions using Amberlite XAD-7 resin impregnated with a newly-synthesized naphthol-derivative Schiff base 1-[(1E,9E)-10-(2-hydroxy-1-naphthyl)-4,7-dioxa-2,9-diaza-1,9-decadienyl]-2-naphthol (EHND) (Fig. 1), prior to their determination by flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

Reagents

All reagents were of pro-analysis grade, purchased from the Merck Company. Gallium and indium 1000 mg L^{-1} stock solutions were supplied by Perkin Elmer. Stock solutions of diverse elements were prepared from the high purity salts of the cations (all from Merck, Germany). Amberlite XAD-7 (manufacturer Rohm and Hass Co., USA) was supplied by Sigma Aldrich. Amberlite XAD-7 is a highly crosslinked acrylic resin with surface area 450 $m^2 g^{-1}$ and particle size of 0.3–0.9 mm.

Synthesis of Schiff Base EHND

The Schiff-base ligand was prepared by a usual Schiff-base condensation in methanol (50 mL) of 2-hydroxy-1-naphthaldehyde (3.44 g, 20 mmol) with 1,8-diamino-3,6-dioxaoctane (1.48 g, 10 mmol). The solution was stirred and refluxed for 4 h. The orange precipitate was filtered, washed by a small amount of methanol and dried in vacuum. Yield 82%, m.p. 158–160°C. Anal. Calcd. for $C_{28}H_{28}N_2O_4$: C: 73.66; H: 6.18; N: 6.14%. Found: C: 73.48; H: 6.02; N: 6.25%. Main IR bands (KBr, cm^{-1}): 2955, 2908, 2863, 1617 (C=N), 1494, 1438, 1242, 1171, 847, and 832. ^1H NMR ($CDCl_3$): δ 15.2 (2H, s, –OH), 9.3 (2H, s, CH=N), 7.48 (4H, s, naphthyl), 7.52 (4H, s, naphthyl), 7.75–8.33 (4H, s, naphthyl), 2.85 (8H, t, $N-CH_2-CH_2-O-$), 3.34 (4H, t, $-O-CH_2-CH_2-O-$). In UV-visible spectra, the Schiff-base ligand exhibits two intense bands at ca. 320 and 400 nm. The former absorption at 320 nm can be assigned to the $\Pi \rightarrow \Pi^*$ transition of the benzene rings as well as the phenol rings. The latter absorption at 400 nm can be attributed to the charge transfer transition within the delocalized psystem in the molecular structure.

Apparatus

The determination of gallium and indium was performed on a Varian model Spectra AA-200 atomic absorption spectrometer using an adjusted

Table 1. Parameters for AAS determination of gallium and indium

Element	Wavelength (nm)	Slit width (nm)	Lamp current (mA)
Ga	294.4	0.5	4.0
In	303.9	0.5	5.0

air-acetylene flame. The analytical parameters for the AAS determinations of gallium and indium are presented in Table 1. A Cary-3 UV-visible spectrophotometer with 10 mm quartz cells was used to record the absorption spectra and measure the absorbance. A Metrohm model 744 digital pH meter, equipped with a combined glass-calomel electrode, was employed for the pH adjustments.

Preparation of Chelating Resin

Amberlite XAD-7 resin obtained from the supplier contained organic and inorganic impurities. To remove the contaminants, it was washed successively with methanol, water, 1.0 M HNO_3, water, 1.0 M NaOH and water. For the impregnation of the resin, 1.0 g of clean and dry XAD-7 resin beads were added to the solution of EHND in acetone (25 mL of 5×10^{-3} M) and equilibrated with constant stirring for 1 h. The Schiff base penetrated into the resin bed and was held up strongly. The amount of ligand deposited on the Amberlite XAD-7 was estimated by spectrophotometric measurements from the residual amount of Salen in the solution ($\gamma_{max} = 415$ nm). The maximum sorption of Salen on the copolymer was found as 0.042 mmol g^{-1} dry Amberlite XAD-7 resin. The treated beads were loaded in a glass column (10 cm long and 1 cm i.d.) and washed successively with methanol and deionized water for removing unadsorbed reagent.

Recommended Procedure for Preconcentration and Determination

The general procedure for the extraction of Ga^{3+} and In^{3+} ions on the impregnated resin was as follows. The column was first washed with 25 mL water. This step pre-wets the surface of the resin prior to ion extraction. Then 50 mL of the sample solution containing 20 μg Ga^{3+} and In^{3+} (pH = 5), was passed through the column (flow rate = 4 mL min^{-1}). The extracted gallium and indium was then stripped from the column using 5 mL of a 1 M solution of nitric acid (flow rate = 4 mL min^{-1})

into a 5.0 mL volumetric flask. The gallium and indium concentrations were then determined by flame atomic absorption spectrometry.

Analysis of the Real Samples

A 250 mL of tap water, well water, wastewater, and seawater samples were filtered through 0.45 μm membrane filter, adjusted to the optimum pH and subjected to the recommended column procedure for the preconcentration and determination of metal ions. For digestion of serum samples, 2 mL concentrated HNO_3 and 2 mL H_2O_2 were added to 25 mL of serum. The solution was then filtered and the general procedure was applied for the preconcentration and determination of gallium and indium.

RESULTS AND DISCUSSION

In order to obtain a clue about the stoichiometry and stability of EHND complexes with the Ga(III) and In(III) ions, preliminary studies were conducted for the investigation of the EHND complexation with the Ga(III) and In(III) ions in acetonitrile solution spectrophotometrically. In these experiments, the EHND concentration in acetonitrile was kept constant at 1.0×10^{-4} M and a concentrated Ga(III) or In(III) solution in the same solvent was then added. The UV-Visible spectra of the resulting solution at various M^{3+}/EHND mole ratios were recorded, until the desired mole ratio was reached. The corresponding spectra's and the resulting mole ratio plots obtained at 415 nm are depicted in Fig. 2. As is obvious from Fig. 2, the EHND absorption spectra show distinct inflection points upon complexation with the metal ions in the solution at a molar ratio of about 1, indicating the formation of a stable 1:1 (EHND:M(III)) complex in acetonitrile solution. The overall stability constant of the resulting 1:1 complexes was evaluated by computer fitting the absorbance vs the cation/ligand mole ratio plots to a corresponding equation (34). The resulting log K values for Ga(III) and In(III) complexes with EHND were 5.12 ± 0.07 and 4.75 ± 0.11, respectively. Based on the above observations, we decided to examine the suitability of EHND as a complexing agent for the solid phase extraction of the gallium(III) and indium(III) ions.

Effect of pH

Most chelating ligands are conjugate bases of weak acid groups and accordingly, have a very strong affinity for hydrogen ions. The pH of

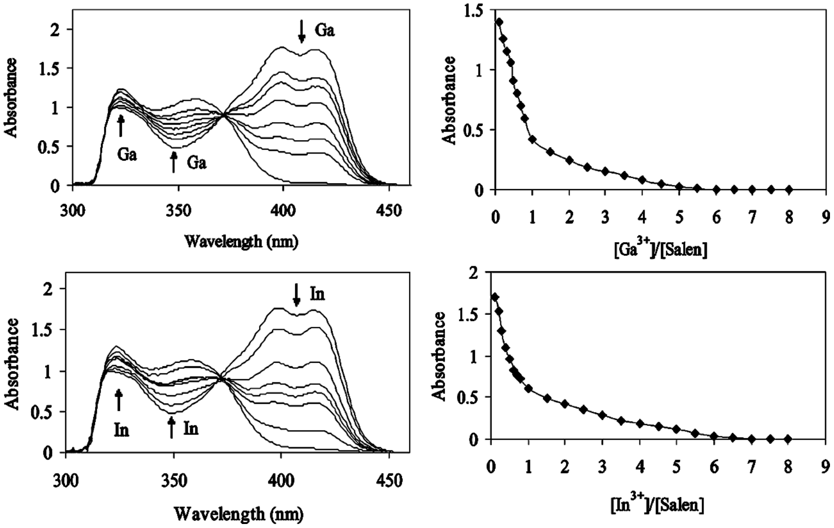

Figure 2. Absorption spectra of a 1.0×10^{-4} M EHND solution in acetonitrile upon addition of increasing amounts of gallium and indium ions together with the corresponding mole ratio plots.

the sample solution is a very important factor in the separation of metal ions by chelation, and determines the values of the conditional stability constants of the metal complexes on the surface of the sorbent. Due to the presence of two hydroxy groups on the EHND structure, it was expected that the extent of its complexation is sensitive to pH. Thus, the effect of pH on the extraction of gallium and indium ions was studied. To do this, the pH of 50 mL aqueous samples containing 20 µg Ga^{3+} and In^{3+} was varied from 2.0 to 8.0. The pH was adjusted by using 0.1 M of nitric acid and sodium hydroxide solutions. The resulting percent recovery-pH plots are shown in Fig. 3, which indicate that sorption is maximum and quantitative in the pH range 4.0–6.0 for gallium and 4.5–8.0 for indium. The decreased extraction of gallium at higher pH values may be attributed to the formation of anionic hydroxide complexes of the metal ion. Consequently, a solution pH of 5.0 was used in further experiments.

Choice of Eluent

In order to choose a proper eluent for the retained Ga^{3+} and In^{3+} ions after extraction of 20 µg of gallium and indium in a 50 mL solution by

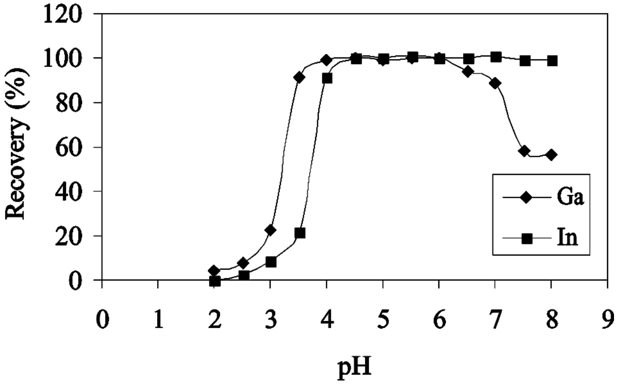

Figure 3. Effect of pH of sample solution on extraction efficiency of Ga^{3+} and In^{3+} ions. Conditions: sample volume, 50 mL; amount of Ga^{3+} and In^{3+}, 20 µg; amount of resin, 1 g; eluent, 5 mL of 1 M HNO_3; flow rate, 2 mL min^{-1}.

the impregnated resin, the gallium and indium ions were stripped with 5 mL of varying concentrations of different mineral acids, and the results are listed in Table 2. The results revealed that a 5.0 mL of 1.0 M concentration of all acids could afford the quantitative elution of Ga^{3+} and In^{3+} from the column. Subsequent elutions of Ga^{3+} and In^{3+} were carried out with 1 M HNO_3 solution. The reason for the choice of nitric acid as eluent was that nitrate ion is reported to be a more acceptable matrix for the both flame and electrothermal AAS experiments than chloride and sulfate ions (9).

Effect of Flow Rate

The effect of flow rates of the sample and stripping solutions through the Amberlite XAD-7-EHND column on the retention and recovery of

Table 2. Percent recovery of gallium and indium from the modified Amberlite XAD-7 using different stripping acid solutions

Stripping acid	Recovery (%)					
	0.1 (M)		0.5 (M)		1.0 (M)	
	Ga^{3+}	In^{3+}	Ga^{3+}	In^{3+}	Ga^{3+}	In^{3+}
HNO_3	84.2	87.4	96.6	97.0	100.0	99.8
HCl	82.6	80.9	94.1	93.5	99.8	100.0
H_2SO_4	77.3	79.8	94.8	94.4	99.6	99.1

gallium and indium was investigated. It was found that, in the range of 0.5–5.0 mL min^{-1}, the retention of gallium and indium by the impregnated resin is not affected by the sample solution flow rate. On the other hand, quantitative stripping of Ga^{3+} and In^{3+} ions from the column was achieved in a flow rate range of 0.5–8.0 mL min^{-1}, using 5 mL of 1 M nitric acid. At higher flow rates, quantitative stripping of gallium and indium required larger volumes of 1 M HNO_3. In consequence, a flow rate of 4.0 mL min^{-1} was selected for both sample loading and sample elution from the XAD-7-EHND column.

Effect of the Amount of Resin

The effect of the sorbent amount on the retention and the recovery was studied for both Ga^{3+} and In^{3+} ions and the results are shown in Fig. 4. As is seen from Fig. 4, the recovery yields increased with increasing amounts of impregnated resin up to 0.8 g and remained almost constant in the range 0.8–1.8 g. However, a further increase in the amount of sorbent resulted in some decreased recovery of the metal ions, most probably because the retained metals cannot be completely eluted with 5 mL of eluent (1 M HNO_3). According to these results, the optimum amount of resin for the column was found to be 0.8–1.8 g using 5 mL of eluent.

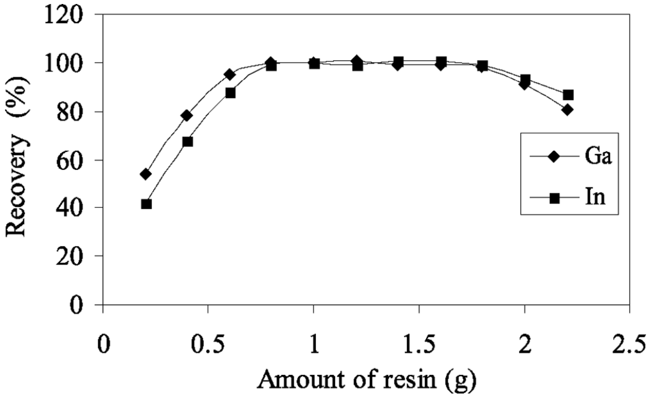

Figure 4. Effect of amount of resin on extraction efficiency of Ga^{3+} and In^{3+} ions. Conditions: sample volume, 50 mL; pH, 5; amount of metal ions, 20 µg; eluent, 5 mL of 1 M HNO_3; flow rate, 4 mL min^{-1}.

Effect of Sample Volume

In order to deal with real samples, especially water samples containing very low concentrations of the metal ions, the maximum applicable sample volume must be determined. The recoveries of 20 μg of Ga^{3+} and In^{3+} ions from different volumes of aqueous solutions are shown in Fig. 5. As seen, the recoveries were found to be quantitative until a sample volume of 1000 mL is reached; hence, 1000 mL was chosen as the largest sample volume to work. Consequently, since the final solution volume to be measured by FAAS was 5 mL, the preconcentration factors for gallium and indium ions were evaluated as 200.

Reusability of the Resin

The stability and potential reusability of the impregnated Amberlite XAD-7 resin was assessed by monitoring the change in the recovery of gallium and indium through several extraction-elution cycles (Fig. 6). For each cycle, a 100 mL sample solution containing 20 μg Ga^{3+} and In^{3+}, adjusted to a pH 5.0 was then passed through column at a flow rate of 4.0 mL min^{-1}. Gallium and indium extracted on resin was eluted with 1.0 M HNO_3 at a flow rate of 4.0 mL min^{-1}. The recoveries of Ga^{3+} and In^{3+} ions were quantitative with reproducible results up to 20 cycles using the same Amberlite XAD-7-EHND column.

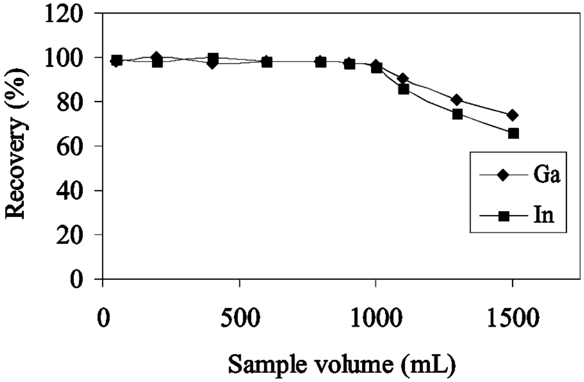

Figure 5. Effect of sample volume on extraction efficiency of Ga^{3+} and In^{3+} ions. Conditions: pH, 5; amount of resin, 1 g; amount of metal ions, 20 μg; eluent, 5 mL of 1 M HNO_3; flow rate, 4 mL min^{-1}.

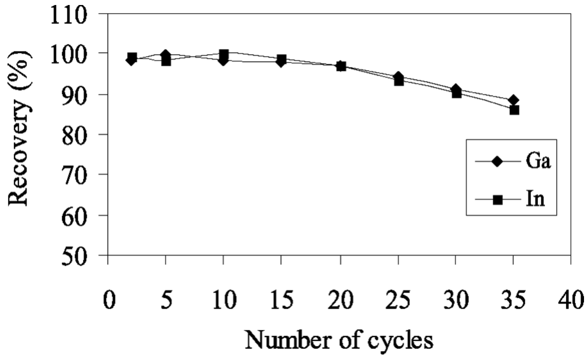

Figure 6. Reusability of modified Amberlite XAD-7 resin. Conditions: pH, 5; amount of resin, 1 g; amount of metal ions, 20 µg; eluent, 5 mL of 1 M HNO_3; flow rate, 4 mL min^{-1}.

Total Sorption Capacity

The total sorption capacity of modified Amberlite XAD-7-EHND was determined for each of Ga^{3+} and In^{3+} ions by the batch method. Here, 0.2 g of the chelating resin was equilibrated with each metal ion solution (50 mL, 50 µg mL^{-1}) for 3 h at the optimum pH. Then, the metal ions were stripped off from the resin with 10 mL of 1 M HNO_3 and their concentrations were determined with FAAS. The sorption capacities calculated for gallium(III) and indium(III) ions were found to be 1.1 and 1.3 mg g^{-1}, respectively.

Effect of Diverse Ions on the Recovery

In order to assess the possible analytical applications of the recommended procedure, the effect of foreign ions on the separation and preconcentration of gallium and indium ions was studied. A fixed amount of analytes was taken with different amounts of foreign ions and the recommended procedure was followed. The tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding ±5% in the determination of investigated analyte ions by the combination of the column solid phase extraction and the flame atomic absorption spectrometric determination methods. The results are summarized in Table 3. As it is seen, large numbers of ions used do not have considerable effect on the determination of gallium and indium ions.

Table 3. Separation of gallium and indium from binary mixtures in the presence of different diverse ions

Ion	Added as	Concentration (μg mL^{-1})	Recovery (%)	
			Ga^{3+}	In^{3+}
Na^+	NaCl	20000	98.3	98.6
K^+	KCl	5000	99.1	101.3
Ca^{2+}	$CaCl_2$	2000	98.1	96.8
Mg^{2+}	$MgCl_2$	2000	97.5	96.7
Ba^{2+}	$BaCO_3$	1000	99.3	98.6
Ni^{2+}	$Ni(NO_3)_2$	50	97.2	95.3
Mn^{2+}	$Mn(NO_3)_2$	50	98.0	98.3
Co^{2+}	$Co(NO_3)_2$	50	97.4	96.8
Zn^{2+}	$Zn(NO_3)_2$	50	97.9	98.2
Fe^{3+}	$Fe(NO_3)_3$	50	97.6	96.8
Cu^{2+}	$Cu(NO_3)_2$	50	96.4	96.2
Cd^{2+}	$Cd(NO_3)_2$	500	98.1	97.6
Pb^{2+}	$Pb(NO_3)_2$	200	97.8	98.7
Hg^{2+}	$HgCl_2$	500	99.4	100.3
Ag^+	$AgNO_3$	500	98.9	99.5
Pd^{2+}	$Pd(NO_3)_2$	500	99.4	97.4
Tl^+	$Tl_2(SO_4)$	500	100.0	98.4
Al^{3+}	$Al(NO_3)_3$	25	96.3	95.4

Conditions: sample volume, 50 mL; amount of metal ions, 20 μg; pH, 5; amount of resin, 1 g; eluent, 5 mL of 1 M HNO_3; flow rate, 4 mL min^{-1}.

Table 4. Recovery of gallium and indium from water samples ($N = 3$, sample volume: 250 mL)

Sample	Gallium amount (μg)		Recovery (%)	Indium amount (μg)		Recovery (%)
	Added	Found		Added	Found	
Tap water	0.0	BDL	–	0.0	BDL	–
	20.0	20.9 ± 0.25[a]	105	10.0	10.2 ± 0.15	102
	50.0	49.3 ± 1.05	99	20.0	20.6 ± 0.3	103
Well water	0.0	BDL	–	0.0	BDL	–
	20.0	19.5 ± 0.45	98	10.0	9.7 ± 0.35	97
	50.0	48.6 ± 0.20	97	20.0	21.3 ± 0.40	106
Seawater	0.0	BDL	–	0.0	BDL	–
	20.0	19.2 ± 0.55	96	10.0	9.6 ± 0.15	96
	50.0	47.6 ± 0.95	95	20.0	19.4 ± 0.65	97

BDL: Below the detection limit.

[a] Standard deviation.

Table 5. Recovery of gallium and indium from serum samples ($N = 3$, sample volume: 25 mL)

Sample	Gallium amount (μg) Added	Gallium amount (μg) Found	Recovery (%)	Indium amount (μg) Added	Indium amount (μg) Found	Recovery (%)
Serum 1	0.0	BDL	–	0.0	BDL	–
	20.0	19.3 ± 0.45[a]	97	10.0	10.1 ± 0.30	101
	50.0	48.4 ± 0.65	97	20.0	19.2 ± 0.55	96
Serum 2	0.0	BDL	–	0.0	BDL	–
	20.0	19.5 ± 0.40	98	10.0	9.8 ± 0.26	98
	50.0	49.7 ± 0.36	99	20.0	19.7 ± 0.25	99

BDL: Below the detection limit.

[a] Standard deviation.

Precision Studies and Limit of Detection

The limit of detection (LOD) of the proposed method for the determination of gallium and indium was studied under the optimal experimental conditions. The LOD, defined as three times the standard deviation of 10 measurements of the blank solution divided by the slope of the calibration curve and the enrichment factor, was evaluated as 2.82 and 0.74 μg L^{-1} for gallium and indium, respectively. The reproducibility of the proposed method for extraction and determination of 20 μg gallium and indium from 100 mL water was also studied. In both cases, the results obtained on 10 replicate measurements revealed a RSD of 2.5%.

Applications

The accuracy of the proposed method was tested by separation and determination of Ga^{3+} and In^{3+} ions in tap water, well water, synthetic

Table 6. Determination of gallium and indium in the wastewater samples ($N = 3$, sample volume: 250 mL)

Sample	Gallium found (μg L^{-1}) Proposed method	Gallium found (μg L^{-1}) GFAAS	Indium found (μg L^{-1}) Proposed method	Indium found (μg L^{-1}) GFAAS
Wastewater 1	BDL	BDL	32.4 ± 0.20	30.8
Wastewater 2	48.6 ± 0.45[a]	49.3	62.7 ± 0.55	64.1

BDL: Below the detection limit.

[a] Standard deviation.

Table 7. Comparative data from some studies on solid-phase extraction of gallium and indium

Analytes	System	Detection technique	Eluent	Enrichment factor	Detection limit ($\mu g\ l^{-1}$)	R.S.D (%)	Reference
In	Chromosorb 108/ bathocuproinedisulfonic acid	GFAAS	2 M HNO_3	30	0.012	<5.0	4
Ga, In	Amberlite XAD-4/5-phenylazo-8-quinolinol	XRF	–	–	81	<5.0	35
In	Naphthalene/1-(2-pyridylazo)-2-naphthol	Differential pulse polarography	1 M HCl	25	200	<1	36
Ga, In	Poly(acryl-phenylamidrazone phenylhydrazide)	ICP-AES	4 M HCl	50	–	<2.7	37
Ga	Polyurethane foam	FAAS	MIBK	40	6	<3.3	2
Ga, In	Poly(Acrylphenylamidrazone-Phenyl-Hydrazide-Acylphenylhydrazine)	ICP-AES	4 M HCl	85	–	<2.5	38
Ga	Activated carbon/8-Quinolinol	GFAAS	–	100	1	<3.2	39
Ga, In	Amberlite XAD-2/1-(2-pyridylazo)-2-naphthol	GFAAS	0.1 M HCl/2 M HNO_3	200	0.3, 2.1 $\mu g\ g^{-1}$	<4.6	40
Ga, In	Amberlite XAD-7/EHND	FAAS	1 M HNO_3	200	2.82, 0.74	<2.5	Present work

seawater, and human blood serum samples. In order to validate the method, analytes were determined in spiked real samples. The results obtained are shown in Tables 4 and 5. As is evident, the gallium and indium ions added can be quantitatively recovered from the biological and water matrices. Also, this method was applied for the determination of gallium and indium in two wastewater sample (electronic industry). The results are given in Table 6. As seen, there is good agreement between the results obtained by the proposed method and graphite furnace atomic absorption spectrometry (GFAAS) method.

Comparison of the Proposed Method with other Solid-Phase Extraction Methods

The comparative data for the figure of the merits of some previous reports (2,4,35–40) on solid-phase extraction of gallium and indium ions using various sorbents and those for the proposed method are summarized in Table 7. As is obvious from Table 7, the preconcentration factor of 200 reported in this work for the Amberlite XAD-7 impregnated with EHND for Ga^{3+} and In^{3+} ions is improved over most of the methods given in Table 7. The detection technique applied in this study (FAAS) is more available and easier to use in comparison with that used in other methods. The elution was easily performed with 5 mL of 1 M HNO_3 and there is no need to use any organic solvent for the desorption of metal ions. The lower acid concentration required for desorption of metal ions avoids the requirement of further dilution for AAS measurement and is among the advantages of the present adsorbent, which also does not suffer from the leaching problems. The low matrix effects, as is evident from the analyses of sea and well water samples and blood serum, good tolerance towards most foreign ions, and low values of relative standard deviations are the additional advantages of the present method.

CONCLUSIONS

It can be concluded that EHND loaded Amberlite XAD-7 is an effective sorbent for trace amounts of Ga(III) and In(III) ions that can be used for their preconcentration or removal from their dilute sample solutions. Under optimal conditions, quantitative sorption is achieved for Ga(III) and In(III) ions on the modified resin and these metals can be desorbed with 1 M nitric acid. XAD-7-EHND resin has high mechanical and chemical strength, as it is unaffected even after 20 cycles. The developed SPE method possesses a high potential for the separation of gallium and indium ions from host of coexisting alkali, alkaline earth, transition, and heavy metal ions. The RSD of the method is 2.5%, and the time taken for the separation and analysis of gallium and indium from a 500 mL sample is at the most 60 min. The method can be successfully applied to the separation and determination of gallium and indium in real samples.

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