Amberlite XAD-4 Impregnated With a New Pentadentate Schiff base: a Chelating Collector for Separation and Preconcentration of Trace Amounts of Gallium (III) and Indium (III)

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Abstract

A new solid-phase extraction method for separation and preconcentration of trace amounts of Ga(III) and In(III) in biological and water samples is proposed. The procedure is based on the adsorption of Ga(III) and In(III) ions on a column of Amberlite XAD-4 resin loaded with newly-synthesized pentadentate naphthol-derivative Schiff base 1-{[(6-{[(E)-1-(2-hydroxy-1-naphthyl)methylidene]amino}-2-pyridyl)imino]methyl}-2-naphthol (HMPN) prior to their determination by flame atomic absorption spectrometry (FAAS). The optimum pH values for quantitative sorption of Ga(III) and In(III) are 4.5–6.0 and 4.5–8.0, respectively, and their desorptions can be achieved by using 5 mL of 0.5 M HNO_3. The sorption capacities of the resin for Ga(III) and In(III) were 1.27 and 1.45 mg g^{-1}, respectively. The enrichment factor for preconcentration of Ga(III) and In(III) 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 3% for both elements. The proposed procedure was applied to the analysis of synthetic seawater, natural waters, wastewater and human blood serum using flame AAS.

Keywords: Solid phase extraction; Amberlite XAD-4; gallium(III); indium(III); Schiff base

1. Introduction

Gallium and indium have emerged as important strategic metals because they are vital for the electronic industry. Gallium and its compounds are used in the production of low-melting alloys and intermetallic compounds used for manufacturing of semiconductors, lasers, special optical glasses and thermometers.[1,2] It is a low-order toxic element and its citrate and nitrate salts are used as tumor-scanning and antitumoral agents in medicine. The role of gallium in pharmacokinetics and its toxicity have been investigated thoroughly.[3,4]

Indium is an important element in the semiconductor industry, in the nuclear studies and in the production of high purity materials.[5–7] Indium and its compounds have numerous industrial applications including the manufacture of liquid crystal displays (LCD), semiconductors, low-temperature solders and infrared photodetectors.[5,6] Indium salts play important roles in alkaline batteries. Indium is, however, widely distributed in the earth's crust at low concentrations. Indium compounds damage 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.[8]

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[9] and electrothermal atomic absorption spectrometry[10] are very capable for ultra trace analysis; however, these techniques are expensive, time consuming and requiring high operator's skill. On the other hand, flame atomic absorption spectrometry (FAAS) technique,[11] 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,[12,13] coprecipitation,[14,15] ion exchange and chelating resins[16,17] and cloud point extraction.[18,19] 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},[20,21] glycerol–silica gel,[22] chelating adsorbents,[23,24] Amberlite XAD resins,[25,26] Chromosorb resins[27,28] and other sorbents[29,30] have been used for 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,[31] Amberlite XAD-4,[32] Amberlite XAD-7,[33] Amberlite XAD-16[34] and Amberlite IRC-718[35] 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.[36] The Schiff base ligands are able to coordinate metal ions through imine nitrogen and other groups usually linked to the aldehyde.[37] 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.[38,39] 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 the recent years, the Salen ligands have been employed as ion carriers in a variety of analytical applications, including liquid-liquid and solid phase extractions,[40–42] liquid membrane transport [43] and ion selective PVC membrane electrodes.[44,45]

In this paper, we introduce a procedure for the separation and preconcentration of trace amounts of Ga(III) and In(III) ions using Amberlite XAD-4 resin impregnated with a newly-synthesized pentadentate naphthol-derivative Schiff base 1-{[(6-{[(E)-1-(2-hydroxy-1-naphthyl)methylidene]amino}-2-pyridyl)imino]methyl}-2-naphthol (HMPN) (Figure 1), prior to their determination by flame atomic absorption spectrometry (FAAS).
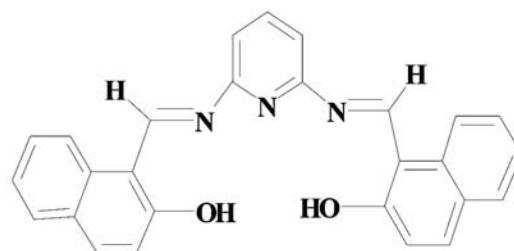

Fig. 1. Structure of HMPN

2. Experimental

2. 1. Reagents

All reagents were of pro-analysis grade, purchased from the Merck Company. Gallium (III) and indium (III) 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-4 resin (polystyrene divinyl benzene type, 20–60 mesh and surface area of 725 m^2 g^{-1}) was obtained from Aldrich. Other reagents and solvents used were of analytical reagent grade purchased from the Merck Company.

2. 1. 1. Synthesis of Schiff Base HMPN

The Schiff-base ligand was prepared by a usual Schiff-base condensation in methanol (50 mL) of 2-hydroxy-1-naphthaldehyde (10 mmol, 1.72 g) with 2,6-diaminopyridine (5 mmol, 0.55 g). The solution was stirred and refluxed for 12 h. The yellow precipitate was filtered, washed by a small amount of methanol and dried in vacuum. Yield 86%, m.p. 250 °C. Anal. Calcd. for $C_{27}H_{19}N_3O_2$: C: 77.68; H: 4.59; N: 10.07. Found: C: 77.48; H: 4.40; N: 10.22%. Main IR bands (KBr,cm^{-1}): 1620 (C=N), 1613 (C=C), 1311 and 1272 (C-O). ^{1}H-NMR (400 MHz, CDCl$_3$, internal reference TMS): δ 15.14 (2H, s, O...H...N), 9.49 (2H, s, CH=N), 7.28–7.40 (3H, d, pyridine), 7.48 (4H, s, naphthyl), 7.52 (4H, s, naphthyl), 7.75–8.33 (4H, s, naphthyl).

2. 2. Apparatus

The determination of gallium and indium was performed on a Varian model Spectra AA-200 atomic absorption spectrometer using an adjusted air-acetylene flame. The analytical parameters for the AAS determinations of gallium and indium are presented in Table 1. The operating parameters for GFAAS determination of gallium and indium (section 3.9) were set as recommended by the manufacturer given in Table 2. A Metrohm model 744 digital pH meter, equipped with a combined glass-calomel electrode, was employed for the pH adjustments. The flow rate of solution through the column was controlled using a peristaltic pump (Watson-Marlow Model 101/U/R, Falmouth, UK).

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

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.

3. Results and Discussion

To obtain quantitative recovery of gallium and indium ions on modified Amberlite XAD-4 resin, the procedure was optimized for various analytical parameters such as pH, sample volume and amounts of resin. The percentage of metal adsorbed on the column was calculated from the amounts of metal in the starting sample and the amounts of metal eluted from the column.

3. 1. 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 the sample solution is a very important factor in the separation of metal ions by chelation, and determines the values of the conditional stability

Table 2 Operating conditions for GFAAS determination of gallium and indium

Parameters	Gallium	Indium
Drying	120 °C, Ramp 10 S, Hold 20 S	120 °C, Ramp 10 S, Hold 20 S
Pyrolysis	1000 °C, Ramp 20 S, Hold 10 S	1200 °C, Ramp 20 S, Hold 10 S
Atomization	2200 °C, Ramp 0 S, Hold 5 S	2000 °C, Ramp 0 S, Hold 5 S
Cleaning	2600 °C, Ramp 1 S, Hold 3 S	2600 °C, Ramp 1 S, Hold 3 S
Sample Volume (µL)	20	
Measurement mode	Peak area	
Argon flow (mL min^{-1})	250	
Atomization site	Pyrolytic graphite-coated tubes and L'vov platforms	

2. 3. Preparation of Chelating Resin

Amberlite XAD-4 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-4 resin beads were added to 25 mL of HMPN solution (5 × 10^{-3} M in acetone) and equilibrated with constant stirring for 1 h. The Schiff base penetrated into the resin bed and was held up strongly. 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.

2. 4. Recommended Procedure for Preconcentration and Determination

The general procedure for the extraction of Ga(III) and In(III) ions on the impregnated resin was as follows.

The column was first washed with 25 mL of 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(III) and In(III) (pH = 5), was passed through the column (flow rate = 5 mL min^{-1}). The extracted Ga(III) and In(III) was then stripped from the column using 5 mL of a 0.5 M solution of nitric acid(flow rate = 5 mL min^{-1}) into a 5.0 mL volumetric flask. The gallium and indium concentrations were then determined by flame atomic absorption spectrometry.

2. 5. Analysis of the Real Samples

A 250 mL of tap water, wastewater, well water 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 of concentrated HNO$_3$ and 2 mL of H$_2$O$_2$

constants of the metal complexes on the surface of the sorbent. Due to the presence of two hydroxy groups on the HMPN 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(III) and In(III) 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 Figure 2, which indicate that quantitative recovery values for Ga(III) and In(III) ions were obtained in the pH ranges of 4.5–6.0 and 4.5–8.0, respectively. The decreased extraction of Ga(III) and In(III) 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.
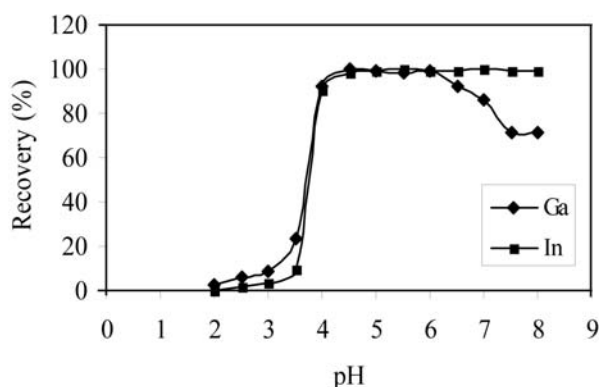

Fig. 2. Effect of pH of sample solution on extraction efficiency of Ga(III) and In(III) ions. Conditions: sample volume, 50 mL; amount of metal ions, 20 μg; amount of resin, 1 g; eluent, 5 mL of 0.5 M HNO$_3$; flow rate, 2 mL min^{-1}.

3. 2. Choice of Eluent

In order to choose a proper eluent for the retained Ga(III) and In(III) ions after extraction of 20 μg of gallium and indium in a 50 mL solution by the impregnated resin, the Ga(III) and In(III) ions were stripped with 5 mL of varying concentrations of different mineral acids, and the results are listed in Table 3. The results revealed that a 5.0 mL of 0.5 M concentration of all acids could afford the quantitative elution of Ga(III) and In(III) from the column. Subsequent elutions of Ga(III) and In(III) were car-

Table 3 Percent recovery of gallium and indium from the modified Amberlite XAD-4 using different stripping acid solutions

| Stripping acid | Recovery (%) | | | | | |
| | 0.1 (M) | | 0.5 (M) | | 1.0 (M) | |
	Ga(III)	In(III)	Ga(III)	In(III)	Ga(III)	In(III)
HNO$_3$	94.2	96.4	99.6	99.8	99.8	99.7
HCl	91.6	90.2	98.9	100.1	101.3	99.5
H$_2$SO$_4$	88.3	89.4	99.5	99.8	100.0	100.4

ried out with 0.5 M HNO$_3$ solution. The reason for choice of nitric acid as eluent was that nitrate ion is reported to be a more acceptable matrix for both flame and electrothermal AAS experiments than chloride and sulfate ions.[11]

3. 3. Effect of Flow Rate

The effect of flow rates of the sample and stripping solutions through the Amberlite XAD-4-HMPN column on the retention and recovery of Ga(III) and In(III) was investigated. It was found that, in the range of 0.5–6.0 mL min^{-1}, the retention of Ga(III) and In(III) by the impregnated resin is not affected by the flow rate of sample solution. On the other hand, quantitative stripping of Ga(III) and In(III) ions from the column was achieved in a flow rate range of 0.5–8.0 mL min^{-1}, using 5 mL of 0.5 M nitric acid. At higher flow rates, quantitative stripping of gallium and indium required larger volumes of 0.5 M HNO$_3$. In consequence, a flow rate of 5.0 mL min^{-1} was selected for both sample loading and sample elution from the XAD-4-HMPN column.

3. 4. Effect of the Amount of Resin

The effect of sorbent amount on the retention and the recovery was studied for both Ga(III) and In(III) ions and the results are shown in Figure 3. As it is seen from Figure 3, 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. If the amount of sorbent is more than 1.8 g, the retained analytes cannot be eluted completely with 5 mL of 0.5 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.
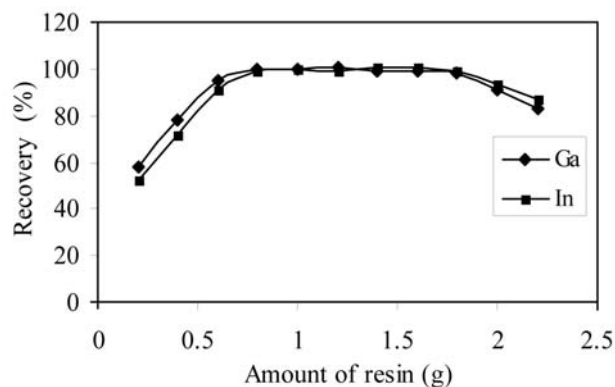

Fig. 3. Effect of amount of resin on extraction efficiency of Ga(III) and In(III) ions. Conditions: sample volume, 50 mL; amount of metal ions, 20 μg; pH, 5; eluent, 5 mL of 0.5 M HNO$_3$; flow rate, 5 mL min^{-1}.

3. 5. 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(III) and In(III) ions from different volumes of aqueous solutions are shown in Figure 4. 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. Consequently, since the final solution volume to be measured by FAAS was 5 mL, the preconcentration factors for Ga(III) and In(III) ions were evaluated as 200.
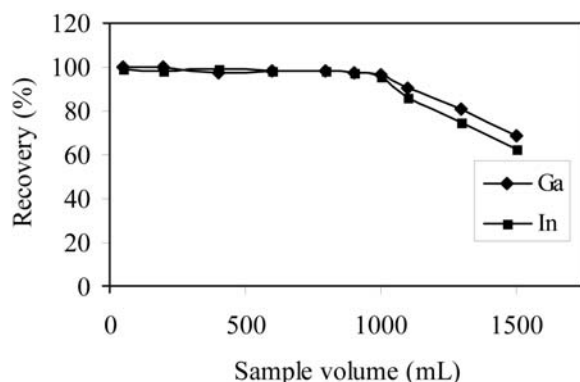

Fig. 4. Effect of sample volume on extraction efficiency of Ga(III) and In(III) ions. Conditions: pH, 5; amount of resin, 1 g; amount of metal ions, 20 µg; eluent, 5 mL of 0.5 M HNO_3; flow rate, 5 mL min^{-1}.

3. 6. Total Sorption Capacity

The total sorption capacity of modified Amberlite XAD-4-HMPN was determined for each of Ga(III) and In(III) ions using the batch mode. 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 0.5 M HNO_3 and their concentrations were determined with FAAS. The sorption capacities calculated for Ga(III) and In(III) ions were found to be 1.27 and 1.45 mg g^{-1}, respectively.

3. 7. 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 Ga(III) and In(III) ions was studied. A fixed amount of analytes was taken with different amounts of foreign ions and the recommended procedure was followed. 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 4. As it is seen, most of ions used have no considerable effect on the determination of Ga(III) and In(III) ions.

Table 4 Separation of Ga(III) and In(III) from binary mixtures in the presence of different diverse ions.

Ion	Added as	Concentration (µg mL^{-1})	Recovery (%) Ga(III)	In(III)
Na^+	NaCl	20000	99.4	99.3
K^+	KCl	5000	99.1	99.5
Ca^{2+}	$CaCl_2$	2000	98.9	98.9
Mg^{2+}	$MgCl_2$	2000	99.5	98.0
Ba^{2+}	$BaCO_3$	1000	99.8	97.7
Ni^{2+}	$Ni(NO_3)_2$	50	98.6	98.3
Mn^{2+}	$Mn(NO_3)_2$	50	98.7	97.3
Co^{2+}	$Co(NO_3)_2$	50	97.3	96.7
Zn^{2+}	$Zn(NO_3)_2$	50	98.4	98.5
Fe^{3+}	$Fe(NO_3)_3$	50	99.1	97.8
Cu^{2+}	$Cu(NO_3)_2$	50	96.4	95.3
Cd^{2+}	$Cd(NO_3)_2$	500	98.5	97.6
Pb^{2+}	$Pb(NO_3)_2$	200	97.8	98.7
Hg^{2+}	$HgCl_2$	500	99.4	99.0
Ag^+	$AgNO_3$	500	98.9	99.5
Pd^{2+}	$Pd(NO_3)_2$	500	98.3	98.4
Tl^+	$Tl_2(SO_4)$	500	100.0	98.6
Al^{3+}	$Al(NO_3)_3$	25	96.9	96.7

Conditions: sample volume, 50 mL; pH, 5; amount of Ga(III) and In(III), 20 µg; amount of resin, 1 g; eluent, 5 mL of 0.5 M HNO_3; flow rate, 5 mL min^{-1}.

3. 8. 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 3.4 and 0.92 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 3%.

3. 9. Applications

The accuracy of the proposed method was tested by separation and determination of Ga (III) and In (III) ions in tap water, well water, synthetic 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 5 and 6. As is evident, the Ga(III) and In(III) ions added were quantitatively recovered from the biological and water matrices. Also this method was applied to the determination of gallium and indium in two wastewater sample (electronic industry). The results are given in Table 7. As seen, there is good agreement between the results obtained by proposed method and graphite furnace atomic absorption spectrometry (GFAAS) method.

Table 5 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	19.3 ± 0.17[a]	97	10.0	10.1 ± 0.20	101
	50.0	51.3 ± 0.96	103	20.0	20.4 ± 0.42	102
Well water	0.0	BDL	–	0.0	BDL	–
	20.0	20.4 ± 0.34	102	10.0	9.8 ± 0.25	98
	50.0	48.5 ± 0.26	97	20.0	20.8 ± 0.35	104
Sea water	0.0	BDL	–	0.0	BDL	–
	20.0	19.1 ± 0.30	96	10.0	9.6 ± 0.15	96
	50.0	47.8 ± 0.75	96	20.0	19.3 ± 0.35	97

BDL: Below the detection limit. [a] Standard deviation.

Table 6 Recovery of gallium and indium from serum samples (*N* = 3, sample volume: 25 mL)

Sample	Gallium amount (µg)		Recovery (%)	Indium amount (µg)		Recovery (%)
	Added	**Found**		**Added**	**Found**	
Serum 1	0.0	BDL	–	0.0	BDL	–
	20.0	19.4 ± 0.35[a]	97	10.0	9.9 ± 0.45	99
	50.0	48.6 ± 0.55	97	20.0	19.2 ± 0.35	96
Serum 2	0.0	BDL	–	0.0	BDL	–
	20.0	19.6 ± 0.40	98	10.0	9.7 ± 0.35	97
	50.0	49.2 ± 0.60	98	20.0	19.8 ± 0.25	99

BDL: Below the detection limit. [a] Standard deviation.

Table 7 Determination of gallium and indium in the wastewater samples (*N* = 3, sample volume: 250 mL)

Sample	Gallium found ($\mu g\ L^{-1}$)		Indium found ($\mu g\ L^{-1}$)	
	Proposed method	**GFAAS**	**Proposed method**	**GFAAS**
Wastewater 1	BDL	BDL	29.1 ± 0.30	30.8
Wastewater 2	51.2 ± 0.35[a]	49.3	63.2 ± 0.48	64.1

BDL: Below the detection limit. [a] Standard deviation.

3. 10. Comparison of the Proposed Method With Other Solid-phase Extraction Methods

The comparative data for the figure of the merits of some previous reports[3,5,46–51] 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-4 impregnated with HMPN for Ga (III) and In (III) 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 0.5 M HNO₃ 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.

4. Conclusions

It can be concluded that HMPN loaded Amberlite XAD-4 is an effective sorbent for trace amounts of Ga(III) and In(III) ions that can be used for their preconcentration

Table 8 Comparative data from some studies on solid-phase extraction of gallium and indium

Analytes	System	Detection technique	Eluent	Enrichment factor	Detection limit (µg l$^{-1)}$)	R.S.D. (%)	Reference
In	Chromosorb 108/bathocuproinedisulfonic acid	GFAAS	2 M HNO$_3$	30	0.012	<5.0	5
Ga, In	Amberlite XAD-4/5-phenylazo-8-quinolinol	XRF	–	–	81	<5.0	46
In	Naphthalene/1-(2-pyridylazo)-2-naphthol	Differential pulse polarography	1 M HCl	25	200	<1	47
Ga, In	poly(acryl-phenylamidrazone phenylhydrazide)	ICP-AES	4 M HCl	50	–	<2.7	48
Ga	Polyurethane foam	FAAS	MIBK	40	6	<3.3	3
Ga, In	Poly(Acrylphenylamidrazone-Phenyl-Hydrazide-Acylphenylhydrazine)	CP-AES I	4 M HCl	85	–	<2.5	49
Ga	Activated carbon/ 8-Quinolinol	GFAAS	–	100	1	<3.2	50
Ga, In	Amberlite XAD-2/1-(2-pyridylazo)-2-naphthol	GFAAS	0.1 M HCl/2 M HNO$_3$	200	0.3, 2.1 µg g^{-1}	<4.6	51
Ga, In	Amberlite XAD-4/HMPN	FAAS	0.5 M HNO$_3$	200	3.42, 0.92	<3	Present work

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 0.5 M nitric acid. XAD-4-HMPN 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 below 3%, and the time taken for 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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Povzetek

Predlagana je nova metoda ekstrakcije na trdnem nosilcu za ločbo in predkoncentracijo Ga(III) in In(III) v vodi in bioloških vzorcih. Postopek temelji na adsorpciji Ga(III) in In(III) ionov na koloni polnjeni z Amberlite XAD-4 ionsko izmenjalno smolo, ki je obdelana z novo sintetizirano pentadentatno Schiffovo bazo 1-{[(6-{[(E)-1-(2-hidroksi-1-naftil) metiliden] amino}-2-piridil) imino] metil}-2-naftolom (HMPN). Sama določitev koncentracij analitov je izvedena s plamensko atomsko absorpcijsko spektrometrijo FAAS. Optimalni območji za kvantitativno adsorpcijo Ga(III) in In(III) sta 4,5–6,0 oziroma 4,5–8,0, desorpcija pa je možna z uporabo 5 mL 0,5 M HNO_3. Sorpcijski kapaciteti 1,27 mg g^{-1} za Ga(III) in 1, 45 mg g^{-1} za In(III) omogočata doseganje predkoncentracijskega faktorja 200. Relativni standardni odmik desetih zaporednih meritev je bil za oba elementa pod 3 %. Predlagana metoda je bila uporabljena za analizo naravnih in odpadnih vod, sintetične morske vode in krvne plazme.