A solid phase extraction procedure for Indium prior to its graphite furnace atomic absorption spectrometric determination

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Abstract

A procedure based on solid phase extraction of indium ions at trace level on Chromosorb 108 resin as bathocuproinedisulfonic acid chelate is presented for its preconcentration. The optimum pH value for quantitative sorption is 8.0–9.0, and desorption can be achieved by using 10.0 ml of 2 M HNO$_3$. The effects of diverse ions on the sorption and recovery of indium have been studied. The capacity of sorbent was 3.78 mg In/g resin. Recoveries for indium from water samples were in the range 95–105%. The accuracy of procedure was confirmed by indium determination in certified reference materials. The method developed was applied with varying results to the analysis of real samples including metallic zinc with satisfactory results.
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1. Introduction

Indium is an important element in the semiconductor industry, in the nuclear studies and in the production of high purity materials [1–3]. Industrial importance of indium is growing as the metal, its alloys and chemicals. Indium and its compounds have numerous industrial applications and it is currently used in the manufacture of liquid crystal displays, semiconductors, low-temperature solders and infrared photodetectors [3,4]. Indium salts play important roles in alkaline batteries. High purity indium is used in the manufacture of semiconductors while indium tin oxide is the single most important transparent conducting oxide in LCD and related technologies. Indium is however widely distributed in the earth's crust at low concentrations. It can be found associated at trace amounts to a few ores such as sphalerite (ZnS) and is mainly obtained as a by-product from zinc mining [4,5]. Indium is an impurity in aluminum, lead and zinc affects the properties of these metals [6,7]. Indium compounds damage the heart, kidney, and liver.

Matrix effects of the interfering species in the real samples and low levels of the analyte ions in real samples, a separation-enrichment procedure is necessity prior to spectrometric determination of indium and other metal ions [8–12]. Coprecipitation [7,13,14], solvent extraction [15–18] and electroanalytical techniques [19,20] have been used for the enrichment and separation of indium ions from various matrices including natural waters and metallic zinc, etc.

Solid phase extraction is one of the important techniques for the separation and preconcentration of heavy metals with various advantages including its simplicity, rapidity, short analysis time, low cost and low consumption of organic solvents, high enrichment factor and easier recovery of analyte and extractant [21–23]. Various adsorbents including polyurethane foam [1], synthetic polymers [4], naphthalene [24,25], chelating resins [26], activated carbon [27] and silicagel [28,29] were used in the solid phase extraction of indium ions from various media. Chromosorb series is a well-known stationary phase support material in gas-chromatographic separation of organic compounds and has hydrophilic properties. As a class of solid phase extraction material, important advantage of the Chromosorb series stationary phases over C$_{18}$, Amberlite XAD resins and silicagel is that they can be used strongly acidic and strongly basic pHs [30–33]. In last decade, some solid phase extraction studies for traces

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Table 1
Instrument settings and analytical conditions for GFAAS determination of indium

Wavelength (nm)	303.9
Slit width (nm)	0.7
Argon flow (ml/min)	250
Atomization site	Pyro/platform
Atomization site	Pyro/platform
Reading time	5 s
	Heating program temperature, °C (ramp time (s), hold time (s))
Drying 1	100 (5, 20)
Drying 2	140 (15, 15)
Ashing	1200 (10, 20)
Atomization	2200 (0, 5)
Cleaning	2600 (1, 3)

heavy metal ions on Chromosorb resins have been performed by various authors [31–35]. According to our literature survey, no study has been found for the usage of Chromosorb resins for indium preconcentration. Bathocuproinedisulfonic acid is a chelating agent for metal ions [36,37]. It also has been used by various researchers for the preconcentration and separation of various ions [38,39].

In the present work, solid phase extraction of the traces indium in environmental samples has been performed by using Chromosorb 108 adsorption resin. Several parameters including pH of sample solution, amount of reagents and volume of sample solution, governing the efficiency and throughput of the procedure were evaluated. The presented solid phase extraction method was applied to the graphite furnace atomic absorption spectrometric determination of indium contents of some real samples including metallic zinc and two reference standard materials.

2. Experimental

2.1. Apparatus

A Perkin-Elmer AAnalyst 700 atomic absorption spectrometer equipped with HGA graphite furnace and with deuterium background corrector was used. For graphite furnace measurements, argon was used as inert gas. The operating parameters for working elements were set as recommended by the manufacturer given in Table 1. Pyrolytic-coated graphite tubes (Perkin-Elmer part no. B3 001264) with a platform were used. Samples of $20 + 5\,\mu l$ of mixture of $0.015\,mg\,Pd + 0.010\,mg\,Mg(NO_3)_2$ as matrix modifier during the study were injected into the furnace using Perkin-Elmer AS-800 autosampler. The signals were measured as peak areas. The absolute sensitivity is defined by the mass of an element, which gives a peak absorbance of 0.0044; it was found 17 pg for In. The range of the calibration standards for indium on graphite furnace atomic absorption spectrometric determinations was 0–25 µg/l. The correlation coefficient of the calibration curves were generally 0.999.

A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. Mile-

stone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used.

2.2. Reagents

All solutions were prepared with deionized distilled water. Otherwise stated analytical-grade acids and other chemicals obtained from Merck, Darmstadt, Germany and Sigma Chem. Co., St. Louis. Stock solution of indium, containing 1000 mg/l (Sigma Chem. Co., St. Louis) was used for preparation of the standards for the calibration curve. The calibration standards were not submitted to the preconcentration procedure.

Sodium phosphate buffer (0.1 M) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 M) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6. For pH 7, sodium borate (0.1 M) buffer solution was used. Ammonium chloride buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8–10.

Bathocuproinedisulfonic acid, disodium salt solution (0.1% (m/v)) was frequently prepared by dissolving the requisite amounts of bathocuproinedisulfonic acid, disodium salt (E. Merck, Darmstadt) in water immediately before use. Chromosorb 108 resin (Sigma Chem. Co., St. Louis, USA) was purchased as 60–80 mesh (surface area: 100–200 m^2/g, pore diameter: 140 Å).

The standard reference materials used in the experimental studies were stream sediment standard reference materials (GBW 07309 and GBW 07310) from the National Research Centre for Certified Reference Materials (NRCCRM)-China).

2.3. Preparation of Chromosorb 108 column

The glass column, having a stopcock and a porous disk, was 10 cm long, and 1.0 cm in diameter. A small amount of glass wool was placed on the disc to prevent loss of the Chromosorb 108 resin beads during sample loading. Then, 0.6 g of Chromosorb 108 was slurried in water, and then poured into the column. The bed height of Chromosorb 108 in the column was approximately 20 mm. The resin was washed successively with water, acetone, and water. It was conditioned with 10–15 ml of pH 9 buffer. In order to condition of Chromosorb 108 for working pH, the resin in the column was washed with pH 9 buffer after each use.

2.4. Preconcentration procedure

The procedure was tested with model solutions prior to the determination of indium in real samples. A 50 ml of solution containing 0.25 µg of indium(III) ion was added 10 ml of buffer solution (the desired pH between 2 and 10) and then bathocuproinedisulfonic acid solution was added for complex formation. The column was preconditioned by passing buffer solution. The solution was permitted to flow through the column under gravity at the flow rate of 4 ml/min. After passing of

this solution ending, the column was rinsed with twice 10 ml of water. The adsorbed indium chelates on the column were eluted with 5–10 ml portion of 2 M HNO_3. The eluent was analyzed for the determinations of indium concentrations by graphite furnace atomic absorption spectrometer.

2.5. Procedure for the stream sediment standard reference material (SRM) sample

The presented procedure was applied for two stream sediment standard reference materials (GBW7309 and GBW7310). For this purpose, 0.25 g of stream sediment standard reference material was digested with HCl:HNO_3 (6:2) in microwave system. Digestion conditions for microwave system for the samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min. After digestion, the volume was made up to 25.0 ml with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples.

2.6. Application to real samples

The water samples analyzed were acidified with 1% HNO_3 after collection from the sources to prevent any losses from the analytes. The acidified water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pHs of the samples were adjusted to 9 with ammonia/ammonium buffer solution. Then the separation/preconcentration method given above were applied. The concentration of indium in the final solution was determined by graphite furnace atomic absorption spectrometer.

A 0.50 g of coal, river sediment, soil and 0.050 g of zinc samples were weighed and transferred to the Teflon beaker of the microwave digestion unit. Then the samples were digested with the mixture of HCl:HNO_3 (6:2) in microwave system. Digestion conditions for microwave system for the samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min. After digestion, the volume was made up to 25.0 ml with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples.

3. Results and discussion

To obtain quantitative recovery of indium ions on Chromosorb 108 resin, the procedure was optimized for various analytical parameters such as pH, sample volume and amounts of ligand. The percentage of indium adsorbed on the column was calculated from the amounts of indium in the starting sample and the amounts of indium eluted from the column.

3.1. Effects of pH on the retentions

A critical parameter in achieving quantitative adsorption and recovery of trace elements on hydrophilic absorbents is pH
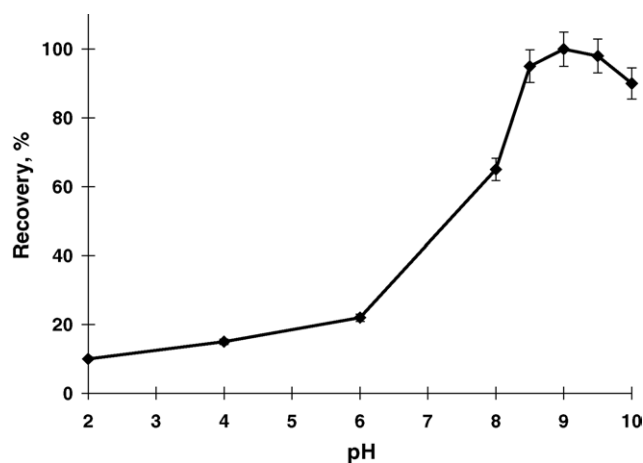

Fig. 1. The pH effects on the recoveries of indium on Chromosorb 108 resin (amounts of indium(III): 0.25 μg, sample volume: 50 ml, eluent: 2 M HNO_3, $N = 3$).

[32,33,40]. The influences of pH on the retentions of indium on Chromosorb 108 resin were investigated in the pH range of 2–10 by using 50 ml of model solutions containing 0.25 μg of indium(III). The results are depicted in Fig. 1. The recoveries of indium at the pH range of 8–9 were found quantitative (>95%). In the pH values of lower than 9, the retentions of indium on the resin were not quantitative. The volume of the buffer solution had no effect. In all further studies, 10 ml of ammonium chloride buffer solution for pH 9 was used.

3.2. Influences of ligand

The proposed method is based on the adsorption of the indium-bathocuproinedisulfonic acid chelates on the Chromosorb 108 resin. In the light of this point the influences of bathocuproinedisulfonic acid on the recoveries of indium were investigated. Firstly, the studies were performed at the pH range of 8.0–10.0 without bathocuproinedisulfonic acid. The recoveries at pH 8.0, 8.5, 9.0, 9.5 and 10.0 without ligand with buffer solution were 68%, 80%, 79%, 89% and 80%, respectively. Then the works were performed with ligand solution at pH 9.0 with ammonium buffer. Quantitative recovery values for indium ions were obtained with 2.0 ml of 0.1% and higher levels of bathocuproinedisulfonic acid. These results show that the ligand is necessity for the quantitative recoveries. On this basis, studies were carried out at 3.0 ml of 0.1% bathocuproinedisulfonic acid.

3.3. Eluent type and eluent volume

The influences of some eluents on the recoveries of indium from Chromosorb 108 were examined with the model solutions containing 0.25 μg of In(III). The results are depicted in Fig. 2. The quantitative recoveries of traces indium were obtained by using 1 M HNO_3 in acetone, 2 M HNO_3 and 2 M HCl. In all further studies, 2 M HNO_3 was preferred as eluent. The effects of volume of 2 M HNO_3 as eluent were also investigated in the range of 4.0–10.0 ml. Quantitative
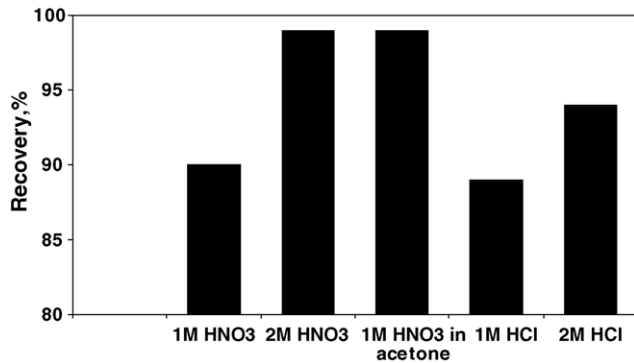
Fig. 2. Influences of the various eluents for desorption of indium ions from Chromosorb 108 column.

recovery values (>95%) for analytes obtained after 8.0 ml of 2 M HNO$_3$.

3.4. Effects of resin amount

The influences of amounts of Chromosorb 108 resin on the mini column were also investigated in the range of 0.3–1.0 g. The amounts of In(III) in the model solutions was 0.25 μg. The results are given in Fig. 3. The recovery values for indium were found quantitative in the resin amounts of 0.5–0.7 g. In all further studies, the short glass column was filled with 0.6 g of Chromosorb 108. If the amount of Chromosorb 108 is more than 700 mg, the retained indium cannot be eluted completely with 10.0 ml of 2 M HNO$_3$.

3.5. Flow rates of sample and eluent solutions

The flow rate of the sample and eluent solutions through the Chromosorb 108 column is a very important parameter, since it not only affects the recovery of indium ions, but also controls the time of analysis [30,31,34]. The flow rates were adjusted to use of the stopcock of the column. The influences of the sample flow rates were investigated in the range of 3.0–10.0 ml/min.
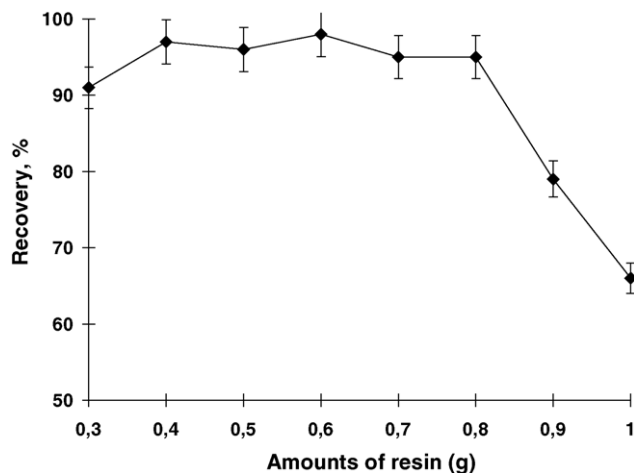

Fig. 3. Amounts of resin and recovery of indium relations (pH 9, amounts of indium(III): 0.25 μg, sample volume: 50 ml, amounts of resin: 0.6 g, eluent: 2 M HNO$_3$, N = 3).
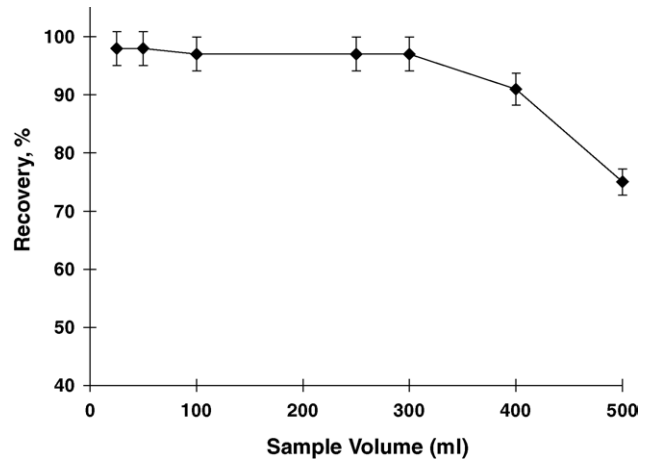

Fig. 4. The influences of sample volume (pH 9, amounts of indium(III): 0.25 μg, amounts of resin: 0.6 g, eluent: 2 M HNO$_3$, N = 3).

The amounts of In(III) in the model solutions was 0.25 μg. The retentions for the analyte ions on Chromosorb 108 were virtually quantitative for sample flow rates up to 8.0 ml/min. Variation of the elution flow rate in the range of 2.0–5.0 ml/min has no effect on the elution efficiency. In consequence, 4.0 ml/min was selected as flow rate for sample loading and sample elution from Chromosorb 108 column.

3.6. Effect of sample volume on the recoveries

The influences of the sample volume on the recovery of indium were also investigated. The amounts of indium were 0.25 μg and in the model solution, indium amounts held constant while increasing the sample volume. The effect of sample volume on the sorption of metal ions was also investigated by passing 20–500 ml volumes through the Chromosorb 108 column at pH 9. The results are depicted at Fig. 4. The adsorption of indium ions with 0.6 g resin was not affected by sample volume till 300 ml. The highest preconcentration factor was 30 for analyte ions when final volume was 10.0 ml.

3.7. Adsorption capacity

To study the adsorptive capacity of Chromosorb 108 resin, batch method was used. To 0.1 g resin was added 50 ml of solution containing 10 mg of indium at pH 9.0 with ammonia buffer. After shaking for 1 h, the mixture was filtered. A 10 ml of the supernatant solution was diluted to 100 ml and determined by atomic absorption spectrometry. The capacity of sorbent was 3.78 mg/g In.

3.8. Effect of concomitant ions

To investigate the possibility of selective recovery of indium on Chromosorb 108 resin in the presence of some metal ions and anions, the presented procedure has been performed with model solutions containing these ions. The amounts of indium were 0.25 μg. The results are given in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller

Table 2
Influences of some ions on the recoveries of indium on the Chromosorb 108 ($N = 4$, sample volume: 50 ml)

Ions	Added as	Concentration (mg/l)	Recovery of indium (%)
Na^+	NaCl	20000	96 ± 2
K^+	KCl	5000	100 ± 1
Ca^{2+}	$CaCl_2$	5000	95 ± 3
Mg^{2+}	$MgCl_2$	5000	97 ± 2
SO_4^{2-}	Na_2SO_4	3000	100 ± 2
Cl^-	NaCl	25000	100 ± 2
F^-	NaF	3000	100 ± 3
NO_3^-	KNO_3	5000	100 ± 1
PO_4^{3-}	Na_3PO_4	3000	99 ± 3
Al^{3+}	$Al_2(SO_4)_3$	25	95 ± 2
Ag^+	$AgNO_3$	25	95 ± 3
Cu^{2+}	$CuSO_4$	25	96 ± 2
Ni^{2+}	$NiSO_4$	25	97 ± 3
Cd^{2+}	$Cd(NO_3)_2$	25	96 ± 1
Fe^{3+}	$FeCl_3$	25	96 ± 2
Mn^{2+}	$MnSO_4$	25	97 ± 3
Co^{2+}	$CoSO_4$	25	98 ± 2
Pb^{2+}	$Pb(NO_3)_2$	25	95 ± 2

than ±5% related to the preconcentration and determination of analytes. The tolerable levels of the some heavy metal ions are suitable for the separation and preconcentration of the analyte ions in the real samples examined present study, because of the levels of transition metals in these samples are lower than their interferic level.

The effects of zinc ions on the recoveries of indium ions were also examined for another application of the presented method for the determination of indium contents of metallic zinc samples. The results were summarized in Table 3. Indium was quantitatively recovered till 2500 mg/l of Zn.

3.9. Figure of merits

Different amounts of indium(III) ions were added to 100 ml of water samples and table salt samples. The resulting solutions were submitted to the preconcentration procedure given in Section 2. The results are shown in Table 4. A good agreement was obtained between the added and measured analyte amounts. The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects. These results confirm the validity of the proposed method.

Table 3
Influences of zinc ions on retentions of indium ions on Chromosorb 108 ($N = 4$, sample volume: 50 ml (Zn^{2+} is added as $ZnSO_4$))

Concentration of zinc (mg/l)	Recovery of indium (%)
100	99 ± 5
500	98 ± 4
1000	97 ± 4
2500	96 ± 3
5000	90 ± 4

Table 4
Tests of addition/recovery in the experiments for indium(III) (sample volume: 100 ml, final volume: 10 ml), $N = 3$

Added (µg)	Found (µg)	Recovery (%)
Tap water		
0.10	0.10 ± 0.01	100
0.20	0.20 ± 0.01	100
0.40	0.40 ± 0.02	100
Sea water		
0.10	0.10 ± 0.01	100
0.20	0.21 ± 0.02	105
0.40	0.39 ± 0.02	98
Refined table salt (4% m/v)		
0.10	0.098 ± 0.004	98
0.20	0.19 ± 0.01	95
0.40	0.38 ± 0.02	95
Unrefined table salt (4% m/v)		
0.10	0.099 ± 0.003	99
0.20	0.20 ± 0.01	100
0.40	0.39 ± 0.02	98

Table 5
The level of indium in the standard reference materials after application of the presented procedure ($N = 4$)

Reference material	Certified value (µg/g)	Our value (µg/g)
GBW 07309 Stream sediment	0.056	0.054 ± 0.003
GBW 07310 Stream sediment	0.067	0.065 ± 0.004

Uncertainty at 95% confidence limit.

The detection limit of the present work was calculated after application of the preconcentration procedure to blank solutions. The limit of detection (LOD) for indium based on three times the standard deviations of the blank ($k = 3$, $N = 21$) on a sample volume 100 ml was 0.012 µg/l. Detection limit can be improved by larger volumes of sample.

3.10. Results for SRMs

The method was applied to two stream sediment standard reference materials (GBW 07309 and GBW 07310) for the separation and preconcentration of indium at trace level. The results in Table 5 are based on the average of four replicates.

Table 6
The concentration of indium in the real samples ($N = 4$)

Sample	Concentration
Coal	68.1 ± 0.4 µg/kg
River water	1.92 ± 0.12 µg/l
Tap water	BDL
Sea water	BDL
River sediment	21.5 ± 1.3 µg/kg
Soil	12.7 ± 0.7 µg/kg
Zinc 10021	10.8 ± 0.6 µg/kg
Zinc 10022	147.3 ± 10.2 µg/kg
Zinc 10023	85.1 ± 5.6 µg/kg

Uncertainty at 95% confidence limit. BDL: below the detection limit.

Table 7
Summary of the some solid phase extraction studies on indium

Detection technique	System	Conditions		PF	DL (µg/l)	R.S.D. (%)	Reference
		pH	Eluent				
Graphite-furnace atomic-absorption spectrometry	Chitosan	7.0–9.0	Acetic acid	100	0.04	3.5–4.5	[7]
Differential pulse polarography	Naphthalene/1-(2-pyridylazo)-2-naphthol	6.5–11.5	1 M HCl	25	200	<1	[25]
Differential pulse polarography	Naphthalene/morpholine-4-dithiocarbamate	3.5–6.4	1 M HCl	–	100	<1	[24]
X-ray fluorescence	Amberlite XAD-4/5-phenylazo-8-quinolinol	6.0–9.0	–	–	81	<5	[26]
Graphite-furnace atomic-absorption spectrometry	Activated carbon/acetylacetone	6.0–8.0	–	–	0.025	<5	[27]
Diffuse reflection spectroscopy	Nacroporous silica gel/2-(5-bromo-2-pyridylazo)-5-diethylaminophenol	4.5–4.8	–	–	–	–	[29]
Graphite-furnace atomic-absorption spectrometry	Amberlite XAD-2/1-(2-pyridylazo)-2-naphthol	6.0–12.0	0.1 M HCl/2 M HNO$_3$	200	2.1 µg/g	<4.0	[41]
Spectrophotometry	Styrene-divinylbenzene/phthalic acid	5.0–8.0	HNO$_3$	666	–	<10	[42]
Graphite-furnace atomic-absorption spectrometry	Chromosorb 108/bathocuproinedisulfonic acid	8.0–9.0	2 M HNO$_3$	30	0.012	<5.0	This Work

DL: detection limit; PF: preconcentration factor. Detection limit for indium by GFAAS without preconcentration is 0.40 µg/l.

The results are in good agreement with the certified values for indium.

3.11. Application to real samples

The presented method was applied to some real samples including waters, soil, sediment and metallic zinc samples for the separation and enrichment of indium. The results are given in Table 6. Some of the samples analyzed in the present work could be determined directly; however, to prevent the interferic effects of the real samples for the accurate determinations of indium in these samples, separation process is a necessity.

4. Conclusion

Chromosorb 108 resin is an effective material for the separation and preconcentration of indium ions in the real samples. Chromosorb 108 resin exhibits good chemical stability and reusability. The high stability of the resin permitted hundreds of adsorption–elution process along the studies without a significant decrease in the recoveries for indium ions. The method presented is most promising for indium ions as the preconcentration factor is 30. A comparison of the presented procedure and some recent preconcentration procedures for indium in the literature were given in Table 7.

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