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SCIENCE DIRECT

Talanta 66 (2005) 646–652

Talanta

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Indium determination in different environmental materials by electrothermal atomic absorption spectrometry with Amberlite XAD-2 coated with 1-(2-pyridylazo)-2-naphthol

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Received 3 June 2004; received in revised form 10 September 2004; accepted 1 December 2004
Available online 12 January 2005

Abstract

Methods were developed for indium (In) determination in complex ores by electrothermal atomization atomic absorption spectrometry using matrix modification after its separation with Amberlite XAD-2 coated with 1-(2-pyridylazo)-2-naphthol (PAN). Palladium–magnesium, nickel, and zinc nitrates were used as matrix modifiers and were compared in terms of maximum pyrolysis temperature, sensitivity and background signal. They have enhanced the absorption signals for indium, respectively eliminating the matrix interferences. The standard additions method was applied. The relative standard deviations for six replicate determinations were in the range 0.3–4.0% for indium in different ores samples for indium concentrations 7.6–209 $\mu g\,g^{-1}$. The recommended method was applied to the indium determination in real samples. The data obtained by this method were in good agreement with those obtained by ICP-AES.

Keywords: Indium determination; Electrothermal atomic absorption spectrometry

1. Introduction

Indium (In) is produced mainly from residues generated during zinc ore processing. In the middle and late 1980s, the development of indium phosphide semiconductors and indium–tin-oxide thin films for liquid crystal displays (LCD) aroused much interest; by 1992, the thin-film application had become the largest end use [1].

Therefore, it is an important element in the semiconductor industry; it is used in such high-technology applications as LCD production, and its use is expected to increase significantly during the present decade [2].

Indium is a rare element in the sense that no part of the world is especially rich in indium minerals, even in sphalerite and chalcopyrite, which are the principal sources of indium, its content ranges from less than 1 to 1000 $\mu g\,g^{-1}$. As a typically dispersed element, it enters into the composition of many rock-forming minerals and its overall abundance in the earth's crust has been estimated as 0.11 $\mu g\,g^{-1}$[3]. There is little information on its occurrence in environmental samples.

The direct determination of trace elements in environmental material-like ore samples by electrothermal atomic absorption spectrometry (ETAAS) is often strongly interfered by co-digested matrix constituents. Due to the presence of various elements in such matrices, suitable pre-concentration and separation methods are often required for the effective separations of analytes before their ETAAS determination [3,4]. In this sense, the Amberlite XAD with different chelating agents has been used to separate and pre-concentrate different metals [5,6,7].

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doi:10.1016/j.talanta.2004.12.002

In the present work, a method for the indium determination in ore samples, such as aluminium mineral, charcoal mineral, fly coal ash, copper concentrates, jarosite, etc. by electrothermal AAS after its separation with Amberlite XAD-2 coated with 1-(2-pyridylazo)-2-naphthol (PAN) was developed. Various chemical modifiers were compared in terms of maximum pyrolysis, sensitivity enhancement effect and background absorption. The accuracy and precision of the method using standard additions method were evaluated by the determination of indium in standard reference materials or the indium determination by ICP-AES.

2. Experimental

2.1. Apparatus

Measurements of pH were made with a Crison standard pHmeter with electrode (Ingold U 455). A Gilson model Minipuls 3 peristaltic pump was used for column experiments. The glass column (200 mm × 10 mm i.d.) had a coarse sintered-glass disc and stopcock at the bottom. A Perkin-Elmer model 1100B atomic absorption atomic spectrometer equipped with deuterium arc background corrector, a Perkin-Elmer HGA 400 graphite furnace and a Perkin-Elmer AS 40 autosampler were used for the measurement of samples. Indium hollow-cathode lamp operated at 20 mA, which provides a wavelength of 287.4 nm, is used. The slit width employed was 0.7 nm. All experiments with the graphite furnace were run with 20 μl samples and measurements were made based on integrate absorbance. Pyrolitic graphite-coated tubes and L‘vov platforms were used throughout. The instrumental parameters are summarised in Table 1.

2.2. Reagents

All solutions were prepared from analytical reagent grade chemicals using ultrapure water, resistivity 18 MΩ cm^{-1}, which was obtained with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Indium stock standard solution 1000 μg ml^{-1} was supplied by Perkin-Elmer.

The Amberlite copolymer (surface area 330 m^2 g^{-1}, pore diameter 90 Å and bead size 20–60 mesh) was supplied by Aldrich Chemie. The resin was washed successively with methanol, water, 1 M HNO_3 in acetone, water, 1 M NaOH and water in order to remove organic and inorganic contaminants [8].

1-(2-Pyridylazo)-2-naphthol (PAN) was supplied by Aldrich–Chemie.

The buffers used were ammonium chloride–hydrochloric acid solution for pH 2–7 and ammonium chloride–ammonia solution for pH 7–12.

Magnesium, aluminium and nickel nitrate stock standard solutions (1000 μg ml^{-1}) were supplied by Merck (Darmstadt, Germany). A Palladium stock standard solution (3.000 g l^{-1}) was prepared according to Welz et al. [9]. Ascorbic acid stock standard solution (3.000 g l^{-1}) was prepared from salt supplied by Merck. All these solutions were used as chemical modifiers.

Certified material ECO-Toxic and Essential Elements in Fly Coal Ash were both supplied by Institute of Radioecology and Applied Nuclear, Czechoslovakia.

Table 1
Temperature programme for the graphite furnace

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow (ml min^{-1})
Drying	110	10	20	300
Pyrolysis	1000	20	10	300
Atomization	1700	0	3	0 (Read)
Cleaning	2700	1	3	300

2.3. Procedures

2.3.1. Preparation of the Amberlite XAD-2 loaded with PAN

The XAD-2 copolymer (2.0 g) was added to 3.6 ml of PAN solution 0.1 M in methanol, and was diluted to 20 ml with methanol using continuous stirring during 20 min; afterwards, it was filtered off, washed with water and dried overnight at 110 °C.

The amount of PAN deposited on the Amberlite XAD-2 was estimated by determining spectrophotometric measurements from the amount of PAN left in the solution. It was found that 0.11% of the PAN had been retained in the copolymer, this corresponds to 0.201 mmol g^{-1} of dry Amberlite XAD-2.

2.3.2. Column preparation

The stopcock of the glass column (200 mm × 10 mm) was covered with a fritted glass disc. The resin column was prepared by adding a mixture of methanol–H_2O (1 + 1) slurry of Amberlite XAD-2 in a certain amount into the column (1.0 g). The height of the column section containing the resin (bed height) was 15 mm. It was conditioned with the buffer solution used for the sample prior to percolation. After elution, the resin was regenerated with a 10–15 ml of eluent and with approximately 100 ml of ultrapure water.

All chemical appliances, such as bottles columns, flask and tubes, were treated with 10% nitric acid overnight and rinsed twice with ultrapure water before use.

2.3.3. Digestion of sample

Accurately weighed 0.300–0.500 g of the samples are taken into a 30 ml Teflon container according to the kind of sample. The dissolution process is as follows.

2.3.3.1. Aluminium mineral. Add 10 ml of concentrated hydrochloric acid (37%) followed by 10 ml of hydrofluoric acid (40%) to 0.300 g of sample and cover the container with a

Teflon cover. Place this container in a sand bath, heating until dryness. Finally, add a sufficient volume of 0.1 mol l^{-1} nitric acid (67%) to dissolve the residue with gentle heating and transfer the solution into a 50 ml calibrated flask. Repeat this procedure several times. Dilute the solution to the mark with ultrapure water.

2.3.3.2. Charcoal mineral. Add 10 ml of concentrated nitric acid (67%) to 0.500 g of sample, heating until dryness. Add 5 ml H_2O_2 (30%) followed by 3 ml of hydrofluoric acid (40%) and cover the container with a Teflon cover. Place this container in a sand bath. Heat until evaporation the acidic residue, keeping bath temperature between 50 and 60 °C. Finally, add a sufficient volume of 0.1 mol l^{-1} nitric acid to dissolve the residue with gentle heating and transfer the solution to the mark with ultrapure water.

2.3.3.3. Copper concentrates. Add 10 ml of concentrated hydrofluoric acid (40%) followed by 10 ml concentrated nitric acid (67%), 10 ml concentrated sulphuric acid and 25 ml of ultrapure water and cover the container with a Teflon cover. Allow the mixture to stand overnight. Place this container in a sand bath. Heat until evaporation the acidic residue, keeping bath temperature between 50 and 60 °C. Finally, add a sufficient volume of 0.1 mol l^{-1} nitric acid to dissolve the residue with gentle heating and transfer the solution into a 50 ml calibrated flask. Dilute the solution to the mark with ultrapure water.

2.3.3.4. Iron mineral (Jarosite) and coal fly ash (ECO). Add 9 ml of concentrated hydrochloric acid (37%) followed by 3 ml concentrated nitric acid (67%) and 5 ml concentrated hydrofluoric acid (40%) and cover the container with a Teflon cover. Place this container in a sand bath. Heat until evaporation the acidic residue, keeping bath temperature between 50 and 60 °C. Finally, add sufficient volume of 0.1 mol l^{-1} nitric acid to dissolve the residue with gentle heating and transfer the solution into a 50 ml calibrate flask. Dilute the solution to the mark with ultrapure water.

2.3.3.5. Copper mineral. Add 10 ml of aqua regia (HCl + HNO_3) (3:1) and cover the container with a Teflon cover. Place this container in a sand bath. Heat until evaporation the acidic residue, keeping bath temperature between 50 and 60 °C. Finally, add sufficient volume of 0.1 mol l^{-1} nitric acid to dissolve the residue with gentle heating and transfer the solution into a 50 ml calibrate flask. Dilute the solution to the mark with ultrapure water.

2.3.4. Separation procedure

Take 3 ml of sample into a beaker and make the pH to about 6.5. Pass through the column containing 1.0 g of Amberlite XAD-2 coated with PAN at flow rate 8 ml min^{-1}. Five millilitres of the acid mixture eluent (0.1 M HCl–2 M HNO_3) was passed at the same flow rate and the contents of In was measured by ETAAS. A blank solution was treated according to the sample preparation procedure.

2.3.5. Measurements procedure by ETAAS

Eluate portions of 200–400 μl were transferred into autosampler cups, and suitable volumes of chemical modifier were also added to complete 1 ml with the acid mixture eluent. Calibration was performed over the range 0–75 μg l^{-1}. Twenty microlitres of each standard solution was injected into the atomizer and was running the sequential drying, pyrolisis, atomization and cleaning steps of the graphite furnace shown in Table 1.

3. Results and discussion

Sample ores are complex in mineral compositions, consisting of 51 types of sulphide minerals including chalcopyrite, pyrite, sphalerite, galena, etc., sulphate minerals: gypsum, barite and quarzt [10,11]. Thus, they contain iron, barium, zinc, copper, and lead as major constituents in the decreasing order, and many other minor elements. The dissolution procedure described under Section 3 was optimized according to each sample.

In order to quantify indium in sample solution containing varying amount of iron, zinc, copper and lead, and due to the high amounts of these in such material, it was necessary to separate indium from the principal matrix. The conditions for the In separation using Amberlite XAD-2 coated with PAN has been studied in a previous work [12].

Due to the necessity of the use of 2 mol l^{-1} nitric acid and −0.1 mol l^{-1} hydrochloric acid as eluent mixture, it was therefore necessary to modify the eluent matrix to eliminate serious chloride interference.

Therefore, various chemical modifiers, such as Pd–$Mg(NO_3)_2$, $Ni(NO_3)_2$, and $Zn(NO_3)_2$ were compared in terms of maximum pyrolysis temperature, characteristic mass, maximum atomization temperature, detection limit and quantification limit.

3.1. Pyrolysis and atomization temperature

Pyrolysis and atomization temperature were determining using palladium–magnesium nitrate, nickel nitrate and zinc nitrate as chemical modifiers, employing the programme shown in Table 1. The absorbance signals from aqueous standard of 75 μg l^{-3} of indium and eluate matrix, the same concentration as the mineral sample were recorded. To each solution was added:

(a) 5 μg ml^{-1} of palladium–10 μg ml^{-1} magnesium nitrate,
(b) 20 μg ml^{-1} of nickel nitrate, and
(c) 20 μg ml^{-1} of zinc nitrate.

The optimum pyrolysis and atomization temperatures obtained for each chemical modifier for an aqueous standard solution, and also for the eluate matrix were studied. The re-

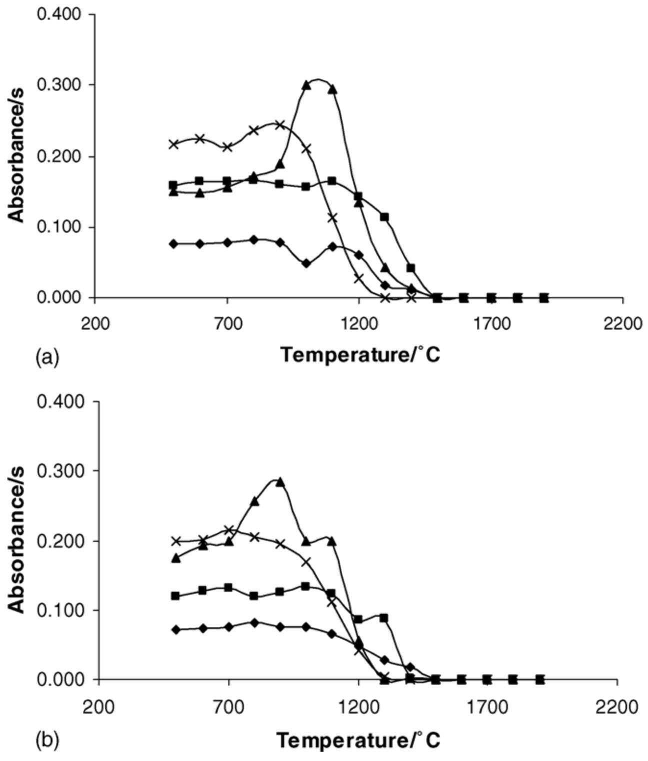

Fig. 1. Pyrolysis curves obtained for 75 μg l^{-1} In aqueous standard (a): without chemical modifier (♦); with Pd–Mg(NO$_3$)$_2$ (■); with Ni(NO$_3$)$_2$ (▲); with Zn(NO$_3$)$_2$ (×); and eluate (b): without chemical modifier (♦); with Pd–Mg(NO$_3$)$_2$ (■); with Ni(NO$_3$)$_2$ (▲); and with Zn(NO$_3$)$_2$ (×).

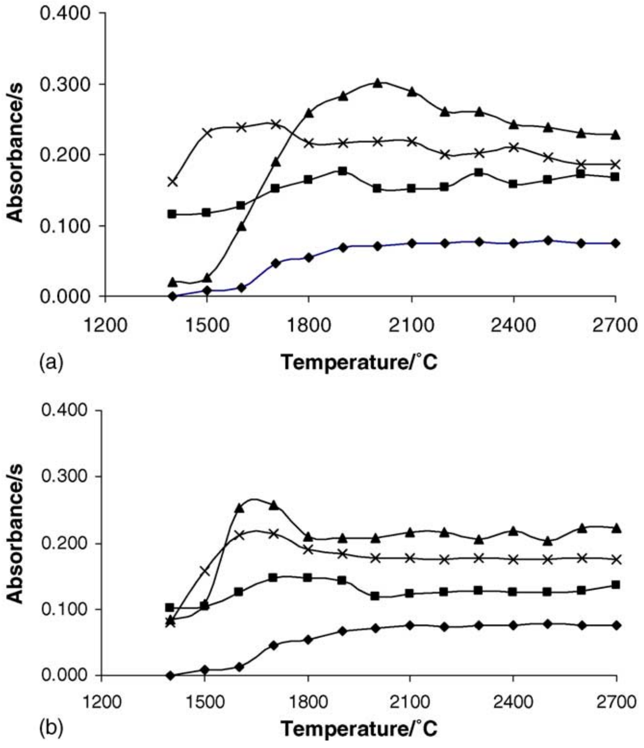

Fig. 2. Atomization curves obtained for 75 μg l^{-1} In aqueous standard (a): without chemical modifier (♦); with Pd–Mg(NO$_3$)$_2$ (■); with Ni(NO$_3$)$_2$ (▲); and with Zn(NO$_3$)$_2$ (×); and eluate (b): without chemical (♦); with Pd–Mg(NO$_3$)$_2$ (■); with Ni(NO$_3$)$_2$ (▲); and with Zn(NO$_3$)$_2$ (×).

sults obtained are shown in Figs. 1 and 2. For the aqueous standard, the behavior without the use of a chemical modifier was different for the different modifiers. The highest pyrolysis temperature was obtained with the Pd–Mg(NO$_3$)$_2$ mixture.

The optimum pyrolysis and atomization temperatures obtained for each chemical modifier for aqueous standard solution, and also for the eluate matrix for each kind of sample (copper minerals) varied between 800 and 1100 °C (aq. matrix), 700 and 1000 °C (eluate matrix), 800 and 1000 °C (copper minerals), and 1700 and 2000 °C (aq. matrix); it was kept in the same valor 1700 °C (eluate matrix) and 1700–1800 °C (copper mineral). These temperatures indicate that they do not produce an appreciable variation of the stabilization by these different chemical modifiers; in the case of aqueous matrix, the highest value of pyrolysis temperature was obtained for Ni(NO$_3$)$_2$ and for eluate matrix with the use of the Pd–Mg(NO$_3$)$_2$ mixture (Figs. 1 and 2).

On the other hand, the atomization temperature for the aqueous standards showed important differences, while for the eluate matrix there are no differences. In all these cases, the atomization temperature was 1700 °C.

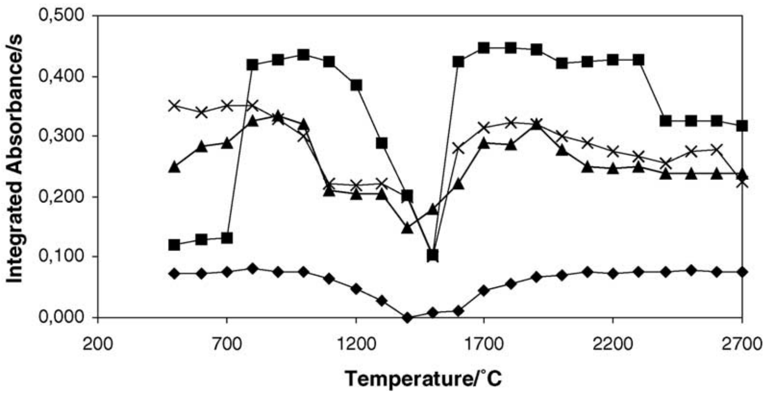

Fig. 3. Charring (left) and atomization (right) curves for copper mineral: without chemical modifier (♦); Pd(NO$_3$)$_2$ (■); with Ni(NO$_3$)$_2$(▲); and with Zn(NO$_3$)$_2$ (×).

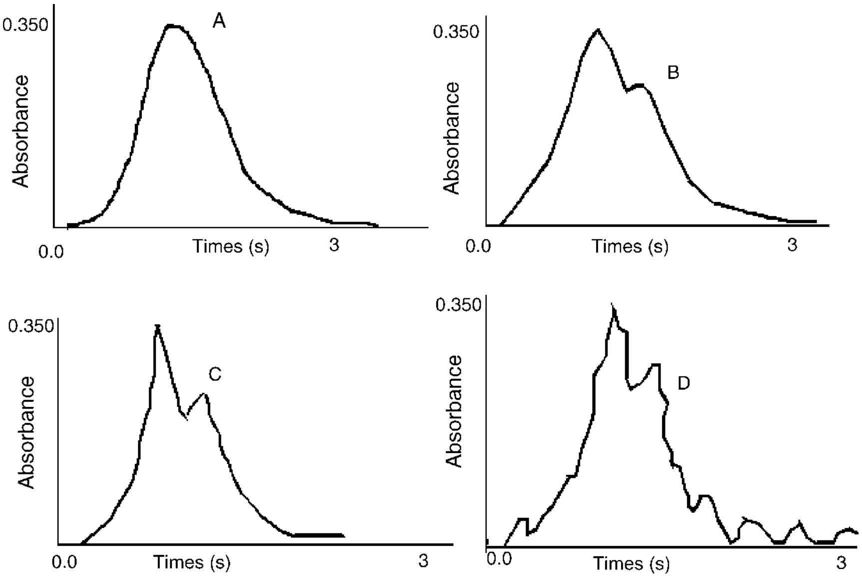

Fig. 4. Effect of atomization temperature on form of peak (A) 1700 °C; (B) 2000 °C; (C) 2300 °C; and (D) 2700 °C.

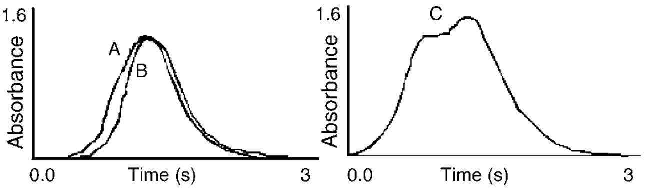

Fig. 5. Effect of Pd amount on the profile peak (A) Pd (5 μg/ml); (B) Pd (5 μg/ml)–$Mg(NO_3)_2$ (10 μg/ml); and (C) Pd (10 μg/ml).

Under the optimum pyrolysis and atomization conditions for all chemical modifiers, the background absorption was very low between 0.001 and 0.003 units of integrated absorbance.

Pyrolysis and atomization curves were also performed with a real sample of a copper mineral and the results are shown in Fig. 3. It can be seen that best stabilization was obtained with Pd–$Mg(NO_3)_2$ mixture, 1700 °C being the optimum atomization temperature. At higher temperatures than 1700 °C, the presence of double peaks was observed (Fig. 4).

The presence of magnesium in the mixture with palladium was essential in order to avoid a low analytical recovery. It can be seen that large amounts of Mg added improved the peak shape (Fig. 5). Nevertheless, when bigger Pd amounts was used, a double peak was observed (Fig. 5C). This can be explained by the presence of species between In and Pd having more refractories, and thus, difficult to atomize. Bozsai et al. [13] studied this effect; Qiao and Jackson [14] indicated that a sharper absorbance peak and in many instances, a higher recovery were obtained when Mg was also present.

3.2. Calibration and addition curves

A study of the calibration and addition graphs obtained for all chemical modifiers tested was performed. The optimum pyrolysis and atomization temperatures, related to a copper mineral sample obtained, were used with each chemical modifier. To obtain the calibration curves, suitable volume of chemical modifiers were added to standard aqueous solution to eluate matrix and copper minerals, respectively containing indium concentration in the 0–75 $\mu g\,l^{-1}$ range. The standard addition method was used for the same range of concentrations using a copper mineral sample.

The calibration slopes obtained for all chemical modifiers tested related to aqueous standard and eluate matrix were different to those achieved when a copper mineral sample was used. Thus, the standard addition method was used for the indium determination in various copper minerals.

Table 2
Characteristic mass (m_0), limit of detection (LOD), limit of quantification (LOQ) and mean R.S.D. (%) corresponding to each chemical modifier

Chemical modifier	m_0 (pg)		LOD ($\mu g\,l^{-1}$)		LOQ ($\mu g\,l^{-1}$)		Mean R.S.D. (%)	
	Eluate matrix	Copper mineral	Eluate matrix	Copper mineral	Eluate matrix	Copper mineral	Eluate matrix	Copper mineral
$Pd/Mg(NO_3)_2$	18.1 ± 1.4	0.5	0.30	2.6	0.98	7.0	–	0.9
$Ni(NO_3)_3$	24.0 ± 0.2	0.3	0.68	4.1	2.25	13.5	–	0.3
$Zn(NO_3)_2$	21.7 ± 0.8	0.3	0.86	2.30	2.86	7.5	–	0.07

3.2.1. Sensitivity

A study of the sensitivity achieved for each chemical modifier was performed. The pyrolysis and atomization temperatures employed were related to copper mineral sample. The LOD was three times the standard deviation (S.D.) of 11 replicates of the blank of the addition, and the slope used for each case was the slope of standard addition graph.

In Table 2 is shown the characteristic mass (m_0), limit of detection (LOD), and limit of quantification (LOQ) [12] obtained for each chemical modifier.

As can be seen, the use of palladium–magnesium nitrate offers the best sensitivity (LOD between 0.3 and 2.6 $\mu g\, l^{-1}$) in comparison with nickel and zinc nitrates.

3.2.2. Precision

The within-batch precision is expressed as R.S.D. (%) obtained for 11 replicates of three copper mineral samples digestion spiked with different concentrations of indium (0, 25, 50 $\mu g\, l^{-1}$). These amounts were investigated for each chemical modifier at the above concentrations. Results are shown in Table 2.

3.2.3. Accuracy

The accuracy of the methods using $Pd/Mg(NO_3)_2$, nickel and zinc nitrates was studied by the analytical recoveries of standard additions, corresponding to 0, 25, 50, 75 and 100 $\mu g\, l^{-1}$ added to a copper mineral since the digestion procedure. In all cases good recoveries has been obtained (Table 3).

Table 3
Analytical recovery

Chemical modifier	In added $\mu g\, l^{-1}$	In found $\mu g\, l^{-1}$	Recoveries (%)
$Pd/Mg(NO_3)_2$	0	–	–
	25	24.3	97.2
	50	50.1	100.2
	75	74.6	99.5
	100	100	100.0
$Ni(NO_3)_2$	0	–	–
	25	25.4	101.6
	50	51.3	102.6
	75	73.7	97.7
	100	98.4	98.4
$Zn(NO_3)_2$	0	–	–
	25	25.0	100.0
	50	49.1	98.0
	75	76.0	101.3
	100	99.9	99.9

3.2.4. Interferences

A comparison was made between the maximum concentrations of interference achievable with these chemical modifiers under the optimum ETAAS operating conditions. The major components for each samples and chloride ion were chosen as possible interferents. The reasons for this choice were as follows.

(1) The mineral samples obtained from natural deposit contained as major constituents 30–40% of iron, copper, sulphur, aluminium, calcium, cadmium, magnesium, lead, zinc, etc.
(2) Due to presence of acidic mixtures (2 $mol\, l^{-1}$ HNO_3–0.1 $mol\, l^{-1}$ HCl) in the eluent mixture, the interference produced by halides is known.

In order to examine the applicability of the recommended method for the real sample analyses, a series of experiments were undertaken to test the interference effects of a variety of foreign ions. To 133 μl of 75 $\mu g\, l^{-1}$ In solution containing 20 $\mu g\, ml^{-1}$ of each chemical modifier, the same volume of various foreign ions was introduced to the pyrolytically coated graphite furnace and the ETAAS procedure was followed.

The results for the permissible maximum concentrations are listed in Table 4. The abilities of the three modifiers to remove these interferences including Cl^- interference were similar for these three chemical modifiers ($Pd/Mg(NO_3)_2$, $Ni(NO_3)_3$ and $Zn(NO_3)_2$).

3.2.5. Application

The method of $Pd/Mg(NO_3)_2$ as chemical modifier was applied to the determination of indium in different mineral

Table 4
Effect of various interferent ions on the recovery of 75 $\mu g\, l^{-1}$ of indium

Interferent	Maximum concentration of interferent ion ($\mu g\, ml^{-1}$)	Variation of signal of In		
		$Pd/Mg(NO_3)_2$	$Ni(NO_3)_2$	$Zn(NO_3)_2$
Al^{3+}	2307	+12.0	+11.0	+19.4
Ca^{2+}	680	+1.5	+3.0	+3.0
Cd^{2+}	500	−1.2	−3.0	−5.0
Cu^{2+}	750	+15.0	−20.0	+10.0
Fe^{3+}	864	+23.0	+15.0	+26.0
Mg^{2+}	480	+4.0	+15.0	+5.0
Mn^{2+}	500	−58.6	−17.0	−35.0
Ni^{2+}	900	+45.0	+18.0	+50.0
Pb^{2+}	800	−11.0	−8.6	−9.0
Zn^{2+}	900	+20.0	+36.0	+22.2
Cl^-	1775	−15.9	−13.6	−13.2
$SO_4{}^{2-}$	416	+2.8	+11.0	+12.0

Table 5
Results for In determination in different minerals obtained ($n = 6$)

Sample	X (αg g^{-1})	±CL[a] (αg g^{-1})	S.D. (αg g^{-1})	R.S.D. (%)	ICP-AES (αg g^{-1})
Aluminium mineral	9.5	±0.3	0.256	2.7	9.7 ± 0.8
Charcoal mineral	7.6	±0.3	0.301	4.0	7.6 ± 0.3
Copper concentrates (Minas de Matahambre)	120.4	±1.2	0.753	0.6	120.8 ± 1.2
Copper concentrates (Mina Grande del Cobre)	209.2	±1.9	2.8	1.3	212.8 ± 1.3
Copper mineral	184.4	±2.7	2.54	1.4	185.9 ± 2.6
Iron mineral (Jarosite)	125.3	±0.4	0.421	0.3	126.7 ± 0.8
Coal fly ash (ECO)	34.9	±1.3	1.21	3.5	35.1 ± 1.9

[a] Confidence level of 95%.

samples. The standard addition method was used as evaluation method. The indium concentrations obtained are given in Table 5.

The results obtained by this method were compared to those found by ICP-AES, and there is no significant difference between both results (paired *t*-test for a confidence level of 95%).

4. Conclusion

The use of palladium/magnesium nitrate for indium determination after its pre-concentration on Amberlite XAD-2 coated with PAN in different mineral samples provides more consistent performances than the use of nickel nitrate and zinc nitrate. The recovery yields obtained with standard solutions in the presence of interferents were always higher than 95%, thus confirming the accuracy of the procedure and its independence from matrix effects. The results obtained in the analysis of In in different mineral samples indicate a relative error <5% for In determination using this method.

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