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Determination of trace impurities in some nickel compounds by flame atomic absorption spectrometry after solid phase extraction using Amberlite XAD-16 resin

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Abstract A simple flame atomic absorption spectrometric (FAAS) procedure for the determination of lead, bismuth, gold, palladium and cadmium as impurities in Raney nickel and nickel oxide was developed using a preconcentration step on an Amberlite XAD-16 resin packed column. Lead, bismuth, gold, palladium and cadmium were quantitatively recovered and separated from a solution containing 1 M HCl and 0.3 M NaI by the column system. Effects of the various parameters such as reagent concentrations, sample volume, matrix effects, etc. have been investigated. Under optimized conditions, the relative standard deviation of the combined method of sample treatment, preconcentration and determination with FAAS ($n = 7$) is generally lower than 12%. The limit of detection (3s, $n = 20$) was between 10–270 ng/g. The results were used for separation and preconcentration of five trace elements from nickel matrices.

Introduction

The mechanical, electrical, catalytic or chemical properties of metallic nickel, nickel-base alloys, compounds and catalysts can be affected by certain impurities [1]. Therefore, the determination of trace impurities in these materials is important. The direct determination of lead, bismuth, gold, palladium, cadmium and silver in nickel compounds by FAAS is difficult because of the matrix effects and the low levels of those elements present [2, 3]. To avoid matrix effects, the trace impurities must generally be separated prior to their determinations. The separation of some elements as impurity from nickel-based products

has been carried out using ion exchange [2, 4, 5], hydride generation [6–8], coprecipitation [9, 10], solvent extraction [11] and adsorption [3, 12, 13]. On the other hand, a method which allows to adsorb chemical species directly onto a solid phase as an adsorbent provides an effective separation.

Several authors reported that the trace metals as various complex forms were adsorbed onto Amberlite XAD-2, XAD-4, XAD-7, XAD-1180 and XAD-16 resins and the metals can be easily separated from matrix components [14–19]. These resins adsorb complexes formed between trace metal ions and inorganic ligands as well as metal chelate complexes. The adsorption of inorganic complexes on the resins is advantageous concerning the adsorption capacity because the free inorganic ligands are not retained. Especially, the metal halogeno complexes can be selectively adsorbed on these resins. The applications based on the retention of halogeno complexes on Amberlite XAD-16 resin are limited for the isolation of trace metal ions from matrix components. However, Amberlite XAD-16 has not been widely used for the preconcentration of trace heavy metal ions as inorganic complexes.

In this work, the retention of trace metal ions as a mixture of iodo complexes on a column filled with Amberlite XAD-16 resin was investigated for the subsequent determination of some metal ions in nickel and nickel compounds. The optimum conditions for retention were also discussed.

Experimental

Apparatus. The measurements were carried out by means of a Perkin-Elmer Model 3110 atomic absorption spectrometer, using an acetylene-air flame. All measurements were carried out without background correction. The instrumental parameters and operating conditions were set as recommended by the manufacturer.

Reagents. All reagents were of analytical-reagent grade, unless stated otherwise. Doubly distilled water was used for the preparation of the reagent solutions. Metal stock solutions of the working elements, containing 1000 mg/L were prepared by dissolving their

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respective nitrates in 1% (w/w) HNO_3 , and diluting with water. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with 1 M HCl. Sodium iodide (suprapur) used to prepare the solutions of NaI and acetone (extra pure) used for elution were purchased from Merck, Darmstadt. Concentrated hydrochloric and nitric acids were from Merck in extrapure quality.

Resin and column preparation. Amberlite XAD-16 resin (particle size, 20–40 mesh; Sigma Chem. Co., St. Louis) was ground and sieved to 80–100 mesh fraction. It was washed successively with methanol, water, 1 M HNO_3 in acetone, water, 1 M NaOH and water, respectively.

A short glass column with an inner diameter of 10 mm and a length of 100 mm, equipped with porous frits, was filled up to a height of about 25 mm with a suspension of 400 mg Amberlite XAD-16 resin in water. Prior to use, the resin was preconditioned with a high-purity solution of 0.3 M NaI and 1 M HCl. After each experiment, the column was rinsed with water and stored for the next experiment.

Test procedure for preconcentration. Volumes of 25–150 mL of spiked solutions containing 2 μg Cd, 5 μg Cu, Ni, Pd, Ag and Au, 10 μg Fe, Pb and Bi were used. The solutions were prepared in a mixture of 1 M HCl and 0.3 M NaI unless stated otherwise. The solution was passed through the column at a flow rate of 10 mL/min., the retained analyte ions were eluted by 8–10 mL of acetone at a flow rate of 2–3 mL/min. Then, the eluate was carefully evaporated to 1–2 mL. The solution was transferred into a 5 mL volumetric flask with 1 M HCl solution. The analytes in the final solution were determined by FAAS.

Analysis of Raney nickel and nickel oxide. 0.5–1.5 g of Raney nickel or nickel oxide were suspended in 2 mL water and decomposed in 2–20 mL *aqua regia*, nearly evaporated to dryness and the residue was dissolved in 75–100 mL 1 M HCl containing 0.3 M NaI. The analytes in this solution were determined by applying the preconcentration procedure given above.

Results and discussion

Effect of HCl and NaI concentration

A thorough understanding of the extraction behavior of different metal ions possibly present in given samples is necessary before a system can be firstly used for preconcentration and/or matrix isolation of metal ions. Recovery profiles for metal ions with HCl or HCl plus NaI give insight into the selectivity of XAD-16 resin and help to choose the practical operating parameters. As can be seen from Fig. 1, gold, iron and silver with $R \geq 50\%$ were only partly recovered from hydrochloric acid solutions. Especially at high HCl concentrations such as in the range of 5–10 M HCl, the recovery for iron was nearly quantitative ($R \geq 95\%$). The recovery values for the other elements were not almost effected from the increasing concentration of HCl and were under 40%.

To increase the number of elements quantitatively recovered, the effect of NaI concentration on the retention was also investigated in the presence of 1 M HCl. The results are shown in Fig. 2. The recoveries of lead, bismuth, gold, palladium, cadmium and silver could be increased up to nearly quantitative values ($\geq 95\%$) with concentration ranges of 0.1–0.4 M NaI in the presence of 1 M HCl. The recovery value for Cu was quantitative only in the

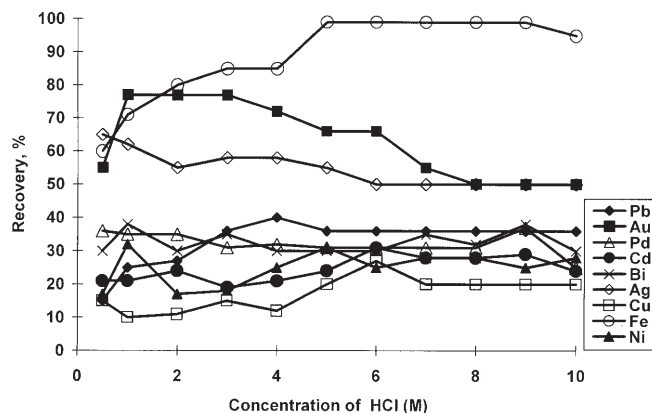


Fig. 1 Effect of HCl concentration on the recoveries of the working elements ($n = 4$, sample volume : 25 mL, eluent: acetone)

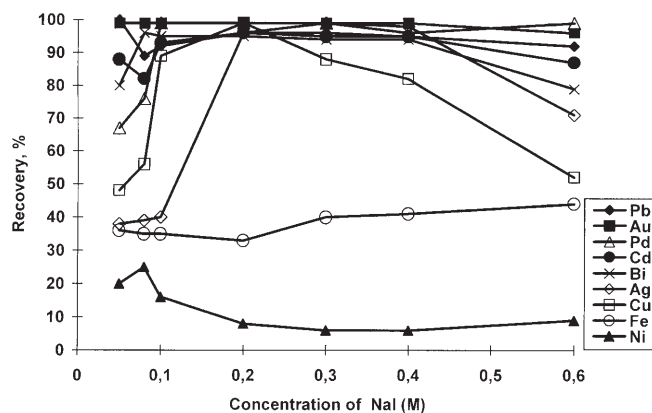


Fig. 2 Effect of NaI concentration on the recoveries of the working elements ($n = 4$, concentration of HCl: 1 M, sample volume: 25 mL, eluent: acetone)

presence of 0.2 M NaI. As known, Cu(II) is reduced to Cu(I) by iodide in acidic solution giving the scarcely soluble CuI. However, CuI is dissolved in the presence of excess iodide by the formation of CuI_2^- . Accordingly, the retention of copper increases with increasing concentration of NaI, due to the formation of CuI. All of Cu(II) in the solution is reduced to CuI in the presence of 0.2 M NaI. Thus, quantitative retention for Cu is obtained. The retention of copper decreases due to the formation of CuI_2^- , with increasing of NaI > 0.2 M. It might be concluded that copper was retained as Cu(I) by Amberlite XAD-16 resin.

It can be concluded that there is a considerable decrease in the recoveries of iron because of the reduction of Fe (III) to Fe (II) by iodide. The effect of 0.5, 1, 2 and 4 M HCl on the recoveries of lead, bismuth, gold, palladium and cadmium were also investigated using 0.1–0.6 M NaI. The recovery values obtained with each acid concentrations were almost the same. The improvement observed in the recoveries by adding of NaI to the HCl solutions might be due to a synergistic effect that is very well known in solvent extraction [20]. The increase in the recoveries of some analytes can be explained by formation of more stable complexes with iodide than with chloro-

ride. As a result, the optimum concentrations of NaI and HCl were taken as 0.3 M and 1 M, respectively. Nickel was not recovered under the optimum conditions. These results show that lead, bismuth, gold, palladium, cadmium and silver can be selectively separated from the nickel compounds.

Sample and eluent flow rates

Sample and eluent flow rates are important parameters to obtain quantitative retention and elution, respectively. The retentions for the analytes were quantitative up to a sample flow rate of 15 mL/min. As in our previous studies [16, 18, 21] it was found that acetone was the most suitable eluent for the elution of the analytes retained using inorganic and organic ligands on the Ambertite XAD-16 resin column. The minimum volume of acetone required for the quantitative elution of the retained analyte complexes was found to be 8.0 mL. Variation of the elution flow rate in the range of 1.0–4.0 mL/min has no effect on the elution efficiency.

Effect of sample volume

In the analysis of a real sample using preconcentration, the sample volume is one of the important parameters to obtain high concentration factors. Therefore, the effect of sample volume on the retention behavior of the analytes examined was studied by varying the sample volume from 25 mL to 150 mL prepared using 0.3 M NaI and 1 M HCl, containing 2–5 µg of analyte depending on the elements studied. According to the results given in Table 1, the recoveries of copper and silver are considerably influenced by an increasing volume and distinctly decrease using volumes of more than 25 mL. Palladium, lead and cadmium were quantitatively preconcentrated up to 125 mL. Gold and bismuth have nearly 100% recovery values up to the examined maximum volume of 150 mL.

Effect of matrix components

The findings above showed that lead, bismuth, gold, palladium and cadmium can be selectively separated from

Table 1 Influences of the sample volume on the recoveries of Pb, Cd, Bi, Pd, Au and Ag ($n = 3$)

Sample volume (mL)	Recovery (%)						
	Pb	Cd	Bi	Pd	Au	Ag	Cu
25	92	96	92	96	97	98	95
50	96	99	100	99	100	72	68
75	96	99	93	99	100	56	28
100	95	96	95	97	100	28	20
125	73	76	97	76	100	20	13
150	70	65	96	64	100	25	10

Table 2 Effect of nickel compounds on recovery ($n = 3$, sample volume 50 mL)

Sample	Concentration of Ni ²⁺ (mg/mL)	Recovery, %				
		Pb	Cd	Bi	Pd	Au
Ni(NO ₃) ₂ · 6H ₂ O	20	95	100	98	97	100
	30	96	100	97	97	101
	50	98	100	95	96	105
	100	43	94	54	103	110
NiSO ₄ · 7H ₂ O	20	94	98	96	94	100
	30	96	105	92	96	104
	50	105	108	97	96	100
	100	74	104	48	80	104
NiCl ₂ · H ₂ O	20	95	102	93	96	102
	30	97	107	55	94	102
	50	96	104	94	108	106
	100	65	108	68	40	105

the nickel containing matrices (Fig. 2). To investigate the effect of high concentrations of various nickel compounds on the recovery of the elements examined, the procedure has been carried out with 50 mL of sample solutions containing 1.0 to 5.0 g Ni (II) as nitrate, sulfate and chloride (Table 2). Lead, bismuth and palladium can be preconcentrated quantitatively up to 50 mg/mL Ni (II). In the working range of Ni (II) from 20 mg/mL to 100 mg/mL, the recoveries of cadmium and gold were quantitative. No influence from the anions such as nitrate, sulfate and chloride was observed. The analysis of the eluates showed residual nickel of 25–125 µg/mL for a sample solution with an initial nickel amount of 20–100 mg/mL. According to these data, it can be concluded that lead, bismuth, gold, palladium and cadmium in nickel matrices can be determined by the procedure proposed.

Analytical performance of the method

The analytical performance of the proposed procedure can be shown for the results from FAAS measurements. The relative standard deviations ($n = 10$) in the case of 16–18 µg/L of the ions examined in 100.0 mL sample volumes were found to be lower than 12%. The recoveries obtained for lead, bismuth, gold, palladium and cadmium with the model solutions in doubly distilled water and in the presence of nickel salts as interferent up to 50 mg/mL were higher than 95%, thus confirming the accuracy of the procedure. The detection limits ($3s$, $n = 20$) for lead, cadmium, bismuth, palladium and gold were found to be 90, 10, 270, 30 and 40 ng/g, respectively.

Application

The procedure proposed was applied to the determination of lead, bismuth, gold, palladium and cadmium in Raney

Table 3 Commercial Raney nickel and nickel oxide analysis ($n = 5$)

Sample	Concentration ^a ($\mu\text{g/g}$)				
	Pb	Bi	Pd	Au	Cd
Raney nickel	11.231 ± 0.906	5.692 ± 0.609	N.D.	N.D.	N.D.
Nickel oxide	0.099 ± 0.006	0.470 ± 0.062	N.D.	N.D.	N.D.

^a $\pm t.s/\sqrt{N}$, N.D.: Not Detected

nickel and nickel oxide. Average values and confidence limits are summarized in Table 3. The concentration found for lead were less than the contents guaranteed by the distributor of the reagents, typically $< 0.005\%$ for lead in NiO. The relative standard deviations for lead and bismuth were in the range of 8.1–12.8%. A reference procedure was applied to the determination of gold and palladium in the samples [3]. The gold and palladium contents of nickel oxide and Raney nickel were also not detected by the reference procedure.

Conclusions

The application of the procedure proposed showed that lead, bismuth, gold, palladium and cadmium can be effectively separated/preconcentrated from Raney nickel and nickel oxide on Amberlite XAD-16 columns. The method may be used for the preconcentration of traces of heavy metals from other matrices, such as natural water samples and geological materials, etc. after a thorough investigation of the effects of the matrix ions on the recoveries of lead, bismuth, gold, palladium and cadmium.

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