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Application of Sorbent Extraction for Preconcentration/ Separation of Trace Amounts of Cadmium(II), Silver(I), Gold(II) and Lead(II) from Metallic Zinc Samples and Their Determinations by Atomic Absorption Spectrometry

A. UZUN, M. SOYLAK*, L. ELCI† and M. DOGAN‡
Erciyes University, Faculty of Art and Science, Department of Chemistry
38039, Kayseri, Turkey
E-mail: soylak@erciyes.edu.tr

The determinations of cadmium(II), silver(I), gold(II) and lead(II) in metallic zinc samples were performed using separation-preconcentration procedure on an Amberlite XAD-16 adsorption resin column. Cadmium, silver, gold and lead were quantitatively recovered and separated from a solution containing 1 M HCl and 0.3 M NaI. Effects of the matrix have been investigated. The recoveries of interesting elements wre found to be in the range of 95–103% through the use of proposed method. The procedure was successfully applied to the determination of trace impurities in four metallic zinc samples (recoveries > 95%, relative standard deviations < 10).

Key Words: Preconcentration, Separation, Metallic zinc, Amberlite XAD-16, Atomic absorption spectrometry.

INTRODUCTION

The properties of the high purity materials, catalyzers and alloys etc. are affected by their impurities and doping elements[1–5]. By using modern analytical techniques like inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption spectrometry (GFAAS) etc., the determinations of impurities in the high metal content samples can be easily performed. However, the main disadvantage of the direct graphite furnace atomic absorption spectrometric determination of the metal impurities in the high metal content samples is the strong contamination with the matrix metal in the graphite furnace[6–8]. This point is an important determination of the matrix metal in the other samples. In order to prevent this problem, an enrichment and separation technique is used[9–11].

†Pamukkale University, Faculty of Art and Science, Department of Chemistry, 20020, Denizli, Turkey.
‡Hacettepe University, Faculty of Science, Department of Chemistry, 06532, Ankara, Turkey.

Adsorption, chromatography, coprecipitation, electrolytic deposition, evaporation, extraction, floatation, cloud point extraction, freezing and ion exchange were well known as separation and preconcentration of trace metal in analytical chemistry[12–16]. These separation/preconcentration methods have frequently been joined with instrumental analysis for the determination of ultra trace metals in complex matrix samples.

Sorbent extraction of the metal ions is an attractive separation and preconcentration technique[17–19]. It has some advantages: simple, economic, rapid, selective separation is possible, easily adaptable to on-line systems etc. Natural and synthetic adsorbents like activated carbon, Diaion HP-20, silica gel etc.[20–27] have been used for sorbent extraction procedures. Amberlite XAD adsorption resin family has an important place in the sorbent extraction of the metal ions trace quantities. Especially Amberlite XAD-16 resin has been preferred for the adsorption of the metal ions, because of its high adsorption capacity, its surface area and porosity[28–32]. The determination of the trace metal impurities in metallic zinc samples after preconcentration procedure has been performed by various researchers[33].

In the present study, applicability of the Amberlite XAD-16 solid phase extraction method is demonstrated for the atomic absorption spectrometric determination of cadmium(II), silver(I), gold(III) and lead(II) ions in metallic zinc samples. Effects of the zinc matrix on the quantitative recoveries of analyte ions were also discussed.

EXPERIMENTAL

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 receptive 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. The calibration standard was not applied to the preconcentratin procedure.

Sodium iodide used to prepare the solutions of NaI and acetone used for elution were purchased from Merck, Darmstadt. Concentrated hydrochloric and nitric acids were from Merck. All solutions were prepared at the time of experiments.

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. A pH meter, Nel pH-900 model glass-electrode was employed for measuring pH values in the aqueous phase.

Column preparation: 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 500 mg of Amberlite XAD-16 resin in water. Prior to use, the resin was preconditioned with buffer solution. After each experiment, the column was rinsed with water and stored for the next experiment.

Model procedure for preconcentration: To obtain quantitative recovery values, the Amberlite XAD-16 method was tested prior to application of the real samples. 50 mL of spiked solutions containing 2–5 μg of analyte ions 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. The sample solution was permitted to flow through the column under gravity. Then, the eluate was carefully evaporated to 1–2 mL. The solution was transferred into a 2–5 mL volumetric flask with 1 M HCl solution. The analytes in the final solution were determined by atomic absorption spectrometry.

Applications to the zinc samples: The separation/preconcentration method was applied to the atomic absorption determination of some metal ions in high purity zinc samples. 40–50 mg of the samples of zinc present as metal turnings were weighed in a beaker and dissolved by slow addition of a minimum amount of concentrated hydrochloric acid. The solutions were evaporated to near dryness on a sand bath. The residue was dissolved and diluted to 25 mL with water. Then the procedure given above was applied to this solution.

RESULTS AND DISCUSSION

The optimized conditions for the preconcentration/separation were established using 50 mL of deionized water containing 2–5 μg of each element and submitting these solutions to the preconcentration procedure. The percentage of metal adsorbed on the column was calculated from the amount of metal in the starting sample and the amount of metal eluted from the Amberlite XAD-16 column.

The optimal conditions for preconcentration and separation were previously examined in detail[34]. The recoveries of cadmium, silver, gold and lead could be increased up to nearly quantitative values (≥ 95%) with concentration ranges of 0.1–0.4 M NaI in the presence of 1 M HCl. The amount of amberlite XAD-16 in the column was 500 mg. The quantitative recoveries were obtained for all working elements with acetone. Analyte ions have nearly 100% recovery values up to the examined maximum volume of 150 mL. The detection limits of the investigated elements are varying 12 ng/L for Cd to 65 ng/L for Pb.

Matrix Effects: The influences of the zinc matrix on the recoveries of the investigated elements were also investigated. In this study zinc(II) nitrate was used as matrix. The results are given in Table-1. The analyte ions were quantitatively recovered from the zinc matrix at the range of 2500–20000 mg/L Zn^{2+}. It can be concluded that cadmium, silver, gold and lead ions can be recovered quantitatively from zinc.

Analytical performance of the method

To estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked in 25 mL solution of 40 mg of A-1 zinc samples and the resulting solutions were submitted to the separation/preconcentration procedure. 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.

TABLE-1
EFFECT OF ZINC CONCENTRATIONS ON THE RECOVERIES (as $Zn(NO_3)_2$, N = 3)

Zn^{2+} (mg/L)	Recovery, %			
	Cd	Ag	Au	Pb
2500	98	96	97	97
5000	100	98	97	97
10000	100	92	95	98
20000	100	96	100	95

Application of the Method to Metallic Zinc Samples

The high purity samples were analyzed in triplicate to determine the analytes using the procedure given in the experimental section. The concentrations, which are given in Table-2, have been calculated on the assumption of 100% recovery of analytes. The relative standard deviations of the procedure were below 10% with exception of a few.

TABLE-2
CADMIUM, SILVER, GOLD AND LEAD CONTENTS OF THE ZINC SAMPLES

Sample	Concentration, % × 10^{-3}*			
	Cd	Ag	Au	Pb
A–1	BDL	0.28 ± 0.01	0.72 ± 0.02	0.97 ± 0.01
B–2	BDL	0.17 ± 0.01	0.85 ± 0.02	1.07 ± 0.03
C–3	0.37 ± 0.02	0.27 ± 0.01	0.53 ± 0.05	1.15 ± 0.02
D–4	0.49 ± 0.01	0.14 ± 0.01	BDL	1.48 ± 0.20

*$\pm t \cdot S/\sqrt{N}$, n = 5, P = 0.95. BDL: Below the detection limit.

In conclusion, the preconcentration/separation method applied for determination of trace metal contents of metallic zinc samples provides a good precision with < 10% relative standard deviations and high accuracy obtained with the quantitative recoveries of spiked analytes.

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