Sorbent Extraction of Some Metal Ions on a Gas Chromatographic Stationary Phase Prior to Their Flame Atomic Absorption Determinations

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An enrichment/separation system for atomic absorption spectrometric determinations of Cu(II), Fe(III), Ni(II) and Co(II) has been established. The procedure is based on the adsorption of the analytes as calmagite chelates on Chromosorb-102. The effects of some parameters including pH, amount of ligand, salt matrix, flow rates of sample and eluent solutions were investigated. Under optimized conditions, the relative standard deviation of the combined method of sample treatment, preconcentration and determination with FAAS (N=5) is generally lower than 5%. The limit of detection (3σ) was between 6.0-112.9 $\mu g/L$. The results were used for preconcentration of analytes from some sodium and ammonium salt.

Key Words : Trace metals, Impurities, Chromosorb-102, Preconcentration, Calmagite

Introduction

The determination of trace impurities in salt samples is important, because of the effects of the impurities on some electrical, mechanical and chemical properties of the salt sample and the necessity of the high purity salt samples in certain areas such as semiconductors, nuclear industry etc.[1,2] Atomic absorption spectrometry (AAS) is the one of the important technique for the determination traces metals. To determine trace metals in various samples by AAS, a separation and preconcentration technique is frequently required, because of the low concentration of metals ions and the presence of interference.[3]

Many methods include membrane filtration, coprecipitation, solvent extraction, cloud point extraction etc. have been developed for preconcentration of trace metals.[3-6] The adsorption of trace elements onto stationary phases has proved to be a valuable preconcentration technique because it provides very high concentration factors, compared the other techniques, and often permits an interference free determination.[3-7] The key to a successful separation of an analyte is the choice of the chemical interaction between the analyte and column material. Adsorption of complexed metals on sorbents, such as activated carbon, Amberlite XAD resins, naphthalene, C-60, silicagel etc have been widely applied to the preconcentration of metals from various samples.[8-12] Chromosorb resins (Chromosorb -101, -102, -105, -108 etc.) are synthetic polymeric materials[13,14] and have been used for gas chromatography as stationary phases, because they have good physical and chemical properties such as porosity, high surface area, durability and purity and are resistant in concentrated mineral acid, concentrated bases and organic solvents for a long time.

They have been used for the preconcentration of traces heavy metal ions in the various samples.[13-21]

Calmagite is widely used chelating agent that has a larger formation constant with metal ions and is also used in preconcentration of metal ions. Ferreira *et al.*[22] have been used calmagite as complexing agent for copper with the on-line sorption of the complexes on XAD-2. The determination of Cu by FAAS was performed after preconcentration of calmagite complex on XAD-2.[23] Calmagite was also used for the enrichment of Mo(VI) on activated carbon.[24] The preconcentration of calmagite metal complexes on cellulose nitrate membrane filter have been performed by Soylak *et al.*[25] The same reagent was used for the preconcentration of some metal ions from seawater samples on XAD-1180.[26]

In the present work, the analytical conditions for the quantitative recoveries of some metal ions as chelates with calmagite on Chromosorb-102 were investigated.

Experimental Section

Reagents and Solutions. Analytical reagent-grade chemicals were employed for the preparation of all solutions. Freshly prepared doubled distilled water, from a quartz still, was used in all experiments. Stock metal ion solutions, 1000 mg/L (E. Merck) were diluted daily to obtaining reference and working solutions. Calmagite (1.0×10^{-2} M) was dissolved in water and prepared daily. Chromosorb-102 (80-100 mesh) (Sigma) was washed successively with methanol, water, 1 M HNO_3 in acetone, water, 1 M NaOH and water.

Sodium phosphate buffer (0.1 M) was prepared by adding an appropriate amount of phosphoric acid (Merck) 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 (Merck) to ammonium acetate solutions to result in solutions of pH 4-6 and ammonium chloride buffer solutions (0.1 M) were

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prepared by adding an appropriate amount of ammonia (Merck) to ammonium chloride solutions to result in solutions of pH 8-10.

Instrument. The instrumental detection system used was a Perkin-Elmer Model 3110 AAS. The operating parameters were those recommended by the manufacturer. All measurements were carried out without background correction with air/acetylene flame. A pH meter, Nel pH-900 Model was employed for measuring pH values in the aqueous phase. The samples were introduced to the nebulizer of AAS by using micro injection method.[27] 100 μL of sample was injected to a mini home-made Teflon funnel with a Eppendorf Pipette. The Teflon funnel was connected to the nebulizer with capillar tubing. The peak height signals were recorded.

Column Preparation. A 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 resin in water. Prior to use, the resin was preconditioned with buffer solution. After each experiment, the column was rinsed with water and stored.

Test Procedure for Preconcentration. A required volume of a 1.0×10^{-2} M solution of calmagite was added to 50 mL of solution containing 10 μg of the each metal ion and brought to desired pH between 2 and 10. The column was preconditioned with 10-15 mL of the water brought to the same pH of working pH. The sample solution was permitted to flow through the column at a flow rate of 5 mL/min. After passing of this solution, the column was rinsed twice with 10 mL of water. The retained metal-chelates were eluted with 10 mL portion of 1 M HNO$_3$ in acetone at a flow rate of 5 mL/min. The eluate was evaporated to near dryness. The residue was diluted to 2-5 mL with 1 M HNO$_3$. The metal concentrations in the final solution were determined by flame AAS.

Application to Real Samples. Five gram of salt sample was dissolved in 50 mL of distilled water. 2 mL of calmagite was added to this solution and the pH of solution was adjusted to 8 with ammonium chloride buffer solution. The sample was passed through the column at a 5 mL/min, then, the adsorbed metal chelates to the column were eluted with 10 mL 1 M HNO$_3$ in acetone. The eluate was evaporated to near dryness. It was diluted to 2 mL with 1 M HNO$_3$. To determine the analytes in the concentrated solutions, an aliquot 100 μL of the solution was introduced to the nebulizer of FAAS by microinjection method.

Results and Discussion

Effect of the pH on the Retentions. pH is a very important factor for efficient recoveries of analyte ions. The influence of pH on the solid phase extraction was studied in the range of 2-10. The pHs of the each solution were adjusted by the addition of relevant buffer solution given in the Experimental and were controlled by pH meter. The results are presented in Figure 1. The recovery depended on the pH that was nearly constant in the pH range of 6-10, 4-10
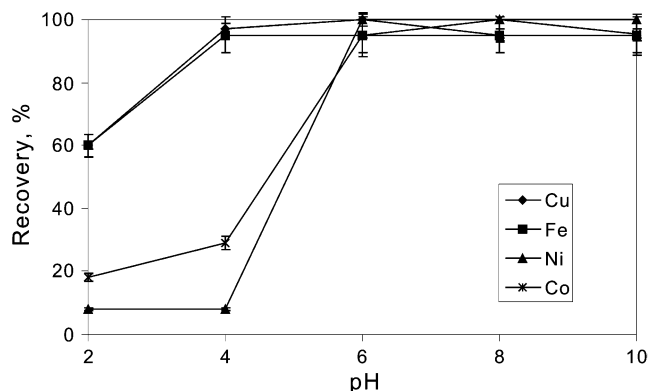

Figure 1. pH dependence of the recoveries of the metal ions (eluent: 10 mL of 1 M HNO$_3$ in acetone, metal amounts: 10 μg, N = 3).
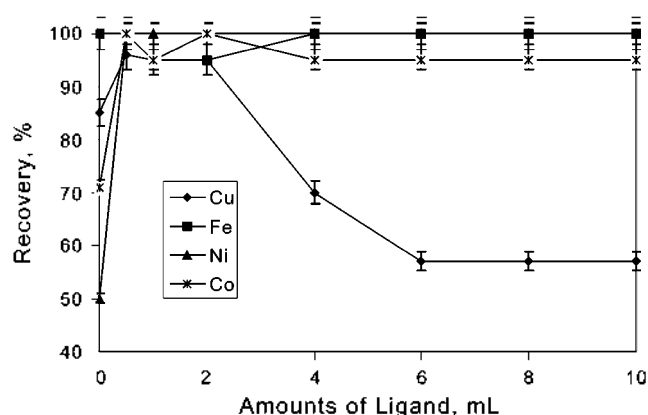

Figure 2. Changes on the recoveries of metal ions with calmagite amounts (N = 3, eluent: 10 mL of 1 M HNO$_3$ in acetone).

for Ni and Co, Cu and Fe respectively. pH 8 was selected as working pH. The volume of the buffer solution had no efficient effects on the recoveries.

Influences of the Amounts of Calmagite. The influences of the amounts of calmagite on the recoveries were also examined. The results are given in Figure 2. The recoveries, ≥ 95%, are quantitative for each of Fe, Ni and Co in the examinated range, for Cu in the range 0.5-2 mL calmagite. The recoveries obtained from the sample solution without calmagite were not quantitative except for Fe. All further studies 2 mL of calmagite was used as ligand.

The Effect of Eluent Type. The effects of eluents on the recoveries of analytes from Chromosorb-102 were also investigated. Quantitative recoveries for all analytes were obtained with 10 mL of 1 M HNO$_3$ in acetone. The recovery of nickel was quantitative with all of investigated eluent. While with 1 M HNO$_3$, Cu, Fe and Ni were quantitatively recovered, with acetone, only Ni and Co were quantitatively recovered. Also, selective eluation of metal ions were possible with some eluents. For example with 5 mL of 0.5 M HNO$_3$, only nickel was recovered quantitatively. All further studies 10 mL of 1 M HNO$_3$ in acetone was used as eluent.

Sample and Eluent Flow Rates. Sample and eluent flow rates are important parameters to obtain quantitative reten-

Table 1. Influences of the certain sodium and ammonium salts as matrix on the recoveries of trace impurities (N = 3, V = 50 mL)

Salt	Concentration, g/50 mL	Recovery, %			
		Cu	Fe	Ni	Co
NaCl	1	97	100	100	95
	5	97	100	100	100
	10	100	100	100	95
NH₄Cl	1	41	96	100	100
	5	71	95	100	100
	10	44	95	100	100
(NH₄)₂SO₄	1	95	100	100	100
	5	96	100	100	100
	10	96	100	100	95

tion and elution of analyte, respectively. The retentions for the analytes were virtually quantitative for sample flow rates up to 10 mL/min. Variation of the elution flow rate in the range of 1.0-6.0 mL/min has no effect on the elution efficiency. In consequence, 5 mL/min was selected as flow rate for loading and elution from the trap.

Effect of Salt Matrix. To investigate the effect of high concentrations of ammonium chloride, ammonium sulfate and sodium chloride salts on the recovery of analytes, the procedure were carried out with samples containing salts in the range of 1-10 g (Table 1). Quantitative recovery values for Cu, Fe, Ni and Co up to 10 g of sodium chloride, for Fe, Ni and Co up to 10 g of ammonium chloride, for Cu, Fe, Ni and Co up to 10 g of ammonium sulfate were obtained. It was concluded that Cu(II), Fe(II), Ni(II) and Co(II) occurring as impurities in ammonium and sodium salts can be determined with presented procedure.

Analytical Performance of the Method. The accuracy of the results was verified by analyzing the concentration after addition of known amounts of analytes into a 50 mL solution containing 5 g NaCl and NH₄Cl. Good agreement was obtained between the recovery of analyte for spiked and control samples using the experimental procedure for Cu, Fe, Ni and Co in NaCl and Fe, Ni and Co in NH₄Cl. Because of the recovery of Cu from NH₄Cl were not quantitative, the determination of Cu in NH₄Cl was not performed.

The reproducibility of the method was evaluated by passing 50 mL of solution containing 10 μg of each analyte ion through Chromosorb-102 and repeating this procedure five times. The relative standard deviations were ± 2.7%,

± 2.1 %, ± 1.6 %, ± 2.1% for copper, iron, nickel and cobalt, respectively. The detection limits of the analytes based on three times the standard deviations of the blank ($k = 3$, N = 20) on a sample volume 50 mL for Cu, Fe, Ni and Co were 17.0 μg/L, 112.9 μg/L, 11.0 μg/L, 6.0 μg/L, respectively. The detection limits of the analytes can be decreased by one order of magnitude by increasing the sample volume.

Application to Salt Samples. The method has been employed for the determination copper(II), iron (III), nickel(II) and cobalt(II) ions in NaCl, NH₄Cl and (NH₄)₂SO₄ salts. The results, which are shown in Table 2, have been calculated by assuming 100% recovery of the working elements. The relative standard deviations ($n = 5$) with related to the determinations in the salts for Cu, Fe, Ni and Co were in the range of 4.0-9.7%.

Conclusion

Because of 500 mg of Cromosorb-102 resin can be used repeatedly for 300-400 samples at least with 5 mL/min of sample and eluent flow rates and the time required for the preconcentration and determination was about 25 min, the proposed preconcentration system provides a fast and simple method for enrichment on Chromosorb-102. The determination procedure was characterized by good reproducibility and accuracy.

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Table 2. The concentration of copper(II), iron(III), nickel(II) and cobalt(II) in some sodium and ammonium salts

Sample	Concentration, μg/g^a			
	Cu	Fe	Ni	Co
Refined Table Salt	0.11 ± 0.01	2.90 ± 0.19	0.39 ± 0.02	B.L.D
Unrefined Table Salt	0.09 ± 0.01	2.73 ± 0.19	0.45 ± 0.02	0.32 ± 0.02
NaCl (Analytical Reagent Grade)	0.15 ± 0.02	1.56 ± 0.16	0.31 ± 0.02	0.28 ± 0.02
NaCl (Technical Grade)	0.11 ± 0.01	1.53 ± 0.14	0.34 ± 0.03	0.19 ± 0.02
NH₄Cl (Analytical Reagent Grade)	N.D.	3.24 ± 0.28	0.34 ± 0.02	0.25 ± 0.02
(NH₄)₂SO₄ (Analytical Reagent Grade)	0.07 ± 0.01	0.94 ± 0.10	0.16 ± 0.01	0.10 ± 0.01

^{a}P = 0.95, ± t.s √N, N = 5, BLD: Below the Detection Limit, ND: Not Determined.

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