

PRECONCENTRATION OF Cu (II), Fe(III), Ni(II), Co(II) AND Pb(II) IONS IN SOME MANGANESE SALTS WITH SOLID PHASE EXTRACTION METHOD USING CHROMOSORB-102 RESIN

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Abstract

An enrichment/separation procedure for the atomic absorption spectrometric determinations of Cu (II), Fe(III), Ni(II), Co(II) and Pb(II) ions in $Mn(NO_3)_2$ and $KMnO_4$ has been established. The ammonium pyrrolidinedithiocarbamate (APDC) complexes of the analyte ions were adsorbed on the Chromosorb-102 column and then desorbed with 10 mL acetone. The effects of manganese concentrations as interferent were discussed. The method has been successfully applied to the determination of Cu, Fe, Ni, Co and Pb in analytical reagent grade manganese salts. Under optimized conditions, the recovery values were > 95%. The relative standard deviations ($n=5$) with related to the determinations in the $Mn(NO_3)_2$ and $KMnO_4$ was in the range of 1-9% and 6-14%, respectively.

Introduction

Metallic manganese of relatively pure grade is the basic material for a series of alloys with special electrical and thermal characteristics. Impurities are generally in the range of ppm and less. Of different manganese compounds, $Mn(NO_3)_2 \cdot 4H_2O$ and MnO_2 are of particular technical importance. For this reason, the quantitative determination of impurities in these compounds is important.

The direct determination of metal impurities by flame atomic absorption spectrometer (FAAS) in analytical reagent-grade salts is often difficult or even impossible because of their low levels and matrix effects. For this reason, a preconcentration and separation procedure is required. In trace element analysis,

preconcentration and separation methods also enhance the sensitivity and precision of the determination.¹

Separation and preconcentration techniques such as adsorption, membrane filtration, cloud point extraction, solvent extraction and coprecipitation have been carried out.²⁻⁷ Among these techniques used in trace element preconcentration, solid phase extraction is an attractive technique based on the use of a sorbent that retains the analytes. The retained analytes are eluted from the sorbent using relatively small volume of a suitable solvent. This feature provides a high analytical preconcentration factor for large volume samples. Various sorbents such as Amberlite XAD resins,⁸⁻¹⁰ silicagel,¹¹ C-18,¹²⁻¹³ activated carbon¹⁴⁻¹⁶ etc. have been used for the solid phase extraction of metal ions from the different matrices.

Chromosorb resins are synthetic polymeric materials^{13,14} and have been used in 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. Chromosorb-102 resin is an adsorbent based on polystyrene divinyl benzene copolymer having hydrophobic character. It has been widely used as adsorbents suitable in gas chromatographic separation of organic compounds.^{17,18} Chromosorb resins have been used for the preconcentration of traces heavy metal ions in various samples.¹⁹⁻²² Ammonium pyrrolidinedithiocarbamate (APDC) as a chelating reagent in solid phase extraction method has been widely applied to the preconcentration of trace metals, prior to their determination by AAS.²³⁻²⁴

This paper presents a separation/preconcentration procedure for ammonium pyrrolidinedithiocarbamate (APDC) complexes of some trace metal ions in some manganese salts on a column filled with Chromosorb-102 adsorption resin prior to their flame atomic absorption spectrometric determinations.

Experimental

Apparatus

A Perkin Elmer Model 3110 atomic absorption spectrometer was used for determination of metals. All measurements were carried out in air/acetylene flame and without background correction. The instrumental parameters were set as recommend by

the manufacturer. pH measurements were performed with a Nel pH 900 digital pH meter and combined glass electrode.

Reagents

Analytical reagent-grade chemicals were employed for the preparation of all solutions. Doubly distilled water was used in all experiments. Metal stock solutions of the working elements (1000 mg/L) were prepared by dissolving their respective nitrates in 1% HNO₃. The stock solutions of the analytes were standardized by titrimetrically. Working standard solutions were prepared in 1 M HNO₃ by diluting just prior to use. Acetone used for elution, concentrated hydrochloric and nitric acids, Mn(NO₃)₂ and KMnO₄ from Merck, Darmstadt in extrapure quality. An ammonium pyrrolidinedithiocarbamate (APDC) solution, 0.05%, was prepared by dissolving the required amount of APDC in water immediately before use.

Resin and Column Preparation

The Chromosorb-102 resin (Phase Separations, 750 614) having a surface area of 300-400 m²/g and a particle size of 80-100 mesh was used as solid phase. A 500 mg Chromosorb-102 resin suspended in water was slurry packed into a glass column (10 mm id x 100 mm length, height of the resin approximately 15 mm). It was washed successively with water, acetone and water, respectively. Before the use, the column was preconditioned with 5-10 mL of blank solution. After each experiment, the resin in the column was washed with large volumes of water.

Procedure for Preconcentration

The performance of column method was tested with model solution prior to its application to manganese salts. For this, 25 mL of the model solution containing 10 µg each of Cu, Fe, Co and Ni and 20 µg Pb was buffered to the desired pH. Three millilitres of 0.05% (w/v) APDC solution was added to form the metal-APDC chelates. The sample solution was permitted to flow through the column under gravity at the flow rate of 5 mL/min. After passage of the solution finished; the column was washed with a blank solution. The retained analyte ions were eluted from the Chromosorb-102 column by 10 mL of acetone at flow rate of 7.5 mL/min. The eluate was evaporated to ~1-2 mL

on a hot plate in a hood. The solution was transferred into a 2-10 mL volumetric flask with 1 M HNO₃ solution. The analyte ions in the final solution were determined by FAAS.

Analysis of Manganese Salts

For the analysis of analyte ions contents of manganese nitrate, 3.000 g Mn(NO₃)₂·4H₂O was dissolved in 100 mL water. Then the preconcentration procedure given above was applied.

Prior to the analysis of KMnO₄, the reduction of KMnO₄ was necessary because of decomposing of Chromosorb 102 resin structure by KMnO₄. For the reduction of Mn(VII) to Mn(II), sodium oxalate was used. 1.000-1.500 g of KMnO₄ was reduced with 90 mL of 0.2 M Na₂C₂O₄ in 1 M H₂SO₄. The solution was neutralized with 6 M NH₃. Then the preconcentration procedure given above was applied to this solution. The analytes ions were determined by FAAS.

Results and discussion

Recently, it has been explained that the determination of some trace metal ions in various samples could be performed after separation and preconcentration by sorbing the metal-APDC complexes on the Chromosorb-102 column.²⁵ In this study, the Chromosorb-102 column method has been modified for the separation/preconcentration of trace metal ions in manganese salts. The optimum conditions for the preconcentration method are given Table 1.

The analyte ions were quantitatively recovered at pH range of 4-7. The volume of the buffer solution (10 mL) has not any effect on the recoveries. 1.5 mg of APDC and 500 mg of Chromorb-102 was used in all experiments. The analyte ions were quantitatively recovered in the sample volume range of 25-600 mL. Quantitative recoveries of the analyte ions were obtained by using 10 mL of acetone at 7.5 mL/min flow rate.

The detection limit was calculated after presented preconcentration procedure applied to 50 mL of the blank solutions. The detection limit for analyte ions based on three times the standard deviations of the blank were in the range of 0.009 µg/g for Cu-0.22 µg/g for Fe (N=20). These results are comparable with the results in reference 25.

Table 1. The Effect of Some Parameters on the Recovery with APDC of Trace Elements with Solid Phase Extraction Method Using Chromosorb 102 Resin.

Parameters	Investigated Range	Best values
pH of Sample Solution	1-10	6
Amount of Chromosorb-102	300-700 mg	500 mg
Amount of APDC	0.5-5 mg	1.5 mg
Types of Eluent	Acetone, 1 M HNO ₃ in acetone, 1 M HNO ₃ , 1 M HCl	Acetone
<i>Volume of Eluent</i>	5-15 mL	10 mL
Flow Rate of Eluent	1-10 mL/min	5 mL/min
Flow Rate of Sample	2-12 mL/min	7.5 mL/min

Matrix Effects

The recoveries were quantitative for Cu (II), Fe(III), Ni(II), Co(II) and Pb(II) in optimum conditions using APDC as a chelating reagent, however the recoveries of Mn(II) was smaller than 5%. For this reason, preconcentration and separation of analyte ions from manganese salts was examined.

In order to investigate the effect of manganese concentrations on the recoveries of the examined elements, the procedure has been carried out with 100 mL of sample solutions containing different amounts of Mn(II). The results are given in Table 2. The retentions of investigated analyte ions were not affected by manganese concentrations as Mn(NO₃)₂·4H₂O set up to 7500 mg/L Mn (II).

Table 2. The Effect of Manganese Concentrations on Recovery of Analyte Ions (N=3).

	Conc. of Mn, mg/L	Recovery, %				
		Cu	Fe	Co	Ni	Pb
Mn(NO ₃) ₂ ·4H ₂ O	2500	95	100	95	95	100
	5000	95	100	95	100	99
	7500	96	95	93	100	100
	10000	89	61	86	100	100
KMnO ₄	1000	96	98	96	95	100
	2000	95	94	92	98	97
	4000	97	95	96	98	100

The effect of the Mn (VII) on the recoveries of analytes was also investigated. The resin was decomposed by the addition of the permanganate solution. Due to this, the preconcentration procedure was applied to the permanganate solutions after reduction of

Mn(VII) to Mn(II) by sodium oxalate.²⁶ We have found that there is no effect of oxalate ions on preconcentration of the examined analytes.²⁵ The quantitative recovery values were obtained with 90 mL of 0.2 M Na₂C₂O₄ in 1 M H₂SO₄. As can be seen from Table 2 in the working range of Mn from 1000 to 4000 mg/L as KMnO₄, the recoveries of examined analytes were quantitative.

According to these data, it can be concluded that Cu (II), Fe(III), Ni(II), Co(II) and Pb(II) in Mn(NO₃)₂ and KMnO₄ can be determined by the preconcentration procedure proposed.

Analytical Performance of the Method

The accuracy of the procedure was confirmed by the recoveries of spikes from Mn(NO₃)₂·4H₂O (Mn content is 7500 mg/L). The results were given in Table 3. Quantitative recoveries of different amounts of the investigated metal ions spikes were obtained. Thus, confirming the accuracy of the procedure and its independence from the matrix effects.

Table 3. The Recoveries of Metal Ions in Manganese (II) Nitrate (Merck) (Volume of Sample: 100 mL, N=3).

Element	Added, µg	Found, µg	Recovery, %
Cu	0	3.8	-
	3.0	6.6	93
	5.0	8.6	96
Fe	0	8.9	-
	5.0	13.7	96
	20.0	28.7	99
Co	0	0.7	-
	0.5	1.2	100
	1.0	1.6	90
Ni	0	4.1	-
	3.0	7.2	103
	5.0	8.9	96
Pb	0	3.8	-
	2.0	5.7	95
	4.0	7.4	90

Applications

The proposed method was applied to the determination of Cu, Fe, Co, Ni and Pb ions in analytical reagent grade $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and KMnO_4 . The levels of the investigated ions are given in Table 4. The results have been calculated on the assumption of 100% recovery of metal ions. The concentrations of Cu, Fe, Co, Ni and Pb in manganese (II) nitrate were less than the contents guaranteed by the distributor of the reagents. The concentration of Pb in potassium permanganate was below the detection limit. The relative standard deviations ($n=5$) with related to the determinations in the $\text{Mn}(\text{NO}_3)_2$ and KMnO_4 was in the range of 1-9% and 6-14%, respectively.

Table 4. Concentrations of Metal Ions in Manganese (II) Nitrate and Potassium Permanganate (N=5).

Sample	Concentration ($\mu\text{g/g}$)*				
	Cu	Fe	Co	Ni	Pb
$\text{Mn}(\text{NO}_3)_2$	1.10 ± 0.06	2.72 ± 0.37	0.20 ± 0.01	1.21 ± 0.04	1.07 ± 0.10
KMnO_4	2.54 ± 0.29	9.29 ± 0.64	0.42 ± 0.06	2.74 ± 0.49	BDL

* $P=0.05$, $\pm ts/\sqrt{N}$, BDL: Below the limit of detection.

Conclusions

The proposed column preconcentration method provides a simple, sensitive, accurate and selective method for the preconcentration and separation of investigated analyte ions in manganese salts. The precision and recovery (>95%) were satisfactory. The proposed method can be used for the preconcentration and separation of traces of Cu (II), Fe(III), Ni(II), Co(II) and Pb(II) ions in the other matrices, such as natural water samples and geological materials, etc.

The present method is promising for enrichment of analyte ions with the preconcentration factor of 50 and is superior to those reported in the literature 26-30. The working pH range (4-7) for all the metal ions is slightly acidic and therefore there is no possibility of their hydrolysis. The effects of manganese salts investigated as matrix for the analyte ions were reasonably tolerable. The relative standard deviations of the determinations were lower comparing to other methods.^{11,20,25-30} Also the apparatus used in the experiments is simple.

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Povzetek

Razvili smo postopek predkoncentriranja/separiranja za določitev Cu(II), Fe(II), Ni(II), Co(II) in Pb(II) z atomsko absorpcijsko spektrometrijo v Mn(NO₃)₂ in KMnO₄. Komplekse določevanih ionov z amonijevim pirolidinditiokarbamatom (APDC) smo adsorbirali na koloni, napolnjeni z nosilcem Chromosorb-102, in desorbirali z 10 mL acetona. Preučili smo interference, ki jih povzročata mangan v različnih koncentracijah. Metodo smo uspešno uporabili za določitev Cu, Fe, Ni, Co in Pb v manganovih solih čistosti p.a. Izkoristek pri optimiziranih pogojih je bil > 95%. Dobili smo relativne standardne odmike (n=5) v območju 1-9% za določevanje ionov v Mn(NO₃)₂ in 6-14% za KMnO₄.