

Preconcentration of Cr(III), Co(II), Cu(II), Fe(III) and Pb(II) as calmagite chelates on cellulose nitrate membrane filter prior to their flame atomic absorption spectrometric determinations

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Abstract

A method for the preconcentration and determination of Cr(III), Co(II), Cu(II), Fe(III) and Pb(II) ions by atomic absorption spectrometry has been described. The method was based the collection of metal–calmagite complexes on a soluble cellulose nitrate membrane filter. The detection of the solution was obtained by flame atomic absorption spectrometry (FAAS) after completely dissolving the membrane with 0.5 ml of nitric acid at 80 °C. The metal ions were recovered quantitatively at pH 8. Various factors which affect the collection and determination of metal ions such as, type and size of the membrane filter, solvent for dissolution of the species retained on the filter were investigated. The detection limits were varying 0.06 $\mu\text{g l}^{-1}$ for Cu to 2.5 $\mu\text{g l}^{-1}$ for Cr. An application of the proposed method for analyte ions in mineral and tap water samples was also described with satisfactory results (recoveries > 95%, relative standard deviations < 10%). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Preconcentration; Cellulose nitrate membrane; Calmagite; Mineral and drinking waters

1. Introduction

Trace heavy metal analysis are an important part of studies in analytical chemistry. The determinations of these ions in the various materials form the industrial samples to environmental samples have been performed continuously [1–4].

Due to the matrix effects and low metal levels in atomic absorption spectrometry, preconcentration/separation methods [5–10] including extraction, coprecipitation, solid phase extraction, ion exchange procedures are a necessity for the determination of the traces metal ions in the highly saline media.

Membrane filters has been used for solid-phase extraction and determination of trace elements in various media [11–16]. The materials of mem-

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brane filters with a strong affinity for hydrophobic species in water are generally useful to retain the species by filtration. The collection is performed very quickly by filtration under suction with the aid of an aspirator. The collected analytes on the filter is dissolved together with the membrane in a small amount of organic solvent or mineral acids. The trace metal ions in the final solution are determined by spectrophotometry, ICP-AES and GFAAS. However, the combination of the membrane filter method with flame atomic absorption spectrometry is very limited. The most attractive features of membrane filtration technique are the simplicity and rapidity of the procedure, an easily attainable high concentration factor and determination with high-precision [17,18].

Calmagite (3-hydroxy-4-[(6-hydroxy-*m*-tolyl)azo]-naphthalenesulfonic acid) is a chelating agent that reacts with transition metal ions to form very stable complexes that has an advantage for preconcentration studies based on differences in formation constants between the transition metals and alkaline and alkaline earth metals for effective separations of trace metals from saline solutions using calmagite [19–21]. Ferreira et al. [20] used calmagite as complexing agent for copper with the on-line sorption of the complexes in a Amberlite XAD-2 column. The same reagent was used for the preconcentration/separation of some metal ions from seawater samples on Amberlite XAD-1180 adsorption resin [21]. In another study, calmagite was used for the preconcentration of molybdenum on activated carbon [22]. The determination of copper by flame atomic absorption spectrometry was performed after preconcentration of copper complex with calmagite, and using an XAD-2 mini column [23]

In the present work, a preconcentration and separation method for the determinations of Cr(III), Co(II), Cu(II), Fe(III) and Pb(II) on cellulose nitrate membrane filter as their calmagite complexes has been established. The optimal analytical parameter for the quantitative recoveries of analyte ions such as pH, amounts of reagents, sample volume, etc. were investigated.

2. Experimental

2.1. Instrument

A Perkin–Elmer model 3110 atomic absorption spectrophotometer equipped with Perkin–Elmer single-element hollow cathode lamps and a 10-cm air–acetylene burner were used for the determination of the metal ions. All instrumental settings were those recommended in the manufacturer's manual book. A pH meter, Nel pH-900 Model glass-electrode was employed for measuring pH values in the aqueous phase. An Erlenmeyer flask with ground stopper was used for filtration the solutions.

2.2. Reagents and solution

Doubly-distilled water and high purity reagents were used for all preparations of the standard and sample solution. Standard stock solutions containing 1000 mg l⁻¹ analyte were prepared from nitrate salts of Cr(III), Co(II), Cu(II), Fe(III) and Pb(II) in 1% of HNO₃ into 1-l calibrated flasks. Diluted standard solutions and model solutions were daily prepared from the stock standard solutions.

Stock solutions of diverse elements were prepared from high purity compounds. The calibration standards were not submitted to the preconcentration procedure. The membrane filters were purchased from Sartorius. A 1.0 × 10⁻³ M solution of calmagite (Sigma Chem. Co., St. Louis, MO) was prepared by dissolving the required amount of calmagite in a water/ethanol (75/25, v/v) mixture. The calmagite solution was prepared daily.

2.3. Preconcentration procedure

In the experiments for the retention of investigated metal ions on cellulose nitrate membrane filter, 30–50 ml portion of an aqueous solution containing an appropriate amount of them, 10 µg for Co, Cu, Fe and 20 µg for Pb and Cr was placed in a glass beaker. Ten milliliters of buffer solution (to give the desired pH between 2 and 10) and calmagite solution were added. After 10 min,

metal–calmagite solution was collected through a cellulose nitrate membrane filter of 0.45 μm size and 47 mm diameter. The collection is performed very quickly by filtration under suction with an aspirator. Then the membrane was completely dissolved in 0.5 ml of concentrated nitric acid at 80 °C on a hot plate. The solution was evaporated to dryness. The residue was diluted to 2–5 ml with 1 M HNO_3 . The metal concentrations in the final solution were determined by FAAS.

2.4. Analysis of the water samples

In order to apply the method, 300 ml of the water sample was placed in a beaker, the pH of the sample was then adjusted to pH 8 with ammonia/ammonium buffer. The separation/preconcentration method given above was then applied. The concentration of the analyte ions in the final solution was determined by FAAS.

3. Results and discussion

The optimised conditions for the preconcentration/separation were established using 30–50 ml of de-ionised water containing 10–20 μg of each element and submitting these solutions to the preconcentration procedure.

3.1. Effect of pH on the recoveries

The effects of the pH on the retention of Cr(III), Co(II), Cu(II), Fe(III) and Pb(II) ions on the cellulose nitrate membrane filter were studied in the pH range of 2–10. For pH 2 phosphate buffer, for pH 4–6 acetate buffers for pH 7 borate buffer, for pH 8–10 ammonium buffers were used. The results were depicted in Fig. 1. The recoveries of the all analyte ions were not quantitative at acidic pH values. Lead was recovered quantitatively in the pH range of 7–10. The quantitative recoveries of Cu(II) and Cr(III) were obtained at pH 8–9. The recoveries of cobalt and iron were $>95\%$ at pH 8–10. Therefore, pH 8.0 was selected for subsequent work, as at this pH, the ammonium buffer shows a good buffer capacity. The volume of buffer added (10 ml) had no effect on the recoveries.

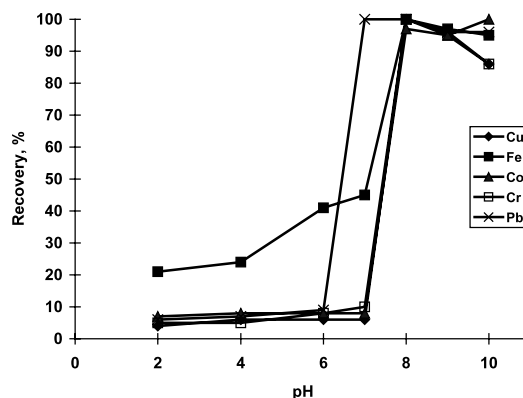


Fig. 1. The influences of the pH on the recoveries of trace metal ions ($N = 3$, ligand: calmagite, membrane: 0.45 μm pore size, 47 mm diameter cellulose nitrate).

3.2. Influences of the ligand amounts

The effects of the ligand amount on the retention of the analyte ions on the cellulose nitrate membrane filter was also examined. The results were given in Fig. 2. The recovery of chromium, cobalt, copper, iron and lead ions increased with increasing concentrations of calmagite added and reached a constant value with at least 2.0 ml of 1.0×10^{-3} M (approximately 0.7 mg of calmagite). The addition of 2.0 ml of calmagite solution is recommended.

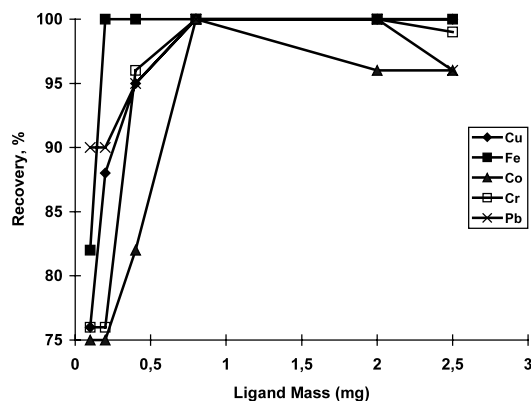


Fig. 2. Effects of the ligand mass on the recovery of analyte ions ($N = 4$, ligand: calmagite, membrane: cellulose nitrate).

Table 1

Effects of the membrane type and size on the recoveries of Cr(III), Co(II), Cu(II), Fe(III) and Pb(II) (pH 8, $N = 4$, ligand: calmagite)

Membrane type and size	Recovery (%)				
	Cr	Co	Cu	Fe	Pb
Cellulose nitrate, 47 mm 0.45 μm	100 \pm 2	97 \pm 2	102 \pm 1	100 \pm 1	100 \pm 2
Cellulose nitrate, 20 mm 0.25 μm	98 \pm 3	96 \pm 3	95 \pm 2	99 \pm 3	98 \pm 2
Cellulose acetate, 47 mm 0.45 μm	100 \pm 3	78 \pm 3	100 \pm 2	95 \pm 3	100 \pm 2
Cellulose ester, 47 mm 0.45 μm	100 \pm 1	56 \pm 2	90 \pm 2	100 \pm 2	100 \pm 3

3.3. Effects of membrane type and size on the retention of metal ions

The effects of the membrane type and membrane size on the recovery values of the analyte ions were also studied. For this purpose, various membrane filters were used. The results are given in Table 1. The recoveries of all the analyte ions at the optimal conditions were quantitative for cellulose nitrate (47 mm, 0.45 μm , and 20 mm, 0.25 μm) and cellulose acetate (47 mm, 0.45 μm) membrane filters. When cellulose ester membrane filter (47 mm, 0.45 μm) used for the preconcentration/separation studies chromium, iron and lead ions were recovered quantitatively.

Various mineral acids including sulfuric acid, hydrochloric acid and nitric acid have been used for the dissolution of the membrane filter. Quantitative recovery values ($> 95\%$) were obtained for the analyte ions by using nitric acid.

3.4. Effect of sample volume

In order to study with high sample volumes, the effect of the sample volume on the recoveries of the analyte ions were also investigated. As can be seen in Fig. 3, the recovery values of copper(II) and iron(III) were quantitative in the sample volume range of 50–500 ml. Lead(II) and chromium(III) were recovered quantitatively in the range of 50–300 ml sample volume. The recovery of cobalt(II) on the cellulose nitrate membrane filter were quantitative up to 150 ml. The low recovery values for cobalt ions at the sample volumes greater than 150 ml may sourced from the competition of the calmagite chelates of other investigated ions.

3.5. Matrix effects

The influences of possible matrix ions in the natural water samples were also examined. The results are summarized in Table 2. The ions normally present in water do not interfere under the experimental conditions used. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the preconcentration and determination of analytes. As can be seen in Table 2, the level of the matrix ions in the final solution was also at low levels. The matrix metal ions were not retained on the column because of their very low stability constants of calmagite complexes.

3.6. Detection limits

The detection limits of the investigated elements based on three times the standard deviations of the blank ($k = 3$, $N = 21$) on a sample volume 100

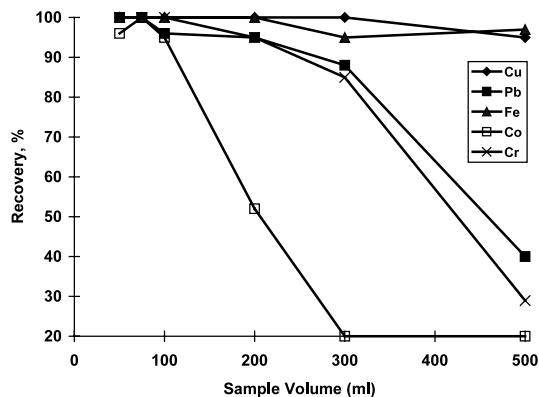


Fig. 3. Effects of sample volume on the recoveries of Cr, Co, Cu, Fe and Pb (filter: cellulose nitrate, $N = 4$).

Table 2
Effects of the matrix ions for recoveries of Cr(III), Co(II), Cu(II), Fe(III) and Pb(II) ($N=4$)

Ion	Concentration in final solution (mg l ⁻¹)	Tolerance Limits (mg l ⁻¹)
Na ⁺	50	5000
K ⁺	20	500
Mg ²⁺	4	1000
Ca ²⁺	40	500
Cl ⁻	–	5000
SO ₄ ²⁻	–	500

ml for copper, cobalt, iron, lead and chromium were 0.06, 0.76, 0.33, 1.18 and 2.5 µg l⁻¹, respectively. The detection limits can be decreased by one order of magnitude by increasing the sample volume.

The preconcentration factors that were calculated from the ratio of highest sample volume obtained quantitative recoveries to 2 ml final volume. The preconcentration factors for Cr, Co, Cu, Fe and Pb were 150, 50, 250, 250 and 150, respectively.

3.7. Recovery of spikes from water sample

In order to estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked in drinking water from Erciyes University and the resulting solutions were submitted to the 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% except cobalt., thus confirming the accuracy of the procedure and its independence from the matrix effects. Because of the recoveries of cobalt from the drinking water were not quantitative, the determination of cobalt in natural water samples was not performed.

3.8. Application of the proposed method

The proposed preconcentration method has been applied to natural water samples. The results are given in Table 3. The relative standard deviations of the determination were less than 10%. The level of the chromium and lead were found below the detection limit in all the water samples.

The concentrations of copper, iron and lead in drinking water-1 and drinking water-2 were also determined by using the Amberlite XAD-4 column method as described previously [24]. The levels of the investigated ions were also found below the detection limits of the Amberlite XAD-4 method. The results found by the proposed method are in agreement with those found by the Amberlite XAD-4 method. The validation shown for the samples studied is also satisfactory.

4. Conclusion

This method has the following advantages: simple, rapid and low analysis cost. The calmagite complex was retained rapidly and quantitatively on a cellulose nitrate membrane filter by filtration under suction. The proposed method has been applied to the separation and determination of

Table 3
Concentration of investigated metal ions in water samples ($N=5$, volume: 300 ml, final volume: 2 ml)

Sample	Concentration of metal ions (µg l ⁻¹)*			
	Cr	Cu	Fe	Pb
Drinking water-1	BDL	BDL	BDL	BDL
Drinking water-2	BDL	BDL	BDL	BDL
Bottled mineral water-1	BDL	8.7 ± 0.3	35.0 ± 3.0	BDL
Bottled mineral water-2	BDL	15.0 ± 1.0	26.5 ± 2.5	BDL
Bottled mineral water-3	BDL	4.7 ± 0.4	9.4 ± 0.9	BDL

* $x \pm t.s./\sqrt{N}$; P , 0.95; BDL, below detection limit.

Cr(III), Cu(II), Co(II), Fe(III) and Pb(II) in water samples from several sources, the recoveries of the analyte ions added to the samples were quantitative except cobalt(II) and the results found are satisfactory.

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