

Separation/preconcentration of silver(I) and lead(II) in environmental samples on cellulose nitrate membrane filter prior to their flame atomic absorption spectrometric determinations

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Abstract

An enrichment method for trace amounts of Ag(I) and Pb(II) has been established prior to their flame atomic absorption spectrometric determinations. The preconcentration/separation procedure is based on chelate formation of Ag(I) and Pb(II) with ammonium pyrrolidine dithiocarbamate (APDC) and on retention of the chelates on cellulose nitrate membrane filter. The influences of some analytical parameters including pH and amounts of reagent, etc. on the recoveries of analytes were investigated. The effects of interferic ions on the quantitative recoveries of analytes were also examined. The detection limits ($k = 3$, $N = 11$) were $4.6 \mu\text{g L}^{-1}$ for silver(I) and $15.3 \mu\text{g L}^{-1}$ for lead(II). The relative standard deviations (R.S.D.) of the determinations for analyte ions were below 3%. The method was applied to environmental samples for the determination of analyte ions with satisfactory results (recoveries >95%).

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1. Introduction

A beneficial level of traces element in humans does not cause deviations from the proper condition of health. The line between the quantity being indispensable and harmful is usually fine and the establishment of a level of traces element ions in food and water is difficult [1–4]. Heavy metal ions should be accurately evaluated in order to prevent the occurrence of harmful effects. The cycle of trace metal ions from environment to human is also an important part of environmental studies [5–8].

Various analytical techniques have been used for determination of traces metal ions including spectrophotometry, atomic absorption spectrometry (AAS), electroanalytical techniques, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), etc. [9–12]. Flame atomic absorption spectrometry (FAAS) has been widely selected and used as the technique of

choice to analysis of trace heavy metal ions owing to its high sensitivity, reproducibility, wide dynamic concentration range, and its relatively low cost [13–15]. However, the determinations of elements at $\mu\text{g L}^{-1}$ concentration level by FAAS are not possible and also interferences caused by coexisting components are often serious problems. In order to solve these two problems, analytical chemists are used to combination of preconcentration and separation methods [16,17]. Preconcentration and separation methods should provide a large enrichment factor, make the composition of the sample the same as that of standard by eliminating basic components effects, can be used in routine analysis and be simple, rapid, and inexpensive [18,19]. Various separation/preconcentration methods including evaporation, solvent extraction, solid phase extraction, ion exchange, electrodeposition, cloud point extraction, and coprecipitation have been used before the atomic absorption spectrometric determinations of traces of heavy metal ions [20–25].

Membrane filtration of trace heavy metals is effective from the point of view of concentration coefficient. Membrane filters including cellulose nitrate, cellulose acetate, etc. have been used for solid-phase extraction of trace species such as organic species, some anions and heavy metal ions in various media

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[26–34]. The most attractive features of membrane filtration technique are the simplicity and rapidity of the preconcentration procedure, an easily attainable high preconcentration factor, and determination with high precision [35,36].

In the present work, membrane filtration method on cellulose nitrate filter for the enrichment/separation of Ag(I) and Pb(II) in environmental samples including natural waters has been established for flame atomic absorption spectrometric determinations. The analytical parameters including reagent amounts, sample volume, and matrix effects, etc. were investigated.

2. Experimental

2.1. Instrumental

A Perkin-Elmer Model 3110 flame 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. The operating parameters for working elements, which were given in Table 1, were set as recommended by the manufacturer. A pH meter, Sartorius PT-10 Model glass-electrode was employed for measuring pH values in the aqueous phase. An Erlenmeyer flask with ground stopper was used for membrane filtration of solutions.

2.2. Reagents and solutions

Aqueous solutions of chemicals were prepared with deionized water (Human RO 180). 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 investigated analyte ions in 1% of HNO₃ into 1 L calibrated flasks. Diluted standard solutions and model solutions were daily prepared from the stock standard solutions. The calibration curve was established using the standard solutions prepared in 1 mol L⁻¹ HNO₃ by dilution from stock solutions. The calibration standards were not submitted to the separation/preconcentration procedure. Membrane filters used in the present study were purchased from Osmonics (Westborough, MA).

Percentage 0.05 (m/V) solution of ammonium pyrrolidine dithiocarbamate (APDC) (Sigma Chem. Co., St. Louis) was prepared by dissolving the required amount of APDC in a water/ethanol (75/25, v/v) mixture. The APDC solution was prepared daily.

2.3. Preconcentration procedure

Twenty-five milliliters portion of an aqueous solution containing 20 µg Pb(II) and 10 µg Ag(I) ions was placed in a glass

beaker in the experiments for the retention of investigated metal ions on cellulose nitrate membrane filter. APDC solution was added and then pH of the solution was adjusted by the addition of 0.1 mol L⁻¹ HCl or 0.1 mol L⁻¹ NH₃. After 10 min, metal-chelates 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 cellulose nitrate membrane was completely dissolved in 0.5 mL of concentrated nitric acid at 80 °C on a hot plate on a hood. The solution was evaporated to dryness. The residue was diluted to 2–5 mL with distilled water. The metal concentrations in the final solution were determined by FAAS.

2.4. Application to real samples

Soil sample (0.5 g) from Mersin city of Turkey was digested with aqua regia (12 mL concentrated hydrochloric acid and 4 mL of concentrated nitric acid) at room temperature then it was heated to 95 °C. After the evolution of NO₂ fumes had ceased, the mixture was evaporated almost to dryness on a sand-bath and mixed with 8 mL of aqua regia. Then the mixture was again evaporated to dryness. After evaporation, 8–9 mL of distilled water was added and the sample was mixed. The resulting mixture was filtered through a blue band filter paper. The filtrate was diluted to 25 mL with distilled water. pH of this solution was adjusted to 4.0 by the addition of diluted HCl. Then the preconcentration procedure given above was applied.

The water samples were collected in pre-washed (with detergent, doubly deionized distilled water, dilute HNO₃ and doubly deionized distilled water, respectively) polyethylene bottles. The samples were filtered through a Millipore cellulose nitrate membrane of pore size 0.45 µm. The samples were stored in 1 L polyethylene bottles and acidified to 1% with nitric acid and were subsequently stored at 4 °C in a refrigerator. To apply the presented method, 100 mL of water sample was taken in a beaker, and then the pH of the sample was adjusted to pH 4 with 0.1 mol L⁻¹ HCl. Then the separation/preconcentration method given above was applied. The concentration of the analyte ions in the final solution were determined by FAAS.

3. Results and discussion

The enrichment/separation procedure was optimized for various analytical parameters such as pH, sample volume, matrix effects, etc. to obtain quantitative recoveries of the metal ions on cellulose nitrate membrane filter. The percent of metal adsorbed on the filter was calculated from the amounts of metal in the starting sample and the amounts of metal in the final solution.

3.1. Effect of pH

The influences of pH of the aqueous solutions on the recoveries of Ag(I) and Pb(II) as APDC chelates on cellulose nitrate membrane filter were investigated in the pH range 2–8. The pH of the solutions was adjusted by the addition of 0.1 mol L⁻¹ HCl or 0.1 mol L⁻¹ NH₃. The results were depicted in Fig. 1. The

Table 1
Instrumental conditions for the measurements of the analytes by FAAS

| Analyte | Wavelength (nm) | Slit width (nm) | Lamb current (mA) |
|---------|-----------------|-----------------|-------------------|
| Pb | 283.3 | 0.7 | 8.0 |
| Ag | 328.1 | 0.7 | 5.0 |

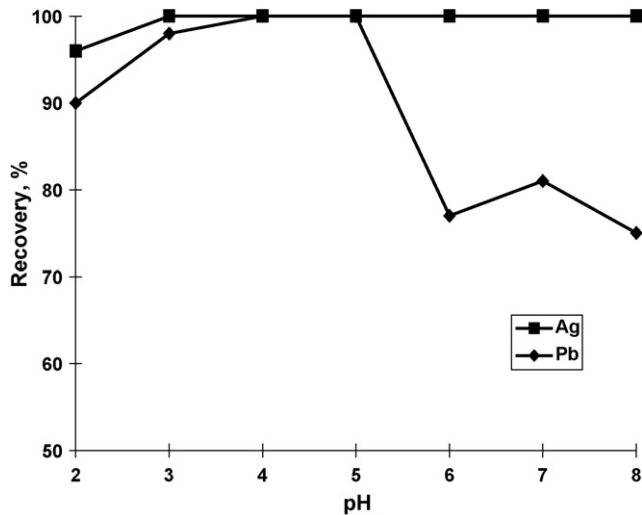


Fig. 1. The influences of the pH of the aqueous solution on the recoveries of Ag(I) and Pb(II) ions ($N=3$, membrane: 0.45 μm pore size, 47 mm diameter cellulose nitrate).

quantitative recoveries (>95%) for silver and lead were found at the pH ranges 3–8 and 3–5, respectively. All subsequent studies were carried out at pH 4. The preconcentration studies were also performed at pH range of 4 without APDC. The recoveries of Ag(I) and Pb(II) were not quantitatively recovered. This situation concluded that ammonium pyrrolidine dithiocarbamate (APDC) as complexing agent is necessary for quantitative recoveries of all the analyte ions on cellulose nitrate membrane filter at our working conditions.

3.2. Influences of amounts of APDC

Due to the amount of ligand, which is also an important factor in the preconcentration studies for the quantitative recoveries of analyte ions from the working media [37–41], the influences of the APDC amounts on the retention of Ag(I) and Pb(II) on the cellulose nitrate membrane filter was also examined in the

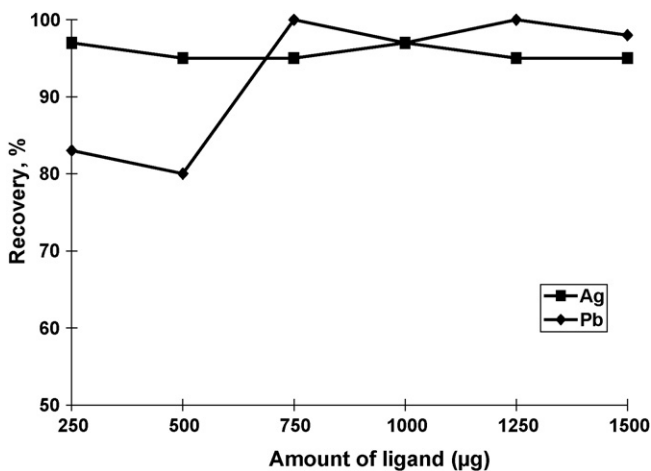


Fig. 2. Effects of the ligand mass on the recovery of Ag(I) and Pb(II) ions ($N=3$, ligand: ammonium pyrrolidine dithiocarbamate (APDC), membrane: cellulose nitrate).

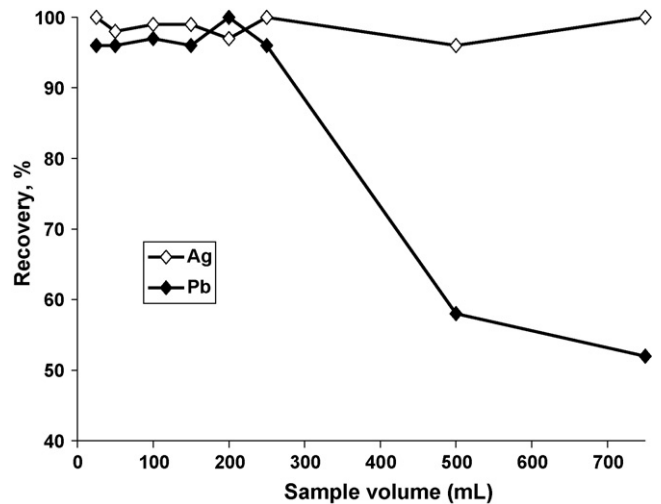


Fig. 3. Effects of sample volume on the recoveries of Ag(I) and Pb(II) (filter: cellulose nitrate, $N=3$).

ligand amount range 250–1500 μg with keeping other analytical parameters constant. The results were given in Fig. 2. Quantitative recoveries for silver and lead ions were obtained in the range of 250–1500 μg of APDC and 750–1500 μg of APDC, respectively. All further works, 1500 μg of APDC was added to the working solutions.

3.3. Effect of sample volume

The membrane filtration technique is a common procedure for extraction and separation of metal ions from large sample volumes to obtain high preconcentration factor. The recovery values as a function of sample volume were shown in Fig. 3. It was found that the recoveries were constant when up to 750 mL for silver(I) and 250 mL for lead(II) of the sample solution was used. At the higher volumes the recoveries for analytes were decreased. Therefore, a preconcentration factor of 375 for sil-

Table 2
Influences of matrix ions on the recoveries ($N=3$)

| Ion | Added as | Concentration (mg L^{-1}) | Recovery (%) | |
|------------------|---------------------|--------------------------------------|--------------|-------------|
| | | | Ag | Pb |
| Na^+ | NaNO_3 | 1000 | 95 ± 3 | 98 ± 3 |
| | | 2500 | 94 ± 1 | 98 ± 5 |
| K^+ | KNO_3 | 1000 | 98 ± 4 | 97 ± 4 |
| Mg^{2+} | $\text{Mg(NO}_3)_2$ | 1000 | 99 ± 5 | 98 ± 3 |
| Ca^{2+} | $\text{Ca(NO}_3)_2$ | 1000 | 95 ± 2 | 96 ± 0 |
| Fe^{3+} | $\text{Fe(NO}_3)_3$ | 5 | 103 ± 2 | 97 ± 5 |
| | | 10 | 101 ± 2 | 94 ± 5 |
| Co^{2+} | $\text{Co(NO}_3)_2$ | 5 | 97 ± 3 | 85 ± 0 |
| | | 10 | 97 ± 3 | 92 ± 5 |
| Cu^{2+} | $\text{Cu(NO}_3)_2$ | 5 | 101 ± 1 | 97 ± 3 |
| | | 10 | 96 ± 4 | 98 ± 5 |
| Mn^{2+} | $\text{Mn(NO}_3)_2$ | 5 | 100 ± 5 | 102 ± 3 |
| | | 10 | 103 ± 2 | 92 ± 1 |

ver(I) and 125 for lead(II) can be achieved when using 750 mL for silver(I) and 250 mL for lead(II) of the sample volume and 2.0 mL of final volume.

3.4. Matrix effects

Due to determination of metal ions by atomic spectroscopic methods, positive or negative effects of matrix components of the analyzed samples are one of the main problems [40–43], the influences of possible matrix ions in the environmental samples and some transition metals were also examined. The effect of potential interfering ions on the determination of Ag(I) and Pb(II) were investigated by adding known concentrations of each ion in a solution containing analytes and then determining the latter. The results were summarized in Table 2. The tolerated amounts of each ion were the concentration values tested that caused less than 5% of the absorbance alteration. The ions normally present in water do not interfere under the experimental conditions used. Also, some of the transition metals at mg L^{-1} levels were not interfered on the recoveries of the analyte ions. The matrix metal ions were not retained on the cellulose nitrate membrane filter because of their very low stability constants of APDC complexes. These results show that the proposed preconcentration/separation method could be applied to the natural water samples.

3.5. Reproducibility and detection limits

The analytical performance of the procedure can be calculated for the results from FAAS measurements. The calibration curves for analyte ions were drawn after setting various parameters of FAAS including wavelength, slit width, lamp current at an optimum level. The optimum linear concentration ranges for Ag(I) and Pb(II) were $0.25\text{--}5.0 \text{ mg L}^{-1}$ and $0.5\text{--}10.0 \text{ mg L}^{-1}$. The statistical calculations are based on the average of triplicate readings for a standard solution analyte ions.

The reproducibility of the preconcentration and separation method was evaluated by passing 25 mL of solution containing $20 \mu\text{g Pb(II)}$ and $10 \mu\text{g Ag(I)}$ ions through cellulose membrane filter and repeating this procedure ten times. The relative stan-

Table 3

Application of the presented procedure for a soil sample from Mersin city of Turkey (Amounts of soil: 0.50 g, $N=3$)

| Analyte | Added (μg) | Found (μg) | Recovery (%) |
|---------|-------------------------|-------------------------|--------------|
| Ag | 0 | BDL | – |
| | 12.5 | 12.0 ± 0.2^a | 96.0 |
| | 25.0 | 24.6 ± 0.6 | 98.4 |
| | 50.0 | 50.7 ± 0.6 | 101.4 |
| Pb | 0 | BDL | – |
| | 12.5 | 12.5 ± 0.5 | 100.0 |
| | 25.0 | 24.7 ± 0.9 | 98.8 |
| | 50.0 | 50.0 ± 1.5 | 100.0 |

BDL: below the detection limit.

^a Mean \pm standard deviation.

dard deviations (R.S.D.) were 3.0% for Ag(I) and 2.6% for Pb(II).

The detection limits for analytes were calculated after presented preconcentration procedure was applied to the blank solutions. The detection limits of the investigated elements based on three times the standard deviations of the blank ($k=3$, $N=11$) on a sample volume of 150 mL were $4.6 \mu\text{g L}^{-1}$ for silver(I) and $15.3 \mu\text{g L}^{-1}$ for lead(II).

3.6. Application to environmental samples

We have explored the feasibility of the methodology given in Section 2 using preconcentration with cellulose nitrate membrane filter for the determination of Ag(I) and Pb(II) in different environmental matrices by standard addition method. Reliability was checked by spiking experiments and independent analysis. The results for this study are presented in Table 3 for a soil samples from Mersin, Turkey and in Table 4 for two different water samples. The recovery of spiked samples is satisfactorily reasonable and was confirmed using addition method, which indicates the capability of the system in the determination of Ag(I) and Pb(II). 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 4

Application of the presented procedure for two water samples (sample volume = 100 mL, final volume: 5 mL, $N=4$)

| Analyte | Added (μg) | Tap water from Eskisehir baglari | | Bottled drinking water | |
|---------|-------------------------|----------------------------------|--------------|-------------------------|--------------|
| | | Found (μg) | Recovery (%) | Found (μg) | Recovery (%) |
| Ag | 0 | BDL | – | BDL | – |
| | 6.25 | 6.66 ± 0.11^a | 106.6 | 6.36 ± 0.19^a | 101.8 |
| | 12.5 | 12.3 ± 0.3 | 98.4 | 12.9 ± 0.1 | 103.2 |
| | 25.0 | 24.3 ± 0.4 | 97.2 | 24.3 ± 0.5 | 97.2 |
| | 50.0 | 48.2 ± 0.5 | 96.4 | 48.8 ± 1.5 | 97.6 |
| Pb | 0 | BDL | – | BDL | – |
| | 12.5 | 12.6 ± 0.8 | 100.8 | 12.5 ± 0 | 100.0 |
| | 25.0 | 25.9 ± 0.5 | 103.6 | 24.4 ± 0.3 | 97.6 |
| | 50.0 | 48.5 ± 0.8 | 97.0 | 49.5 ± 0.7 | 99.0 |
| | 100.0 | 96.3 ± 1.0 | 96.3 | 102.1 ± 1.0 | 102.1 |

BDL: below the detection limit.

^a Mean \pm standard deviation.

4. Conclusion

The presented membrane filtration method has the following advantages: simple, rapid, and low analysis cost. The recoveries of analyte ions at pH 4 were greater than 95% at the optimal working conditions. The time required for the membrane filtration and determination was about 20 min. The analyte ions can be sensitively determined by FAAS without any influence of matrix ions. The membrane filtration method can be applied not only to water samples but also geological and biological samples and similar media.

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