

## Membrane Filtration of Iron(III), Copper(II) and Lead(II) Ions as 1-(2-pyridylazo) 2-naphtol (PAN) for their Preconcentration and Atomic Absorption Determinations

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A membrane filtration procedure for the preconcentration and atomic absorption spectrometric determination of Pb(II), Co(II) and Fe(III) ions in natural water samples has been established. Cellulose nitrate membrane filters (0.45  $\mu$ m and 47 mm diameter) were used in all experiments. The procedure is based on chelate formation of the analyte metals with 1-(2-pyridylazo) 2-naphtol (PAN) and on retention of the chelates on cellulose nitrate membrane filter. The cellulose nitrate membrane and analyte ions were completely dissolved by 500  $\mu$ L of nitric acid at 85 °C on a hood and then metal determinations were performed by flame atomic absorption spectrometry. The method was applied to natural water samples for the determination of analyte ions with satisfactory results, e.g., recoveries > 95%, RSD's < 10%.

**Keywords:** 1-(2-Pyridylazo) 2-naphtol (PAN); Membrane filtration; Separation; Enrichment; Cellulose nitrate membrane; Natural water samples; FAAS.

### INTRODUCTION

Trace heavy metal analysis<sup>1-7</sup> is an important part of environmental studies in order to investigate pollution in the environment and its effects on human life. Because of low costs and easy applications, in determinations of traces of heavy metal ions in environmental samples, atomic absorption spectrometry (AAS) is generally the main instrument. However, matrix effects and lower metal concentrations are limited to AAS determinations.<sup>8-10</sup> In order to solve the problems, the preconcentration/separation methods are necessary for AAS determinations of metal ions.<sup>10-11</sup> Coprecipitation, liquid-liquid extraction, electrodeposition, ion exchange, cloud point extraction and solid phase extraction procedures based on adsorption are important preconcentration techniques.<sup>12-23</sup> Many of these methods are time consuming, and usage of organic solvents in these procedures is generally at high levels.

Membrane filtration is also one of the preconcentration methods for traces of metal ions.<sup>24-31</sup> The metal ions were collected on the membrane as a suitable form including metal chelates. The collection of metal ions is performed very quickly by filtration under suction with the aid of an aspirator. The collected analyte species on the membrane filter are dissolved together with the membrane in a small amount of

suitable solvent including mineral acids. The trace species in the final solution are determined by an instrumental method such as AAS, spectrophotometry, etc. The materials of membrane filters with a strong affinity for hydrophobic species in water are generally useful to retain the species by filtration. Membrane filters, including cellulose nitrate and acetate, have been used for enrichment of trace heavy metal ions in natural waters and biological samples.<sup>22-28</sup> The combination of 1-(2-pyridylazo) 2-naphtol (PAN)-cellulose nitrate membrane filter for the separation and enrichment of the traces of metal ions has not been used, according to our literature survey.

The aim of the present work is to establish a simple, fast and sensitive preconcentration/separation procedure by using membrane filtration for the flame AAS determination of Pb(II), Cu(II) and Fe(II) ions in natural water samples. The analytical conditions (pH, sample volume, reagent amounts, type of the membrane filter, etc.) for the quantitative recoveries of the investigated analyte ions were examined.

### EXPERIMENTAL

#### Instruments

A Perkin-Elmer Model 3110 atomic absorption spec-

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trophotometer 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. A pH meter, Nel pH-900 Model glass-electrode was employed for measuring pH values in the aqueous phase. An Erlenmeyer flask with a ground stopper was used for filtration of the solutions.

### Reagents and Solution

Analytical reagent-grade chemicals were employed for the preparation of all solutions. All aqueous solutions were prepared from doubled-quartz-distilled water. Stock metal ion solutions, 1000 mg/l (E. Merck, Darmstadt) were diluted daily for obtaining reference and working solutions. The calibration curve was established using the standard solutions prepared in 1 M HNO<sub>3</sub> 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). 1-(2-pyridylazo) 2-naphtol (PAN) (E. Merck, Darmstadt) was dissolved in a water/ethanol (20%, v/v) mixture. The pH of the model solution was adjusted to pH 2 with phosphate buffer, pH 4-6 with CH<sub>3</sub>COO<sup>-</sup>/CH<sub>3</sub>COOH buffers, pH 7 with borate buffer and pH 8-10 with NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> buffers.

### Preconcentration Procedure

A 40 mL portion of an aqueous solution containing 10-20 µg of each analyte ion was placed in a glass beaker. Ten mL of buffer solution and 1-(2-pyridylazo) 2-naphtol (PAN) solution were added. 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 membrane was completely dissolved in 500 µL 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<sub>3</sub>. The metal concentrations in the final solution were determined by flame AAS.

### Procedure for Water Samples

For application of the proposed preconcentration/separation method, 150 mL of water sample was taken in a beaker, and then the pH of the sample was adjusted to pH 7 with borate buffer. Then the preconcentration method given above was applied. The concentrations of the analyte ions in the final solution were determined by FAAS.

## RESULTS AND DISCUSSION

To obtain quantitative recoveries of analytes on cellulose nitrate membrane, the procedure was optimized for various analytical parameters such as pH, sample volume and amounts of PAN. The percentage of metal adsorbed on the filter was calculated from the amounts of metal in the starting sample and the amounts of metal eluted from the filter.

### Influences of pH of the Solutions on the Retentions

The pH of the working solution is one of the important factors on the formation of PAN-metal chelates and adsorption of these chelates on the membrane filters.<sup>32</sup> The effect of pH on the retentions of Cu(II), Fe(III) and Pb(II) ions as PAN chelates on cellulose nitrate membrane filter were investigated in the pH range of 2-10. The results are depicted in Fig. 1. The quantitative recoveries (> 95%) for Cu, Fe and Pb were found at the pH ranges 7-8, 2-10 and 6-8, respectively. All subsequent studies were carried out at pH 7 by using borate buffer.

### Influences of the Ligand Amounts

The influences of the 1-(2-pyridylazo) 2-naphtol (PAN) amounts on the retention of Cu(II), Fe(III) and Pb(II) on the cellulose nitrate membrane filter was also examined in the ligand amount range 0.1-1.0 mg with keeping other parameters constant. The recoveries of copper, iron and lead ions were quantitative all through the working range. The addition of 0.2 mg (1.0 mL of 0.02% (w/V) solution) of PAN solution

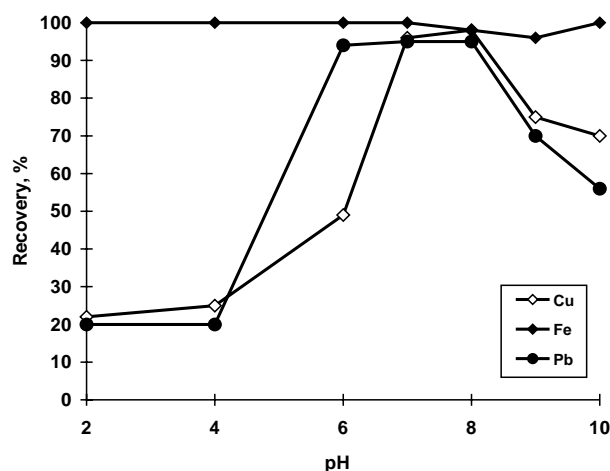


Fig. 1. The influences of the pH of the aqueous solution on the recoveries of analyte ions (N = 3, Membrane: 0.45 µm pore size, 47 mm diameter cellulose nitrate).

is recommended.

### Type and Size of Membrane Filter

The effects of the membrane type and membrane size on the recovery values of the analyte ions were also examined. For this purpose, various membrane filters given in Table 1 were used. The recoveries of analytes were quantitative with cellulose nitrate and acetate membrane filters (0.22  $\mu\text{m}$  and 0.45  $\mu\text{m}$ ). When polysulfone (PES) membrane filter was used for the preconcentration studies, the recovery of copper was not quantitative (Table 1). The recovery values for Cu, Fe and Pb ions were not quantitative with polytetrafluoroethylene (PTFE) membrane filter. In all further studies cellulose nitrate membrane filter (47 mm 0.45  $\mu\text{m}$ ) was used. Concentrated mineral acids including  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$  have been used for the dissolution of the cellulose nitrate membrane filter. Quantitative recovery values for the investigated analytes were obtained by using only nitric acid.

### Effect of Sample Volume

The effect of sample volume on the recoveries was also investigated. 20-500 mL of sample solutions was passed through the system with optimal conditions. Quantitative recoveries (> 95%) were obtained for sample volumes of 150 mL for the analyte ions. In this experiment, 150 mL of sample solution was adopted for the preconcentration of analytes from water samples, the final volume was 2 mL and a precon-

centration factor of 75 is achieved.

### Matrix Effects

The influences of possible matrix ions in natural water samples were also examined on the retention of copper, iron and lead ions on cellulose nitrate membrane. The results are summarized in Table 2. The ions normally present in water do not interfere under the experimental conditions used. The matrix metal ions were not retained on the cellulose nitrate membrane filter because of the very low stability constants of PAN complexes.

### Accuracy Studies

To estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked in tap water and bottled water samples that have 150 mL, and the resulting solutions were submitted to the preconcentration procedure. A good agreement was obtained between the added and measured analyte amounts. The recoveries calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects. The detection limits of the elements based on three times the standard deviations of the blank ( $N = 21$ ) were 3.6  $\mu\text{g/l}$  for Cu, 9.5  $\mu\text{g/l}$  for Fe and 10.3  $\mu\text{g/l}$  for Pb.

### Application to Water Samples

The proposed preconcentration method has been ap-

Table 1. Effects of the membrane type and size on the recoveries of analyte ions (pH = 7,  $N = 3$ )

Membrane Type and Size	Recovery, %		
	Cu	Fe	Pb
Cellulose Nitrate, 0.45 $\mu\text{m}$	98 $\pm$ 1	102 $\pm$ 2	100 $\pm$ 1
Cellulose Nitrate, 0.22 $\mu\text{m}$	95 $\pm$ 2	99 $\pm$ 2	98 $\pm$ 3
Cellulose Acetate, 0.45 $\mu\text{m}$	95 $\pm$ 3	98 $\pm$ 2	95 $\pm$ 3
Cellulose Acetate, 0.22 $\mu\text{m}$	98 $\pm$ 2	98 $\pm$ 1	95 $\pm$ 2
Polysulfone (PES), 0.45 $\mu\text{m}$	84 $\pm$ 2	101 $\pm$ 3	92 $\pm$ 2
Polytetrafluoroethylene (PTFE), 0.45 $\mu\text{m}$	63 $\pm$ 2	89 $\pm$ 3	83 $\pm$ 2

Table 2. Influences of matrix ions of natural waters on the recoveries of the analytes ( $N = 3$ )

Ion	Added As	Concentration (mg/l)	Recovery, %		
			Cu	Fe	Pb
$\text{Na}^+$	NaCl	20.000	98 $\pm$ 2	100 $\pm$ 2	97 $\pm$ 1
$\text{K}^+$	KCl	1.000	101 $\pm$ 2	102 $\pm$ 2	94 $\pm$ 1
$\text{Ca}^{2+}$	$\text{CaCl}_2$	500	96 $\pm$ 2	101 $\pm$ 3	98 $\pm$ 3
$\text{Mg}^{2+}$	$\text{MgCl}_2$	1.000	98 $\pm$ 3	96 $\pm$ 3	100 $\pm$ 1
$\text{SO}_4^{2-}$	$(\text{NH}_4)_2\text{SO}_4$	2.000	95 $\pm$ 1	96 $\pm$ 2	94 $\pm$ 3
$\text{Cl}^-$	$\text{NH}_4\text{Cl}$	25.000	102 $\pm$ 3	98 $\pm$ 2	96 $\pm$ 2

Table 3. The concentrations of copper, lead and iron in some water samples (N = 4)

Sample	Concentration, $\mu\text{g/l}^*$		
	Cu	Fe	Pb
Tap Water-I	$3.4 \pm 0.3$	$22.1 \pm 2.1$	BDL
Tap Water-II	$3.7 \pm 0.3$	$39.1 \pm 2.9$	BDL
Bottled Drinking Water-I	BDL	$17.8 \pm 0.9$	BDL
Bottled Drinking Water-II	$2.9 \pm 0.2$	$16.6 \pm 0.4$	BDL

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

plied to natural water samples for the determinations of analyte ions. The results are given in Table 3. A volume of 150 mL of water samples was used for the analysis. The final volume was 2 mL. The relative standard deviations of the determination were less than 10%.

## CONCLUSION

The presented method has the following advantages: simple, rapid and low analysis cost. The PAN metal complexes were retained rapidly and quantitatively on a cellulose nitrate membrane filter by filtration under suction. After optimization of analytical parameters, the procedure was successfully applied for the preconcentration of the analytes in the natural water samples. The method applied provides good precision with relative standard deviations lower than 9% and high accuracy obtained with the quantitative recoveries (> 95%) of spiked analytes.

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