Determination of trace metal ions by AAS in natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column

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Abstract

A simple preconcentration method is described for the determination of Cu, Mn, Co, Cd, Pb, Ni and Cr in water samples by flame AAS. Trace metal ions in water were sorbed as pyrocatechol violet complexes on activated carbon column at the pH range of 4–8, then eluted with 1 M HNO_3 in acetone. The effect of major cations and anions of the natural water samples on the sorption of metal ions has been also investigated. The concentration of the metal ions detected after preconcentration was in agreement with the added amount. The present method was found to be applicable to the preconcentration of Cu, Mn, Co, Cd, Pb, Ni and Cr in natural water samples with good results such as R.S.D. from 3 to 8% ($N = 10$) and detection limits under 70 ng l^{-1}. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The importance of the determination of trace metal concentration in natural water samples is increasing in contamination monitoring studies. Flame atomic absorption spectrometry (AAS) is a simple and well available technique for the determinations of heavy metals in the natural water samples. However its main problem is the low sensitivity for trace metals at μg l^{-1} level. This limitation can be overcome by the use of a preconcentration procedure. For this purpose, various preconcentration/separation methods such as solvent extraction [1,2], coprecipitation [3–5], ion exchange [6,7] sorbent extraction [8–10], resin chelation [11–13] etc. have been widely used.

Solid phase extraction (SPE) technique has found increasing application for the preconcentration of trace metal ions and elimination of matrix interference prior to AAS analysis. Different sor-

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bents such as Amberlite XAD resins [14–17], activated carbon [18–20], C-18 bonded silica [21,22] and others [23,24] have been used for the preconcentration of trace metal ion from various media.

Solid phase extraction procedures based on sorption of metal complexes on activated carbon have widespread applied [18–20,25,26]. In most of the previous studies metal complexes are collected on an activated carbon filter. The preconcentrated trace metals on the filter are recovered by treating with concentrated nitric acid. Thus, the prepared activated carbon filter is used only for one analysis. On the other hand, the column packed with activated carbon is repeatedly used with sorption–elution techniques. So, time consuming step due to acid digestion of activated carbon in the filter techniques is avoided. However the number of activated carbon studies is limited [27–30].

Pyrocatechol violet is widely used organic chelating agent that has a larger formation constant with metal ions [31]. Pyrocatechol violet is used in chemical enrichment and separation of trace heavy metal ions by various preconcentration techniques prior to their determination [32–35].

In the present work, a column separation–preconcentration method has been established for the flame atomic absorption spectrometric determination of trace amounts of copper, manganese, cobalt, cadmium, lead, nickel and chromium ions on activated carbon as pyrocatechol violet complexes. The proposed method was applied for the determination of the investigated ions in the drinking water samples collected from Kayseri and Nigde, Turkey.

2. Experimental

2.1. Apparatus

A Perkin–Elmer Model 3110 flame atomic absorption spectrometer was used in the studies. Atomic absorption measurements were carried out using air/acetylene flame. The operating parameters for working elements were set of as recommended by the manufacturer.

2.2. Reagents

All solutions were prepared with deionized water. Otherwise stated, analytical-grade acetone, acids and other chemicals used in this study obtained from Merck, Darmstadt, Germany. The calibration curve was established using the standard solutions prepared in 1 M HNO_3 by dilution from 1000 mg l^{-1} stock solutions (Merck). The calibration standard was not submitted to the preconcentration procedure. The chelating agent was pyrocatechol violet (Merck) and was daily dissolved in a water/ethanol (80/20, v/v) mixture.

Ammonium acetate buffer solutions (0.1 M) were prepared by adding an appropriate amount of acetic acid (Merck) to ammonium acetate solutions for pH 2–6 and ammonium chloride buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia (Merck) to ammonium chloride solutions for pH 8–10.

Activated carbon powder used as adsorbent in the preconcentration of metal ions (Merck No. 2186) was treated with concentrated HCl, washed with distilled water and dried at 110°C.

2.3. Preparation of activated carbon column

A column containing 500 mg of activated carbon in water suspension was 10 cm long and 1.0 cm in diameter. The bed height in the column was 2.0 cm. The column was preconditioned with 10–15 ml 1 M HNO_3 in acetone prior to percolation of sample. After elution, the activated carbon column was regenerated with 10–15 ml of acetone.

2.4. Preconcentration procedure

The method was tested with model solutions before its application to the natural waters. Ten ml of buffer solution (to give the desired pH between 2 and 10) and pyrocatechol violet solution were added to 50 ml of solution containing 10–20 μg of the working element. The column was preconditioned with the buffer solution. Metal–pyrocatechol violet solution was passed through the column at a flow rate of 5–10 ml min^{-1} using a vacuum aspirator. After passing of

this solution, the column was rinsed twice with 10 ml of water. The adsorbed metal chelate on the column was eluted with 8–10 ml portion of 1 M HNO_3 in acetone. The eluted solution was evaporated to near dryness and then diluted to 5 ml with 1.0 M HNO_3. The eluent was analyzed for the determination of metal concentrations by atomic absorption spectrometry.

2.5. Collection of water samples

Water samples were collected from the municipal water supplies of Kayseri Merkez at Kayseri and Nigde University, Organize Sanayi and Nigde Sehir Merkezi at Nigde in July 1999. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size.

2.6. Determination of Cu, Mn, Co, Cd, Pb, Ni and Cr in water samples

For the preconcentration, the pH of 500 ml of the sample was adjusted to 6 with acetate buffer. Then, the ligand solution was added. After 10 min, the sample was passed through the column at a 5 ml min^{-1} flow rate. Then, the metal chelates adsorbed on the activated carbon column were eluted with 1 M HNO_3 in acetone. The effluent was evaporated to near dryness and made up to 5 ml with 1 M HNO_3. The concentrations of Cu, Mn, Co, Cd, Pb, Ni and Cr in the eluent were determined by flame AAS.
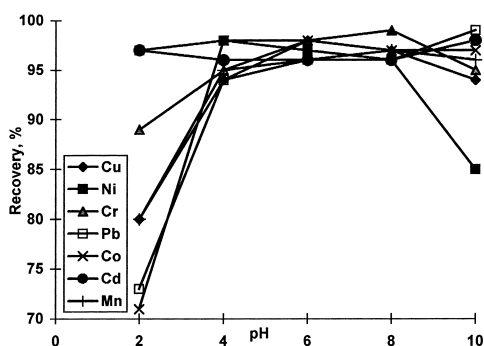

Fig. 1. Influences of pH on the recoveries (N:4; ligand: pyrocatechol violet, eluent: 1 M HNO_3 in acetone; 10 ml eluent volume)

3. Results and discussion

In order to obtain quantitative recoveries of the metal ions on the activated carbon column, the preconcentration procedure was optimized for various analytical parameters such as pH, sample volume and amount of activated carbon, matrix effects etc. The percent of metal adsorbed on the column was calculated from the amounts of metal in the starting sample and the amounts of metal eluted from the column.

3.1. Influences of pH on sorptions

Metal ions were enriched on the activated carbon column in the pH ranges 2–10, keeping the other parameters constant. The recoveries for the heavy metals are shown in Fig. 1. The optimum pH range for quantitative recoveries of Cu, Ni, Pb, Fe, Cd, Co and Mn is 4–8. All subsequent studies were carried out at pH 6. The volume of buffer added (10 ml) had no effect on the recoveries.

3.2. Effects of the amount of activated carbon

The effects of the amount of activated carbon on the sorption of metal ions at pH 6 was examined in the range of 100–800 mg. The results demonstrated that, quantitative recoveries (> 95%) of the working elements were observed in the range of 300–600 mg. Above 600 mg, the recoveries were below 95% with 10 ml of the eluent. When 25 ml of eluent was used, the recoveries were quantitative with 600 mg of activated carbon. In the proposed procedure, 500 mg of activated carbon is recommended.

3.3. Influences of ligand concentration on the recoveries

In order to determine the concentration of the pyrocatechol violet required for quantitative recoveries, the proposed method was applied, changing the pyrocatechol violet concentration from 0.3×10^{-4} to 1.0×10^{-2} M. It was found that, the recovery of the metal ions increased with increasing concentrations of pyrocatechol violet
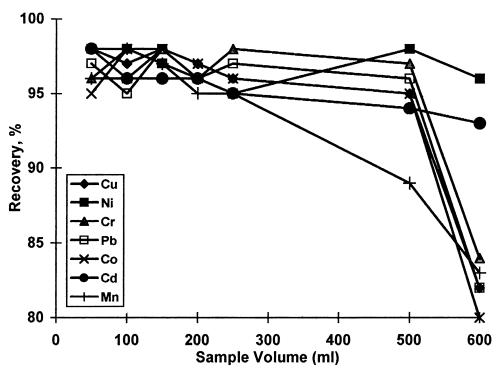
Fig. 2. Effect of the sample volume on the recovery of trace metal ions from the activated carbon column (N:4; eluent: 1 M HNO$_3$ in acetone; 10 ml eluent volume)

added and reached a constant value with at least 0.33×10^{-3} M. On this basis, studies were carried out at a pyrocatechol violet concentration of 1.0×10^{-3} M. This concentration of pyrocatechol violet is enough for the preconcentration procedure because of the very low level of the investigated metal ion concentrations in natural waters.

3.4. Effect of flow rate and desorption studies

The influence of flow rate on the adsorption of trace metals was studied. Flow rate in the range of 5–25 ml min^{-1} had no significant effect on the recoveries of the investigated elements. All subsequent experiments were performed at 25 ml min^{-1} flow rate.

The desorption of the retained metals from the activated carbon column was tested using various eluting agent. The selected volume of the eluent was 5 ml, but the same results were obtained with higher volumes. Quantitative recoveries (>95%) were obtained for the investigated elements with 1 M HNO$_3$ in acetone, 1 M HCl in acetone and 3 M HCl in acetone. These results agree with the data given in our papers [36–38].

3.5. Effect of the sample volume on the recoveries

In order to explore the possibility of enriching low concentrations of the analytes from the large sample volume, the effect of the sample solution volume on the metal sorption was studied by

passing 50–600 ml volumes through the activated carbon column at a 5 ml min^{-1} flow rate. The adsorption of the metal ions with 500 mg activated carbon was not affected by sample volume below 500 ml. Above 500 ml the percent sorption decreased for the analytes (Fig. 2). The recoveries of analytes decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume above 500 ml. In the present study 500 ml of sample solution was adopted for the preconcentration of the investigated ions from drinking water samples, the adsorbed metals can be eluted with 5 ml of 1 M HNO$_3$ in acetone and a preconcentration factor of 100 is achieved by this technique.

3.6. Effect of matrix ions

The effects of matrix ions in water samples on the recovery of Cu, Mn, Co, Cd, Pb, Ni and Cr was also investigated (Table 1). There is no interferences in the presence of large amounts of alkaline, alkaline earth metals and main anions in the water samples. The matrix metal ions are not retained on the column because of their very low stability constants of pyrocatechol violet complexes.

3.7. Detection limits

The detection limits based on three times the S.D. of the blank were 25 ng l^{-1} for Cu, 21 ng l^{-1} for Mn, 36 ng l^{-1} for Co, 13 ng l^{-1} for Cd, 48 ng l^{-1} for Pb, 54 ng l^{-1} for Ni and 69 ng l^{-1} for Cr ($k = 3$, $N = 21$) on a 200 ml of sample volume after applying the preconcentration procedure. The detection limits can be decreased by one order of magnitude by increasing the sample volume to 500 ml.

3.8. Recovery of spikes from a water sample

The recoveries of the trace metal ions from a drinking water sample from Nigde Merkezi were also studied. As can be seen in Table 2, satisfactory results were obtained for the elements examined. These results confirm the validity of the proposed method for the preconcentration of the investigated ions.

Table 1
Effect of the matrix ions on the recovery of metal ions (100 ml volume, $N = 4$)

Ion	Added as	Concentration (mg l^{-1})	Recovery (%)						
			Cu	Mn	Co	Cd	Pb	Ni	Cr
–	–	–	97	99	101	96	98	100	96
Na$^+$	NaCl	500	98	97	96	99	96	102	97
		1000	95	96	98	98	97	99	95
K$^+$	K$_2$SO$_4$	500	98	98	95	96	97	99	96
		1000	96	97	100	96	97	98	96
Ca^{2+}	CaSO$_4$	500	97	98	96	96	98	98	96
		1000	98	97	96	99	98	96	95
Mg^{2+}	MgSO$_4$	500	99	103	96	98	100	101	96
		1000	96	98	97	95	95	96	96
Cl$^-$	NaCl	500	97	99	96	95	96	100	97
		1000	98	96	98	97	97	99	95
(SO$_4$)$^{2-}$	(NH$_4$)$_2$SO$_4$	500	98	97	96	99	96	102	97
		1000	95	96	98	98	97	99	95

3.9. Application to water samples

The present method was applied to the determination of Cu, Mn, Co, Cd, Pb, Ni and Cr in drinking water samples from Kayseri and Nigde, Turkey. A volume of 500 ml of water samples was used for the analysis. The results are summarized in Table 3. The results have been calculated on the assumption of 100% recovery of the trace metal ions. The R.S.D. were less than 10%. The concentrations of cadmium and chromium in the all drinking water samples are below 0.1 and 1 μg l^{-1}, respectively.

4. Conclusion

The proposed preconcentration procedure provides fast and simple method for the enrichment of Cu, Mn, Co, Cd, Pb, Ni and Cr on an activated carbon column from drinking water samples. The application of the proposed method has shown that trace metal ions can be effectively separated and preconcentrated from drinking water samples.

Table 2
Recovery data for the preconcentration of trace metals from a drinking water sample from Nigde Merkezi (250 ml sample volume)

Element	Added (μg)	Found[a] (μg)	Recovery (%)
Cu	10	10.2 ± 0.2	102
	20	20.2 ± 0.3	101
Mn	10	10.6 ± 0.1	103
	20	20.2 ± 0.2	101
Co	10	10.0 ± 0.1	100
	20	20.4 ± 0.3	102
Cd	10	9.7 ± 0.2	97
	20	19.5 ± 0.2	98
Pb	10	9.9 ± 0.1	99
	20	20.1 ± 0.2	100
Ni	10	10.1 ± 0.3	101
	20	19.9 ± 0.3	100
Cr	10	9.9 ± 0.2	99
	20	20.4 ± 0.1	102

[a] Average of four experiments with 95% confidence interval.

Table 3
Cu, Mn, Co, Cd, Pb, Ni and Cr concentrations of drinking water samples from Kayseri and Nigde, Turkey ($N = 5$, 500 ml sample volume, 5 ml eluent volume)

Sample location	Concentration of metals ($\mu g\ l^{-1}$)[a]				
	Cu	Mn	Co	Pb	Ni
Nigde Sehir Merkezi	22.0 ± 0.2	4.0 ± 0.2	1.7 ± 0.1	9.0 ± 0.7	2.2 ± 0.1
Kayseri Merkez	20.6 ± 0.8	6.5 ± 0.4	4.6 ± 0.2	14.3 ± 0.6	8.1 ± 0.3
Nigde Organize Sanayi	10.3 ± 0.8	22.8 ± 1.9	2.5 ± 0.2	8.2 ± 0.5	4.2 ± 0.3
Nigde Universitesi	17.3 ± 1.5	10.3 ± 0.8	1.8 ± 0.2	7.5 ± 0.2	3.7 ± 0.1

[a] Mean expressed as 95% tolerance limit.

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