

Atomic absorption spectrometric determination of copper, cobalt, cadmium, lead, nickel and chromium in table salt samples after preconcentration on activated carbon

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ABSTRACT

Copper, cobalt, cadmium, lead, nickel, and chromium contents of table salt samples were determined by atomic absorption spectrometry after preconcentration/separation on an activated carbon column as pyrocatechol violet (PV) complexes. The PV-metal ion complexes buffered to pH 6 were retained on an activated carbon column and were then eluted from the column with 1 M nitric acid in acetone. The effect of matrix ions on recoveries of the working elements was also examined. The recoveries of metal ions were in the range of 95–103%. The relative standard deviations (RSD) of the metal ion determinations varied from 2 to 9%.

Keywords: Activated carbon; atomic absorption spectroscopy; preconcentration; table salts; trace metals.

INTRODUCTION

The determination of trace heavy metal contents of environmental samples is very important for public health studies (Narin *et al.* 1998, Doğan *et al.* 1999, Narin & Soylak 1999a, Vlasankova & Sommer 1999, Bagheri *et al.* 2000a, Ferreira *et al.* 2000, Soylak *et al.* 2001a, Zhang *et al.* 2000). The heavy metal ions in table salt samples are below the detection limits of modern instrumental techniques including graphite furnace atomic absorption spectrometry (GFAAS), flame atomic absorption spectrometry (FAAS), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) etc. In addition, their determination is generally influenced by the matrix. Therefore, a separation and preconcentration procedure is necessary prior to determination.

Various enrichment procedures including coprecipitation, extraction, ion exchange, membrane filtration and adsorption have been used for this purpose (Ono *et al.* 1997, Ferreira *et al.* 1998, Soylak *et al.* 1998, Narin & Soylak 1999b, Sun *et al.* 1999, Divrikli *et al.* 2000, Melo *et al.* 2000). Procedures based on sorption of metal ions on sorbents such as Amberlite XAD resins, silica gel, naphthalene, C-18, activated carbon etc. (Soylak *et al.* 1997, 1998, Soylak 1998, Dobrowolski 1999, Garg *et al.* 1999, Taher & Puri 1999, Skinner *et al.* 1999, Bagheri *et al.* 2000b, Cesur & Bati 2000, Tokalioglu *et al.* 2000, Soylak *et al.* 2001b) are popular.

Studies on the adsorption of metals and their chelates on an activated carbon filter for atomic absorption spectrometry (AAS) determinations have been reported (Elçi 1993, Soylak *et al.* 1996). In these procedures, an activated carbon filter was prepared and could be used only once. However, the elution techniques for using activated carbon can be applied many times. In adsorption/elution techniques, activated carbon is filled into a column, then a metal-chelate solution is passed through the column. Metal ions adsorbed on the activated carbon column are eluted with a suitable eluting agent for atomic absorption spectrometric measurements (Narin & Soylak 1999b).

In the present study, the concentrations of copper, cobalt cadmium, lead, nickel and chromium in table salt samples were determined by atomic absorption spectrometry as pyrocatechol violet complexes after a preconcentration/separation procedure using an activated carbon column.

MATERIAL AND METHODS

Apparatus

The instrumental detection systems used were Hitachi Model Z-8000 and Perkin-Elmer Model 3110 atomic absorption spectrometers. The operating parameters for working elements, given in Table 1 for the flame atomic absorption spectrometer and in Table 2 for the graphite furnace atomic absorption spectrometer were as recommended by the manufacturers.

Reagents

Unless otherwise stated, all chemicals were super pure grade and all solutions were prepared in double distilled-deionized water. Stock solutions of investigated metal ions were prepared from appropriate amounts of respective nitrates as 1000 mg/L

Table 1. Conditions for flame atomic absorption spectrometric determinations

Element	Wavelength (nm)	Slit (nm)	Lamp current (mA)	Flow rate of flame gases	
				Air (l/min)	Acetylene (l/min)
Cu	324.8	0.7	25	9.5	2.3
Pb	283.3	0.7	15	9.5	2.3
Ni	232.0	0.2	30	9.5	2.2
Co	240.7	0.2	30	9.5	2.2
Cd	228.8	0.7	12	9.5	2.2
Cr	357.9	0.7	12	9.5	2.6

Table 2. Instrument settings and conditions for the analysis

Parameter	Element					
	Cu	Ni	Cd	Pb	Co	Cr
Wavelength (nm)	324.8	232.0	222.8	283.3	240.7	357.9
Slit width (nm)	1.3	0.2	1.3	1.3	0.2	0.7
Lamp current (mA)	7.5	15.0	7.5	7.5	15	12.0

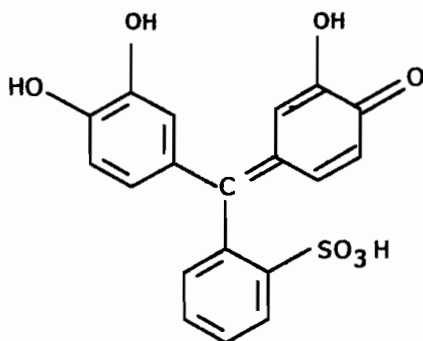
Step	Condition	Cu	Ni	Cd	Pb	Co	Cr
Dry	time (sec)	15	15	15	15	15	15
	temp (°C)	120	120	100	120	100	100
Ash	time (sec)	30	30	30	30	30	30
	temp (°C)	600	700	300	400	600	1200
Atomize	time (sec)	10	10	10	10	10	10
	temp (°C)	2700	2700	1500	2400	2700	2300

solutions in 0.01 M HNO₃ and further diluted daily for obtaining reference and working solutions prior to use.

A 1.0×10^{-2} M solution of pyrocatechol violet (Fig. 1) solution was freshly prepared by dissolving the requisite amount of pyrocatechol violet (E. Merck, Darmstadt) in water immediately before use. 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.

In order to prepare 1 M HNO₃ in acetone, 1 M HCl in acetone and 2 M HCl in acetone, an appropriate amount of concentrated nitric acid or concentrated hydrochloric acid were transferred into a calibrated volumetric flask and made up to 100 ml with the addition of acetone slowly and carefully in a hood.

Activated carbon (500 mg) as a slurry in water was added to a glass column (Fig. 2) 10.0 cm long with 1.0 cm diameter. The bed-height of the activated carbon column was 2.0 cm. The column was preconditioned with 10–15 ml of working buffer solution prior to percolation of the sample. After elution, the activated carbon column was regenerated with a large volume of acetone.

**Fig. 1.** Pyrocatechol violet.

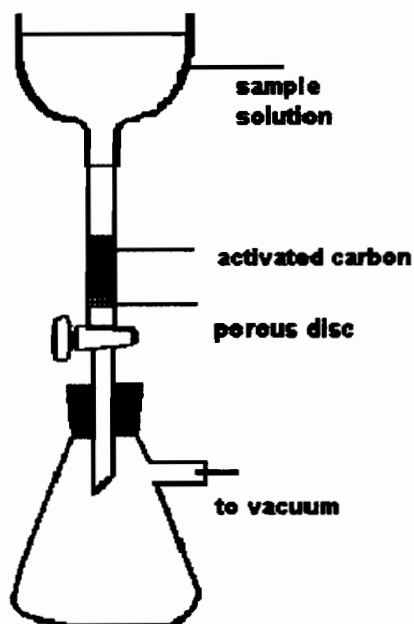


Fig. 2. Preconcentration column.

Preconcentration procedure

The preconcentration method was tested with model solutions before its application to salt samples. A 10 ml aliquot of buffer solution (to give the desired pH between 2–10) and 3 ml of pyrocatechol violet solution (0.02%) were added to the 50 ml of solution containing 10–20 μg of working element. The column was preconditioned with buffer solution. Metal-pyrocatechol violet solution was passed through the column at a flow rate of 5–10 ml/min with the aid of a vacuum aspirator. After passing of this solution, the column was rinsed twice with 10 ml of water. The metal chelates adsorbed on the column were eluted with 8–10 ml of 1 M HNO_3 in acetone. The eluent was evaporated over a hot plate to near dryness at 35°C in a hood. The residue was diluted to 5 ml with 1.0 M HNO_3 and was analysed for the determination of trace heavy metal concentrations by atomic absorption spectrometry.

Recommended procedure for table salts

For the determination of copper, cobalt, cadmium, lead, nickel and chromium ions in salt samples 4.0 g of table salt (bought from a local market) was dissolved in 3 ml of 0.2% HNO_3 and diluted to 25 ml with distilled water. The preconcentration/separation procedure was applied to this solution. The levels of copper, cobalt, cadmium, lead, nickel and chromium in the samples were determined by FAAS and/or GFAAS according to their concentration levels.

RESULTS AND DISCUSSION

The optimal conditions for adsorption of metal ions as pyrocatechol violet complexes on the activated carbon column were previously examined in detail (Narin *et al.* 2000). The recoveries of copper, cobalt, cadmium, lead, nickel and chromium were quantitative (95–102%) in the pH range 5–7. Therefore, all experiments in this study were carried out for metal ions at pH 6. The volume of buffer added (10 ml) had no effect on recovery. The concentration of pyrocatechol violet was 5.0×10^{-4} mol/l. The amount of activated carbon in the column was 500 mg. The activated carbon can be used 60 times for the preconcentration/separation procedure.

Desorption of the retained metals from the activated carbon column was tested with various water-miscible eluting agents. Quantitative recoveries were obtained for all working elements with 1 M HNO₃ in acetone, 1 M HCl in acetone or 2 M HCl in acetone. All subsequent studies were carried out using 8–10 ml of 1 M HNO₃ in acetone for desorption. Quantitative recoveries (> 95–102%) were obtained for the sample volumes in the range of 50–500 ml for all metal ions.

Matrix effects

Because analytical preconcentration/separation procedures for the trace elements can be strongly affected by the matrix constituents of the sample, the effects of NaCl, KCl, CaCl₂, K₂SO₄, CaSO₄, MgSO₄ and (NH₄)₂SO₄ on the recovery of metal ions from the activated carbon column were examined under optimal working conditions in 100 ml of sample solution containing 5 µg of each metal. The results were given in Table 3. Due to the low stability constants of alkaline and alkaline earth metal-PV complexes (The Chemical Society 1964, Cheng *et al.* 1982), these uncomplexed ions were almost completely eluted from the activated carbon column. Quantitative recoveries (> 95%) for copper, cobalt, cadmium, lead, nickel and chromium were

Table 3. Effect of matrix on the recoveries of the metal ions (*N* = 4, Eluent volume: 10 ml)

Salt	Concentration (g/l)	Recovery, %					
		Cu	Co	Cd	Pb	Ni	Cr
–	–	98	96	101	96	95	97
NaCl	5.0	96	95	97	96	96	96
	10.0	95	97	97	95	95	96
KCl	5.0	94	99	94	96	95	96
	10.0	99	96	97	93	96	98
CaCl ₂	5.0	96	97	96	96	96	96
	10.0	95	99	97	99	96	96
K ₂ SO ₄	0.5	98	95	96	97	97	95
	1.0	96	100	96	97	98	96
CaSO ₄	0.5	97	96	98	98	98	96
	1.0	98	96	99	98	96	99
MgSO ₄	0.5	99	96	98	100	99	96
	1.0	96	97	99	95	96	96
(NH ₄) ₂ SO ₄	0.5	98	97	99	96	102	96
	1.0	95	98	98	97	99	95

obtained in the presence of concentrations of the investigated salt samples. The recoveries of alkaline and earth alkaline metal complexes were determined by flame photometry and found to be less than 1%.

Accuracy of the method

To estimate the accuracy of the procedure, different amounts of investigated ions were added to a table salt sample (Sample 3) solution (4.0 g table salt/25 ml), and the resulting solutions were submitted to the preconcentration procedure. The metal contents of the effluent were determined by flame atomic absorption spectrometry. The results are shown in Table 4. Good agreement was obtained between the added and analyte recovered content using the experimental procedure. The recovery values calculated for the standard additions were always higher than 95%, thus confirming the accuracy of the procedure and the absence of matrix effects.

In order to determine detection limits of the working elements, model test solutions were used. The detection limits found on a 200 ml of sample volume after applying the preconcentration procedure for copper, cobalt, cadmium, lead, nickel and chromium by GFAAS based on three times the standard deviations of the blank ($N = 21$, $X_L = X_b + 3\sigma$, X_L : Limits of Detection, X_b : Blank Value) were 25 ng/l, 36 ng/l, 13 ng/l, 48 ng/l and 69 ng/l (IUPAC, 1976) respectively.

Application to the table salt samples

The proposed preconcentration/separation method was applied to the determination of copper, cobalt, cadmium, lead, nickel and chromium in five different table salt samples purchased from local markets at Niğde and Kayseri, Turkey. The results, given in Table 5, have been calculated on the assumption of 100% recovery of the trace metal ions. The relative standard deviations (RSD) of the procedure were less than 9%.

CONCLUSION

The proposed preconcentration/separation procedure provides a fast and simple method for the enrichment of copper, cobalt, cadmium, lead, nickel and chromium on the activated carbon column from drinking water samples (Narin *et al.* 2000). The present method is most promising for copper, cobalt, cadmium, lead, nickel

Table 4. Recovery studies of trace metal ions in sample 3 ($N = 4$)

Ion	Added (μg)	Found (μg)	Recovery, %
Cu	10	9.7	97
Co	10	9.8	98
Cd	5	5.0	100
Pb	15	14.9	99
Ni	10	9.5	95
Cr	15	15.1	101

Table 5. Metal ion levels in table salt samples ($N = 4$)

Sample	Concentration, $\mu\text{g/g}$ ($x \pm \text{SD}$)					
	Cu	Co	Cd	Pb	Ni	Cr
Sample 1	1.79 ± 0.20	BDL	0.79 ± 0.02	BDL	0.26 ± 0.03	1.08 ± 0.10
Sample 2	1.34 ± 0.13	BDL	0.80 ± 0.01	BDL	0.24 ± 0.03	BDL
Sample 3	1.16 ± 0.08	BDL	0.77 ± 0.01	BDL	BDL	BDL
Sample 4	1.27 ± 0.17	BDL	0.83 ± 0.03	BDL	0.32 ± 0.2	BDL
Sample 5	1.18 ± 0.08	BDL	0.82 ± 0.01	BDL	0.41 ± 0.03	BDL

BDL: Below Detection Limit.

$x \pm \text{SD}$: mean \pm standard deviation.

and chromium enrichment as the preconcentration factor is 150–200. The preconcentration factor of the activated carbon/PV system is superior to those of Taher and Puri (1999), Melo *et al.* (2000) and Uzun *et al.* (2001).

The working pH range (5–7) for all the metal ions is slightly acidic and therefore there is no possibility of complex hydrolysis, which could result in low RSD values. The matrix effects with the present method were within reason. The recoveries were quantitative (95–102%). The application of the proposed method has shown that trace metal ions can also be effectively separated and preconcentrated from table salts.

ACKNOWLEDGEMENTS

The authors would like to thank TÜBİTAK (the Scientific and Technical Research Council of Türkiye) for providing the Perkin-Elmer 3110 AAS used in this study.

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(Submitted 1 July 2000)

(Revised 24 December 2001)

(Accepted 13 January 2001)

استخدام طيف الامتصاص الذري لتعيين النحاس، الكوبالت، الكاديوم، الرصاص، النيكل، والكروم في ملح الطعام بعد تركيزه على الكربون النشط

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الخلاصه

تم تعيين المحتوى المعدني (نحاس، كوبالت، كاديوم، رصاص، نيكل، كروم) لعينات من ملح الطعام باستخدام طيف الامتصاص الذري بعد تركيز هذه العينات وفصلها على عمود من الكربون النشط من هيئة متراكبات البيروكاتيكول البنفسجية (PV).

متراكبات البيروكاتيكول البنفسجية (PV) والتي تحتوي على أيونات معدنية والموجودة في محلول منظم $PH = 6$ تمتص من قبل العمود ومن ثم يمكن فصلها من العمود باضافة حمض النيتريك بتركيز 1M والمذاب في الأسيتون. كما وقد تم أيضا فحص تأثير الأيونات المكونة لعمود الفصل على ما تم استخلاصه من الأيونات من العناصر السابقة. استخلاص أيونات المعادن تم في المدى من 95-103%، بينما كانت قيمة الحيوود القياسي النسبي تتراوح بين 2-9%.