

Solid phase preconcentration and separation of copper, nickel and lead in haemodialysis concentrates and urine on Amberlite XAD-1180 resin

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ABSTRACT

In this study, a simple, sensitive separation/preconcentration procedure is presented for the determination of copper, nickel and lead at trace levels by atomic absorption spectrometry. The procedure is based on chelate formation of the investigated metals with calmagite and recovery of the chelates from the Amberlite XAD-1180 column with 0.5 M HNO₃. The presented procedure was applied to the preconcentration and separation of copper, nickel and lead in urine and haemodialysis concentrates with satisfactory results (recoveries in the range of 95-100%).

Keywords: Amberlite XAD-1180, Determination, Haemodialysis concentrates, Preconcentration, Urine.

INTRODUCTION

Trace metal analyses have a gradually increasing importance in various areas such as biological systems, environment and geochemistry. The determination of trace species in environmental, biological and other samples have been performed by various researchers (Narin *et al.* 1998, Kim *et al.* 2000, Totoni & Culla 2001, Dogan & Soylak 2002, Soylak *et al.* 2002a, Turkoglu *et al.* 2003, Divrikli *et al.* 2003). In these determinations spectrophotometry, flame and graphite furnace atomic absorption spectrometry (FAAS & GFAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS) have been widely used.

Determination of the trace metals directly and reliably with most instrumental methods is difficult due to the low concentration of analytes and the interference caused by the sample matrix (Mizuike 1981, Vandecasteeck & Block 1997, Soylak 2001, Soylak *et al.* 2001a). Because of this, preconcentration and separation procedures are applied to samples both to separate the analyte from the sample matrix and to concentrate them in a small volume (Arpadjan *et al.* 1992, Saracoglu *et al.* 2000a). The most widely used separation preconcentration methods are solvent extraction (Williams *et al.* 1986, Koklu & Akman 1992, Tuzen *et al.* 2002), membrane filtration (Divrikli *et al.* 2002, Soylak *et al.* 2002b, Karatepe *et al.* 2002), ion exchange (Kiriyaama & Kuroda 1988, Meeravali & Arunachalam 1997, Namboothiri *et al.* 1991), coprecipitation (Frigge & Jackwerth 1993, Saracoglu *et al.* 2001) and cloud point extraction (Luconi *et al.* 2002, da Silva *et al.* 2001, Chen & Teo 2001a, 2001b, Paleologos *et al.*, 2001).

Solid phase extraction is one of the most effective multi-element separation preconcentration methods because of its simplicity, rapidity and ability to attain a high concentration factor (Mizuike 1981, Dogan *et al.* 1997, Vandecasteeck & Block 1997, Seren *et al.* 2001, Soylak 2001, Soylak *et al.* 2001a, Killian & Pryzyska 2002). Column and/or batch techniques could be applied to solid phase extraction of trace heavy metal ions. In solid phase extraction, various sorbents, including activated carbon, C-18, Diaion HP20, Ambersorb 563, silica gel and others (Okamoto *et al.* 1991, Soylak & Dogan 1996, Soylak 1998, Soylak *et al.* 1998, Hirata *et al.* 2000, Saracoglu *et al.* 2000b, Soylak *et al.* 20001b, Narin *et al.* 2001, Pyrzyska & Szelag 2001, Cai *et al.* 2002, Soylak 2002, Soylak & Akkaya 2002), have been used for the preconcentration/separation of the trace heavy metal ions from various media such as natural water samples, including seawater, urine, geological samples, etc.

Since Amberlite XAD adsorption resins have good physical properties such as porosity, uniform pore size distribution, high surface area, and good adsorbent properties for uncharged compounds, they have been used as supports for the separation and enrichment of metal complexes. Several authors reported that trace metals as various complex forms were adsorbed onto Amberlite XAD-2, XAD-4, XAD-7, XAD-8, XAD-11, XAD-16 and XAD-2000 resins and can be easily separated from other matrix components (Elci *et al.* 2000, Soylak & Elci 2000, Soylak *et al.* 2000, Soylak *et al.* 2001b, Wuilloud *et al.* 2001). Amberlite XAD-1180 is polystyrene divinylbenzene copolymer (surface area: 600 m²/g, pore diameter: 140 Å) which is also a nonionic polymeric adsorbent having excellent sorption characteristics.

Calmagite (3-hydroxy-4-[6-hydroxy-m-tolyl]azo]-naphthalenesulfonic acid)

(Figure 1) is a chelating agent that reacts with metal ions to form very stable complexes. Calmagite has an advantage for preconcentration studies as a result of differences in formation constants between the transition metals and alkaline and alkaline earth metals to effect separations of trace metals from saline solutions (The Chemical Society 1964, Cheng *et al.* 1982, Marczenko 1986). Various studies have been performed by using calmagite as a chelating agent in the separation/enrichment methods. Ferreira and co-workers (2000a) used calmagite as a complexing agent for copper with the on-line sorption of the complexes in an Amberlite XAD-2 column. The determination of copper by flame atomic absorption spectrometry was performed after preconcentration of a copper complex with calmagite, and sorption on a XAD-2 mini column (Ferreira *et al.* 2000b). In another study, calmagite was used for the enrichment and separation of molybdenum on activated carbon (dos Dantos *et al.* 2001). Preconcentration of some calmagite metal complexes in some natural water samples from Kayseri-Turkey on cellulose nitrate membrane filter have been performed by Soylak *et al.* (2002b). The same reagent was used for the preconcentration/separation of some metal ions from seawater samples on Amberlite XAD-1180 (Soylak *et al.* 2002c).

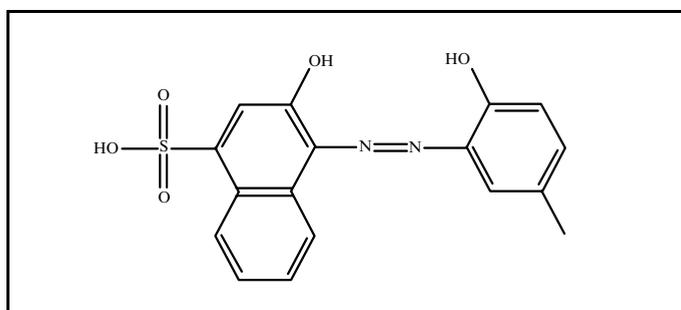


Fig.1. Calmagite

The aims of the present study were to investigate the solid phase extraction conditions for copper, nickel and lead on Amberlite XAD-1180 adsorption resin prior to their atomic absorption spectrometric determination of copper, nickel and lead in urine samples and haemodialysis solutions.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 3110 flame atomic absorption spectrometer was used. Studies were carried out with the use of an air/acetylene flame without any

background correction. Graphite furnace atomic absorption measurements were carried out using a Perkin Elmer atomic absorption spectrometer (Model Analyst 100) equipped with a graphite tube atomizer (Model HGA-800, Perkin Elmer) and deuterium background correction. The operating parameters for the working elements given in Table 1 for the flame atomic adsorption spectrometer and in Table 2 for the graphite furnace atomic absorption spectrometer were as recommended by the manufacturers. A pH meter, Nel pH-900 Model glass-electrode, was employed for measuring pH values in the aqueous phase.

Table 1. Conditions for flame atomic absorption spectrometric determinations

Element	Wavelength		Lamp Current	Flow rate of oxidant and fuel	
	(nm)	Slit (nm)		Air (l/min)	Acetylene (l/min)
Cu	Pb	Ni	324.8	283.3	232.0
0.7	0.7	0.2	15	15	30
9.5	9.5	9.5	2.3	2.3	2.2

Table 2. Instrument settings and conditions for GFAAS

Parameter	Element			
	Cu	Ni	Pb	
Wavelength (nm)	324.8	232.0	283.3	
Slit width (nm)	1.3	0.2	1.3	
Lamp current (mA)	7.5	15.0	7.5	
Step				
Dry	time (sec)	15	15	15
	temp (°C)	120	120	120
Ash	time (sec)	30	30	30
	temp (°C)	600	700	400
Atomize	time (sec)	10	10	10
	temp (°C)	2700	2700	2400

Reagents and solutions

All chemicals used were the same as previously described in Soylak *et al.* (2002c). Calmagite (0.05% w/V) solution was prepared daily by dissolving the requisite amounts of calmagite (E. Merck, Darmstadt) in water.

Stock solutions were prepared from appropriate amounts of the respective nitrates (E. Merck, Darmstadt) as 1000 mg/l solutions in 0.01 M HNO₃ and diluted daily to obtain working solutions prior to use. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with 1 M HNO₃. The calibration standards were not subjected to the separation/preconcentration procedure. Stock solutions of all elements were prepared from the high purity compounds (% 99.99, E. Merck, Darmstadt).

In order to remove organic and inorganic contaminants, Amberlite XAD-1180 adsorption resin (20-50 mesh) (Sigma Chem. Co., St. Louis) was washed successively with methanol, water, 1 M HNO₃ in acetone, water, 1 M NaOH and water.

Sodium phosphate buffer (0.1 M) was prepared by adding an appropriate amount of phosphoric acid (Merck, Darmstadt) to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 M) were prepared by adding an appropriate amount of acetic acid (Merck, Darmstadt) to ammonium acetate solutions to result in solutions of pH 4-6 and ammonium chloride buffers solutions (0.1 M) were prepared by adding an appropriate amount of ammonia (Merck, Darmstadt) to ammonium chloride solutions to result in solutions of pH 8-10.

Haemodialysis samples

The dialysis solutions for haemodialysis were collected from Erciyes Dialysis Hospital (EDH), Kayseri State Hospital (KSH) and Erciyes University Research Hospital (EUH). The concentration (g/l) of each component was as follows:

- a - Concentrated basic solution for haemodialysis (EDH-1B): NaHCO₃ 84.0.
- b - Concentrated basic solution for haemodialysis (KSH-1B): NaHCO₃ 84.0.
- c - Concentrated acidic solution for haemodialysis (EUH-1A): NaCl 214.80; KCl 2.612; CaCl₂ 5.830; MgCl₂ 1.670; CH₃COOH 4.210.
- d - Concentrated basic solution for haemodialysis (EUH-2B): NaHCO₃ 84.0.

Column preparation

A short glass column with an inner diameter of 10 mm and a length of 100 mm, equipped with porous frits, was filled to a height of about 25 mm with a suspension of 500 mg Amberlite XAD-1180 resin in water. Prior to use, the resin was preconditioned with buffer solution. After each experiment, the column was rinsed with water and stored for the next experiment.

Separation/preconcentration procedure

The method was initially tested with model solutions prior to application to urine and dialysis samples. 50 ml of solution containing 10-20 μg of copper, nickel and lead ions was added to 1 ml of a 0.05% (w/V) solution of calmagite and brought to desired pH between 2 and 10 (working pH). The column was preconditioned with 10-15 ml of the sater at the working pH. The metal solution was passed through the column at a 2 ml/min flow rate. The column was then washed with calmagite solution adjusted to the working pH. The retained metal-chelates were eluted with 10.0 ml of 0.5 M HNO_3 . The metal concentrations in the eluant were determined by flame AAS.

In the investigation of the effects of the matrix components on the recoveries of the analyte ions, each matrix component was added to the model solutions. Model solutions containing matrix components underwent the developed separation and preconcentration method. The blank solutions for the preconcentration method did not contain any matrix components of urine and dialysis concentrates on the optimization studies. In the accuracy studies, the blank solutions contained the sample matrix.

Procedure for analysis of haemodialysis solution

The haemodialysis concentrate was used after 1:33 dilution with double-distilled water (3M Ω) obtained in our university hospital. 250 ml of diluted haemodialysis solution was buffered to pH 8. An excess of calmagite solution was then added to the buffered solution. This solution was analysed by using the preconcentration procedure described above. In the final solution metal ions were determined by flame AAS and/or GFAAS according to their concentration levels.

Copper, nickel and lead contents of urine samples

Urine samples were collected from three healthy people living in Kayseri City, Turkey in October 2001 for the application of the procedure developed in this study. The urine samples were collected in pre-washed (with detergent, doubly distilled water (3 M Ω), dilute HNO_3 and doubly de-ionised distilled water) polyethylene bottles. The samples were acidified to 1% with concentrated ultrapure nitric acid (65%). The samples were refrigerated at 4°C and analyzed within a week.

The preconcentration and separation procedure described above was applied to 50 ml of the urine sample. The metal contents were determined by flame AAS and/or GFAAS according to their concentration levels.

RESULTS AND DISCUSSION

Parameters including pH of the solution, eluent solution concentration, eluent solution volume, influences of matrix components of urine and dialysis concentrate and sample flow rate were tested. This was done to achieve best efficiency concerning sorption and elution, which should result in increased sensitivity, as well as high analytical throughput. The optimised conditions for the preconcentration/separation were established using 50 ml of de-ionised water containing 10-20 μg of each element and submitting these solutions to the preconcentration procedure. 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 Amberlite XAD-1180 column.

The optimal conditions for adsorption of metal ions on the Amberlite XAD-1180 mini chromatographic column have been examined previously (Soylak *et al.* 2002c). Cu(II), Pb(II) and Ni(II) ions were quantitatively (95-100)% recovered at pH 8-9. Above pH 10 recoveries were not quantitative. The volume of buffer added (10 ml) had no effect on the recoveries. All subsequent studies were performed at pH 8. Above 0.1 ml of 0.05% (w/V) calmagite, copper, nickel and lead were quantitatively adsorbed. The present studies were performed by using 1.0 ml of 0.05% (w/V) calmagite. The adsorption of the metal ions with 500 mg of XAD-1180 was not affected by sample volume below 750 ml.

A 20-50 mesh resin bead size was selected for the separation/preconcentration procedure in an Amberlite XAD-1180 column. Smaller resin particles may have improved retention capacity, but the flow rates of sample solution and eluent solution would have been reduced, with a subsequent increase in preconcentration/separation time. 500 mg of Amberlite XAD-1180 resin could be used for 200 preconcentration procedures.

The highest preconcentration factor was 375 for all investigated analyte ions. In all studies, 10 ml of 0.5 M HNO_3 was used as eluent. Under optimal constant conditions, the flow rates of sample volume and eluent solution were studied in the range of 0.5-10 ml/min. The best results were obtained at 2.0 ml/min for retention and elution.

Effect of matrix ions on the recoveries of analyte ions

The effect of major components in urine and haemodialysis concentrates such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , CH_3COO^- , dextrose, urea and creatine on the solid phase extraction were studied systematically. Matrix ions were separately added to a solution containing fixed amounts of analytes and the present procedure was followed. The results are given in Table 3. The levels given in Table 3 for each matrix component were the highest tolerable levels of

each component. Quantitative retention (95-100%) for Cu, Ni and Pb were obtained in the presence of high concentrations of these components.

Due to the low stability constants of alkaline and alkaline earth metal calmagite chelate complexes (The Chemical Society 1964, Cheng *et al.* 1982, Marczenko 1986), investigated ions were almost completely rejected from the Amberlite XAD-1180 column. It can be concluded from the results in Table 3 that analyte ions could be recovered quantitatively from urine and haemodialysis concentrate. The results are desirable in view of application of the presented procedure for urine and haemodialysis analysis.

The recovery values of alkaline and earth alkaline metals on the Amberlite XAD-1180 resin were determined by flame photometer and/or FAAS and found to be less than 1%. The matrix contents in the eluent solutions were found to be significantly lower and suitable for flame atomic absorption spectrometric determination.

Table 3. Effect of matrix ions on the recoveries of analyte ions (N = 3)

Ion	Added As	Concentration, mg/l	Recovery, %		
			Cu	Ni	Pb
Na ⁺	NaCl	25000	1000	100	100
Mg ²⁺	MgCl ₂	5000	100	100	100
K ⁺	KCl	1250	95	100	100
Ca ²⁺	CaCl ₂	2500	100	100	100
Cl ⁻	NaCl	75000	100	100	100
SO ₄ ²⁻	Na ₂ SO ₄	2500	100	100	100
CH ₃ COO ⁻	CH ₃ COONa	5000	98	99	96
Urea	-	500	100	90	100
Kreatine	-	500	100	100	100
Dextrose	-	1000	95	100	99

Accuracy, precision and detection limits

For the urine and haemodialysis concentrate analysis, the efficiency of recovery of metal spikes from urine and two haemodialysis concentrates was investigated. As seen from Table 4, good agreement was obtained between the added and found analyte content using the procedure given in the experimental section. The metal contents of the effluent were determined by atomic absorption spectrometry. The correctness of the present method was confirmed by the

recoveries of spikes from the real samples including various salts at high concentration levels.

Table 4. Recovery of analytes spiked into the dialysis concentrate and urine samples (N = 3)

Sample	Element	Added,		%R
		μg	Found, μg	
Urine	Cu	0	Below 2 $\mu\text{g/l}$	-
		10	9.7	97
		20	20	100
	Ni	0	Below 9 $\mu\text{g/l}$	-
		10	10.2	102
		20	14.6	73
	Pb	0	Below 4 $\mu\text{g/l}$	-
		10	10.2	102
		20	19.4	97
Acidic Dialysis Solution	Cu	0	Below 2 $\mu\text{g/l}$	-
		10	9.5	95
		20	19.2	96
	Ni	0	Below 9 $\mu\text{g/l}$	-
		10	10.4	104
		20	17.2	86
	Pb	0	Below 4 $\mu\text{g/l}$	-
		10	10	100
		20	20	100
Basic Dialysis Solution	Cu	0	Below 2 $\mu\text{g/l}$	-
		10	10	100
		20	18.4	92
	Ni	0	Below 9 $\mu\text{g/l}$	-
		10	9.5	95
		20	19.0	95
	Pb	0	Below 4 $\mu\text{g/l}$	-
		10	9.9	99
		20	20	100

The detection limits based on three times the standard deviations of the blank ($N=20$, $X_L = X_b + 3s$, X_L : Limit of Detection, X_b : Blank Value) for copper, nickel and lead were found to be $2 \mu\text{g/l}$, $9 \mu\text{g/l}$ and $4 \mu\text{g/l}$, respectively, for 100.0 ml of sample. The detection limits of investigated elements can be decreased by one order of magnitude by increasing the sample volume.

Application of the proposed method

The proposed separation/preconcentration method was applied to determination of copper (II), nickel (II) and lead (II) in three urine samples and four different haemodialysis concentrates used in various hospitals in Kayseri-Turkey. The results given in Table 5 have been calculated on the assumption of 100% recovery of the trace heavy metal ions.

Table 5. Metal contents of urine samples and dialysis concentrates

Sample	Sample No	Concentration, $\mu\text{g/l}^*$		
		Cu	Ni	Pb
Urine	1020	3.4 ± 1.6	18.5 ± 5.5	3.6 ± 0.2
	1021	4.7 ± 2.0	13.8 ± 4.8	7.8 ± 0.2
	1022	4.5 ± 2.0	13.6 ± 4.8	25.9 ± 0.1
Dialysis	EDH-B	252 ± 31	134.0 ± 4.0	1.3 ± 0.3
	KSH-B	265 ± 31	47.0 ± 3.0	1.1 ± 0.2
	EUH-B	239 ± 26	47.0 ± 3.0	1.5 ± 0.3
	EUH-A	226 ± 10	77.0 ± 3.0	2.8 ± 0.1

* $P=0.95$, $\pm ts/\sqrt{N}$, $N = 5$

CONCLUSION

The method is simple, fast and economical. The determination procedure was characterized by good reproducibility and accuracy. The presented preconcentration procedure shows high tolerance to interference from matrix ions. The application of the proposed method has shown that trace metal ions can also be effectively separated and preconcentrated from urine samples and dialysis concentrates.

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التركيز المسبق والفصل في الحالة الصلبة للنحاس والنيكل والرصاص من عينات مركزة لديلزة الدم والبول على راتينج امبيرلايت XAD-1180

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خلاصة

تعرض في هذه الدراسة طريقة مبسطة ودقيقة للفصل والتركيز المسبق لتصنيف النحاس والنيكل والرصاص بمقادير ضئيلة وذلك بواسطة الامتصاص الذري. وتعتمد الطريقة على تكوين كُلابي (chelate) من تفاعل الفلزات مع كالماجيت (calmagite) وفصل الناتج بواسطة عمود من امبيرلايت XAD - 1180 مع 0.5 مول/ليتر من حمض النيزيك. واستخدمت هذه الطريقة في عملية التركيز المسبق وفصل النحاس والنيكل والرصاص من البول ومن عينات مركزة من ديلزة الدم، وأعطت الدراسة نتائج مقبولة (استخلاص في حدود 90 - 100%).