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Separation/preconcentration of trace heavy metals in urine, sediment and dialysis concentrates by coprecipitation with samarium hydroxide for atomic absorption spectrometry

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Abstract

Multi-element determination of trace elements in urine and dialysis solutions by atomic absorption spectrometry has been investigated. Coprecipitation with samarium hydroxide was used for preconcentration of trace elements and elimination of matrix elements. To 10 ml of each sample was added 500 μl of 2 mg ml^{-1} samarium solutions; the pH was then adjusted to 12.2 in order to collect trace heavy metals on samarium hydroxide. The precipitate was separated by centrifugation and dissolved in 1 ml of 1 mol l^{-1} HNO_3. Coprecipitation parameters and matrix effects are discussed. The precision, based on replicate analysis, is around 5% for the analytes, and recovery is quantitative, based on analysis of spiked samples and solutions including matrix components. The time required for the coprecipitation and determination was about 30 min.

Keywords: Coprecipitation; Samarium hydroxide; Urine; Dialysis concentrate

1. Introduction

Atomic absorption spectrometer (AAS) is generally main instrument of analytical chemistry laboratories for the determination of traces heavy metal ions, due to its relatively low cost. However the main two problem for the determination of heavy metal ions by AAS are low levels of metal ions and interferic influences of main components of samples. In order to solve these problems, the separation/preconcentration procedures including solid phase extraction [1–7], membrane filtration [8], electroanalytical techniques [9,10], solvent extraction [11], ion-exchange [12] are a necessity.

Coprecipitation is also one of the efficient separation/enrichment technique for the traces heavy metal ions [13,14]. The coprecipitation technique has some advantages: simple, fast method and several analyte ions can be preconcentrated and separated from the matrix simultaneously. Coprecipitation of trace metal ions by use

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of organic and inorganic coprecipitants have been developed and well documented [15–18]. For the coprecipitation traces heavy metal ions, metal hydroxides are most popular due to good trace recovery and sufficient separation factors for alkali and alkaline earth metals. Coprecipitation by hydroxides of metals is frequently used in the enrichment and separation of trace amount of analytes, generally using a milligram quantity of carrier element. A number of metal hydroxides such as magnesium [19,20], cerium [21,22], scandium [23], lanthanum [24], indium [25], zirconium [26] and iron [27] hydroxides, etc. [28–30] have been widely used for the preconcentration of trace metal ions.

The aim of the present study to establish a coprecipitation method by using samarium hydroxide for the separation/preconcentration of copper, iron, nickel, cobalt, lead, cadmium, manganese and chromium ions in urine samples, sediment and dialysis concentrates prior to their atomic absorption spectrometric determinations. The experimental conditions for coprecipitation of analyte ions onto samarium hydroxide, pH, samarium (III) concentration, etc. were optimized.

2. Experimental

2.1. Apparatus

A Perkin–Elmer Model 3110 AAS 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 book. A Hitachi Model Z-8000 AAS with a Zeeman background corrector was employed for the determination of analytes ions in the aqueous solution. A Hitachi Model graphite furnace atomizer (Part no. 180-7400) was used for the determination of analyte in the urine and dialysis concentrates. Twenty microliter of sample were introduced into the graphite tube using an eppendorf pipette. The operating parameters for working elements were set of as recommended by the manufacturer. A pH meter, Nel pH 900 Model glass-electrode was employed for measuring pH values in the aqueous phase. Hettich Rotofix 32 model and Mistral 2000 model centrifuges were used to centrifuge of solutions.

2.2. Reagents and solutions

Water, double-distilled in a quartz apparatus, was used in all the experiments. Stock standard solutions of analytes, 1000 mg l^{-1}, was prepared by dissolving appropriate amount of nitrate salts of Cu, Fe, Ni, Co, Pb, Cd, Mn and Cr in 1% nitric acid. Stock metal ion solutions were diluted daily for obtaining reference and working solutions. The calibration curve was established using the standard solutions prepared in 1 mol l^{-1} HNO_3 by dilution from stock solutions. The calibration standards were not subjected to the preconcentration procedure.

Sodium hydroxide (supra pure grade, Merck) was used for preparation of 6 mol l^{-1} NaOH solutions and pH adjustment. Two milligram per milliliter Sm^{3+} was prepared freshly by dissolving samarium (III) oxide (supra pure grade, Merck) (0.116 g) in small amounts of nitric acid and diluting to 50 ml with double distilled water. Nitric acid (65%) used for preparing of diluted acid solution was supra pure grade from Merck.

2.3. Model working

The coprecipitation method was tested with model solutions prior to its application to urine, sediment and dialysis concentrates. Five hundred microliter of 2 mg ml^{-1} samarium solutions were added to 10.0 ml of solution containing 5–20 μg of Cd, Fe, Co, Cr, Cu, Mn, Ni and Pb. Then, a certain amount of 6 mol l^{-1} NaOH solution was added to adjust the pH or NaOH concentration. After 10 min, the solution was centrifuged at 2500 rpm for 20 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 1 ml of 1 mol l^{-1} HNO_3. To determine the analytes, 100 μl of this final solution was injected to nebulizer of flame AAS. The number of replicates for the test workings was three.

2.4. Analysis of stream sediment

0.1 g of standard reference material (SRM) (GBW 07309) 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 evaluation of NO_2 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 was added and the sample was mixed. The resulting mixture was filtered through a blue band filter paper. The filtrate was diluted to 10 ml with distilled water. The subsequent procedures were the same those described in the model working section. The final solution was diluted to 2 ml.

2.5. Analysis of urine

Urine samples were collected in prewashed (with detergent, doubly distilled water, diluted nitric acid and doubly distilled water, respectively) polyethylene bottles. Exactly 10.0 ml of urine is placed into a 15-ml glass centrifugation tube. One milligram Sm^{3+} was added to each urine sample and to form a samarium hydroxide precipitate and to run coprecipitation, pH of the concentrate is adjusted to 12.2 with 6 mol l^{-1} NaOH solution. The tube is slowly and carefully shaked for several seconds and allowed to stand for 10 min. The precipitate is centrifuged at 2500 rpm for 20 min and the supernatant is discarded. A small precipitate adheres to the bottom tube. Then, 1 ml of 1 mol l^{-1} HNO_3 is added to dissolve the precipitate. The analyte ions in this solution are determined with graphite furnace AAS using matrix matching standards.

2.6. Analysis of dialysis concentrate

The six different dialysis solutions for hemodialysis were collected from Erciyes University Research Hospital (EUH), Erciyes Dialysis Hospital (EDH) and Kayseri State Hospital (KSH). The analysis of dialysis concentrate was carried out after dilution 1+2 with the water used in the hospital to form of samarium hydroxide precipitate. Exactly 10.0 ml of diluted dialysis concentrate is placed into a 15 ml glass centrifugation tube. One milligram Sm^{3+} was added to each dialysis sample and the pH of the concentrate was adjusted to 12.2 with 6 mol l^{-1} NaOH solution. This solution was analyzed by the preconcentration procedure described above. In the final solution, metal ions were determined by graphite furnace AAS.

3. Results and discussion

The influence of the various analytical parameters such as amount of samarium, NaOH concentration, etc. on the recovery of copper, iron, nickel, cobalt, lead, cadmium, manganese and chromium from urine and dialysis concentrate were examined. The optimum conditions determined for the preconcentration procedure were as follows.

3.1. Interference of samarium on the absorbance of investigated elements

Initially, an attempt was made to examine the effect of samarium concentration, due to the matrix of samarium, on the determination of the desired elements with flame AAS. For this purpose, increasing concentrations of Sm^{3+} was added to aqueous solution containing an appropriate amount of desired metal ions. These solutions were analyzed by FAAS without any pretreatment. The absorbances for the elements remained almost constant up to about 20 mg ml^{-1} Sm^{3+}. This indicates that the concentration of samarium in the final solution for the combination of coprecipitation method with flame AAS must to be excessed 20 mg ml^{-1}.

3.2. Effects of samarium (III) amounts and pH on the recoveries

The amount of samarium ion needed for the coprecipitation was selected experimentally. The influence of Sm^{3+} was investigated in the range of 0–2000 μg Sm^{3+}. As it can be seen from Table 1,

Table 1
Effect of samarium amount on coprecipitation (amounts of analytes: 5 μg Cd; 10 μg Co, Fe, Cu, Mn, Ni; 20 μg of Cr, Pb, $n = 3$)

Amount of Sm, μg	Recovery, %							
	Cu	Fe	Ni	Co	Pb	Cd	Mn	Cr
0	83	90	100	85	29	87	87	95
100	93	95	100	95	35	94	95	95
200	95	100	100	100	47	95	94	100
400	97	100	100	100	59	95	94	100
800	97	100	100	100	71	95	94	100
1000	100	100	100	100	95	95	95	100
2000	100	100	100	100	100	96	98	95

Table 2
Effect of NaOH concentration on coprecipitation (amounts of analytes: 5 μg Cd; 10 μg Co, Fe, Cu, Mn, Ni; 20 μg of Cr, Pb, $n = 3$)

Concentration of NaOH, mol l^{-1}	Recovery, %							
	Cu	Fe	Ni	Co	Pb	Cd	Mn	Cr
0.005	88	76	100	92	83	97	95	100
0.01	96	94	100	95	92	100	100	100
0.02	100	100	100	100	100	100	100	100
0.05	96	95	100	100	92	100	100	100
0.1	96	95	100	100	50	100	100	100
1	95	100	100	100	< 5	100	100	100

the recoveries of desired metal ions from solution preparing with the increasing amounts of samarium ion in 0.02 mol l^{-1} NaOH (pH 12.2) were quantitative after 0.1 mg Sm^{3+} for Fe, Co and Mn, 0.2 mg Sm^{3+} for Cu and Cd, 1 mg Sm^{3+} for Pb. The recoveries of Ni and Cr were quantitative without Sm^{3+}. The optimum amount of Sm^{3+} was taken as 1 mg in further experiments.

Samarium hydroxide was precipitated at different pH values from model solution containing 1 mg samarium and fixed trace amount of desired elements, such as 10 μg for Cu, Fe, Ni, Co, Mn, 20 μg for Pb and Cr, 5 μg for Cd. pH values were adjusted with different concentration NaOH solution. The results obtained are shown in Table 2. The recoveries for Cu, Fe and Co were quantitative in the range of 0.01–1 mol l^{-1} NaOH, and Pb was at 0.02 mol l^{-1} NaOH concentration. Ni, Cd, Mn and Cr were virtually completely coprecipitated in the investigated NaOH concentration range. In this work, the optimum concentration of NaOH was taken as 0.02 mol l^{-1} (pH 12.2). For the acidified real samples, after neutralization, the pH of the samples were adjusted to pH 12.2 with NaOH.

The analyte ions were quantitatively (95%) recovered in the sample volume range of 10–50 ml. After 50 ml of sample volume, the recoveries of all the investigated ions were not quantitative.

3.3. Effect of matrix ions

To detect potential interference on the coprecipitation of examined elements, various amounts of

Table 3
Effect of matrix components on coprecipitation (amounts of analytes: 5 μg Cd; 10 μg Co, Fe, Cu, Mn, Ni; 20 μg of Cr, Pb, $n = 3$)

Ions	Added as	Concentration, mg l^{-1}	Recovery, %							
			Cu	Fe	Ni	Co	Pb	Cd	Mn	Cr
Na^+	NaCl	20 000	100	100	100	100	100	100	95	100
K^+	KCl	5000	100	100	95	100	100	100	100	100
Ca^{2+}	$CaCl_2$	5000	94	100	95	100	100	100	100	100
Mg^{2+}	$MgCl_2$	5000	100	100	100	100	100	95	100	100
CH_3COO^-	CH_3COONa	5000	100	100	100	100	100	100	100	100
SO_4^{2-}	Na_2SO_4	2500	100	100	100	100	100	100	95	100
Cl^-	NaCl	30 000	100	100	100	100	100	100	95	100
Creatine		5000	94	100	100	100	100	100	95	100
Urea		2500	100	100	100	100	100	100	95	100
Dextrose		1000	95	100	100	95	95	100	100	95

NaCl, KCl, $CaCl_2$, $MgCl_2$, CH_3COONa, creatine, urea and dextrose as major components of urine and dialysis were added to a solution containing the examined elements at the fixed amounts, and then the procedure was followed. The results are listed in Table 3. All of examined analytes are not effected from the all components in the investigated concentration ranges. The results are desired in view of application to the urine and dialysis sample.

3.4. Method validation and analytical performance

To the validation of present method was evaluated, the recoveries of analytes spiked into analysing urine and dialysis were also studied, satisfactory results were obtained as shown in Table 4. Good agreement was obtained between the added and analyte recovered content using the experimental procedure in acidic and basic dialysis solution. The recovery values calculated for the standard additions were always higher than 95%, thus confirming the accuracy of the procedure and tha absence of matrix effects. As can be seen from Table 4, recoveries of Cu, Co and Cd in urine sample were not quantitative.

The relative standard deviations for atomic absorption spectrometric measurements are between 0.2 and 10.2%. The detection limits, defined as the concentration equivalent to three times the standard deviation ($n = 10$) of the reagent blank, for copper, iron, nickel, cobalt, lead, cadmium, manganese and chromium were 1.1, 6.7, 3.1, 4.5, 24.0, 0.4, 1.0 and 0.99 μg l^{-1}, respectively.

3.5. Analysis of standard reference material

The developed preconcentration method was applied a stream sediment SRM (GBW 07309) for the determination of analyte ions. The results are given in Table 5. The results, based on the average of five replicates, which show that the results are in good agreement with the certified values. If the concentration levels of the most common matrix constituents, including 1.07% Na, 1.65% K, 3.04% Fe, 5.60% Al, 3.82% Ca, 1.44% Mg, in the reference stream sediment material and the accuracy of the presented method are considered together, it can be concluded that the proposed method is free from interferences of the various constituents.

3.6. Analysis of the samples

Based on the above findings, the procedure was applied to the determination of Cu, Fe, Ni, Co, Pb, Cd, Mn and Cr in dialysis concentrate and also Fe, Ni, Pb, Mn and Cr in urine samples. The results were summarised in Table 6. The analytes in the final solution obtaining with the coprecipi-

Table 4
Recovery of analyte spikes from urine and dialysis sample ($n = 3$)

Element	Added, μg	Acidic dialysis		Basic dialysis		Urine	
		Found, μg	Recovery, %	Found, μg	Recovery, %	Found, μg	Recovery, %
Cu	0	ND	–	ND	–	ND	–
	5	5.0	100	5.0	100	0.7	14
	10	10.0	100	10.0	100	1.2	12
Fe	0	ND	–	ND	–	ND	–
	5	5.0	100	5.0	100	5.0	100
	10	10.0	100	10.0	100	10.0	100
Ni	0	ND	–	ND	–	ND	–
	5	5.0	100	5.0	100	5.0	100
	10	10.0	100	10.0	100	6.5	65
Co	0	ND	–	ND	–	ND	–
	5	5.0	100	5.0	100	2.9	58
	10	10.0	100	10.0	100	3.3	33
Pb	0	ND	–	ND	–	ND	–
	10	10.0	100	10.0	100	9.5	95
	20	20.0	100	20.0	100	18.0	90
Cd	0	ND	–	ND	–	ND	–
	2.5	2.5	100	2.5	100	0.15	60
	5	5.0	100	5.0	100	3.2	64
Mn	0	ND	–	ND	–	ND	–
	5	4.8	96	4.8	96	5.0	100
	10	9.7	97	10.0	100	9.5	95
Cr	0	ND	–	ND	–	ND	–
	10	10.0	100	10.0	100	10.0	100
	20	20.0	100	20.0	100	20.0	100

tation were determined with graphite furnace AAS using matrix-matching standards. The concentrations given in Table 6 have been calculated on the assumption of 100% recovery of the analytes.

Table 5
Results of the analysis a stream sediment SRM (GBW7309)

Element	Certified value (μg g^{-1})	Our value (μg g^{-1})	(s/x)
Cu	32.1	31 ± 1	0.032
Ni	32.3	30 ± 2	0.067
Co	14.4	14.3 ± 0.03	0.002
Pb	23.0	22.7 ± 0.04	0.002
Cd	0.26	1.1 ± 0.1	0.026
Cr	85.0	90 ± 2	0.022

4. Conclusion

A procedure for the determination of trace amounts of Cu, Fe, Ni, Co, Pb, Cd, Mn and Cr is described, which combines atomic absorption spectrometry with preconcentration of the analyte by inorganic coprecipitation. Coprecipitation with samarium hydroxide offers a useful multielement preconcentration technique in dialysis concentrates and urine analysis. The procedure has been successfully applied to copper, iron, nickel, cobalt, lead, cadmium, manganese and chromium in dialysis concentrate and Fe, Ni, Pb, Mn and Cr in urine with acceptable accuracy and precision. The coprecipitated analyte ions can be sensitively determined by atomic absorption spectrometry without any influence of samarium hydroxide. The procedure would appear to have potential

Table 6
Results of dialysis concentrate and urine analysis

Sample	Concentrations, μg l^{-1}*							
	Cu	Fe	Ni	Co	Pb	Cd	Mn	Cr
EUH1	7.9±0.3	86±3	BDL	1.1±0.1	57±8	0.2±0.1	4.1±0.4	15.2±0.8
EUH2	8.2±0.7	47.8±0.2	102±11	1.3±0.1	61±4	0.3±0.1	12±1	8.4±0.8
EDH1	9.2±0.4	251±24	BDL	0.6±0.1	59±5	0.2±0.1	5.2±0.4	5.3±0.2
EDH2	7.4±0.7	107.6±0.4	58±8	1.0±0.1	3.6±0.3	BDL	18±3	6.2±0.2
KSH1	81±1	195.9±0.2	55.0±0.6	1.2±0.2	40±5	0.3±0.1	7.9±0.6	39±4
KSH2	6.7±0.4	47.8±0.2	33±3	1.1±0.1	5.7±0.6	0.1±0.1	4.3±0.4	5.1±0.4
Urine1	ND	238.9±0.2	BDL	ND	2.9±0.3	ND	0.9±0.1	2.3±0.3
Urine2	ND	423.9±0.1	5.1±0.4	ND	1.7±0.1	ND	0.8±0.2	2.5±0.1

BDL, below the detection limit; ND, not determined.
* $P = 0.95$, $x \pm ts/\sqrt{N}$, $N = 4$.

for application to trace elements determinations in seawater samples.

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