

5-Chloro-2-hydroxyaniline–copper(II) coprecipitation system for preconcentration and separation of lead(II) and chromium(III) at trace levels

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Abstract

A separation–preconcentration procedure based on the coprecipitation of lead(II) and chromium(III) ions with copper(II)–5-chloro-2-hydroxyaniline system has been developed. Effects of pH, sample volume and interferences on the recovery of the metal ions were investigated. The detection limits corresponding to three times the standard deviation of the blank were found to be $2.72 \mu\text{g L}^{-1}$ for lead and $1.20 \mu\text{g L}^{-1}$ for chromium. The preconcentration factor is 50. The effectiveness of the present method was assessed by determining analyte metals in GBW 07309 stream sediment and NIST SRM 1633b coal fly ash certified reference materials. The method was successfully applied to the determination of trace lead and chromium in environmental samples.

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1. Introduction

Heavy metals occur naturally at trace concentrations in our environment; however, the levels of heavy metals are increased in the environment due to mining, industrial activities and traffic [1–4]. Heavy metal contamination of soils through anthropogenic activities is a widespread and serious problem confronting scientists and regulators throughout the world. Many works by many chemists around the world have been performed for the determination of traces heavy metals [5–10]. In these works, flame atomic absorption spectrometry (FAAS) is the main instrumental technique due to its simplicity and its lower costs than other instruments [11–14]. However the direct determinations of heavy metal ions at $\mu\text{g L}^{-1}$ levels by FAAS are not possible due to detection limits of FAAS [15–17]. Also other main problem in FAAS determinations of metals is the interference effects of matrix components of the sample

[18,19]. The use of a separation–preconcentration step prior to heavy metal determination is usually necessary since the presence of heavy metals in environmental samples is at low levels. Methods including cloud point extraction, membrane filtration, solvent extraction, solid phase extraction, ion-exchange, solvent sublation, and electroanalytical techniques are widely used to solve these problems [20–27].

Coprecipitation is a useful technique for isolation of traces of heavy metals determination with flame furnace atomic absorption spectrometry. Short analysis time, high preconcentration factors and low consumption of organic solvent are the main advantages of the coprecipitation technique [28–37]. For the present work, 5-chloro-2-hydroxyaniline and copper(II) were selected as organic reagent and carrier element, respectively. According to our literature survey, this combination is not used for the coprecipitation of heavy metal ions, until now.

In this work, a coprecipitation technique for lead(II) and chromium(III) has been developed. The analytical parameters including pH of the working media, amount of copper(II), amount of 5-chloro-2-hydroxyaniline, sample volume, matrix effects, etc., were investigated.

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2. Experimental

2.1. Instruments

PerkinElmer AAnalyst 700 atomic absorption spectrometer was used in the studies. All measurements were carried out in an air/acetylene flame. 10-cm long slot-burner heads, hollow cathode lamps were used. A pH meter, Nel pH-900 model glass-electrode was employed for measuring pH values in the aqueous phase. Nuve NF 800 model centrifuge was used to centrifuge of solutions.

Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used. Digestion conditions for microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, ventilation: 8 min [38–40].

2.2. Reagents and solutions

All the reagents used were of analytical reagent grade. Deionised double distilled water was used throughout. Laboratory glassware was kept overnight in a 10% (v/v) HNO₃ solution and then rinsed with deionised double distilled water. 5-Chloro-2-hydroxyaniline solution (1.0% (w/v)) was daily prepared in ethanol.

A stock solution of copper(II) (1000 mg L⁻¹) was prepared by dissolving 0.378 g of Cu(NO₃)₂·3H₂O (E-Merck, Germany) in deionised doubly distilled water in 100 mL; it was prepared daily. Stock standard solutions of analytes, 1000 mg L⁻¹, were prepared by dissolving appropriate amount of nitrate salts of analytes 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 HNO₃ by dilution from stock solutions.

The buffer solutions were prepared for pH adjustment: (a) 3.79 g sodium dihydrogen phosphate and 9 mL 85% of phosphoric acid for pH 2; (b) 13.78 g sodium dihydrogen phosphate and 0.60 mL 85% of phosphoric acid for pH 3; (c) 77.0 g ammonium acetate and 413 mL acetic acid for pH 4; (d) 13.1 g sodium dihydrogen phosphate and 2.40 g disodium hydrogen for pH 5; (e) 58.5 g ammonium acetate and 2.5 mL acetic acid for pH 6; (f) 0.69 g sodium borate and 5 mL 1 mol L⁻¹ hydrochloric acid for pH 7; (g) 53.5 g ammonium chloride and 4.0 mL ammonia for pH 8; (h) 500 mL of 0.1 mol L⁻¹ of ammonium chloride and 250 mL of 0.1 mol L⁻¹ of ammonia for pH 9; (i) 37.0 g ammonium chloride, 285 mL ammonia for pH 10; were taken then the volume was completed to 500 mL with distilled water.

2.3. Preconcentration work

25.0 mL portion of an aqueous solution containing 20 µg of Pb(II) and Cr(III) was placed in a centrifuge tube. The pH of solution was adjusted with an appropriate buffer solution. For pH adjustment, different buffer solutions given in Section 2.2 were used for each pH that was worked. Then 1.0 mL of 1000 mg L⁻¹ of copper(II) as a carrier element was added to this solution.

The required volume of 5-chloro-2-hydroxyaniline solution was poured into the tube. After 10 min, the solution was centrifuged at 2500 rpm for 20 min. The supernatant was removed. The precipitate in the tube was dissolved with 500 µL of concentrated HNO₃. Then it was completed to 2.0 mL with deionised water. The analytes in the final solution were determined by flame atomic absorption spectrometry.

2.4. Application to real samples

The water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size. The pH of the samples was adjusted to 8.0 with ammonia/ammonium buffer solution. Then the preconcentration–separation procedure given above was applied to all the samples. The levels of analyte ions in the final solutions were determined by flame atomic absorption spectrometry.

GBW 07309 stream sediment (250 mg) and NIST SRM 1633b coal fly ash (250 mg) certified reference materials, river sediment from Kizilirmak (1.0 g), soil sample from Tokat City (1.0 g) and coal from Tokat City (1.0 g) were digested with 6 mL HCl (37%), 2 mL of HNO₃ (65%) in microwave digestion system and diluted to 50.0 mL with deionised water. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solutions.

3. Results and discussion

3.1. Effects of pH on the coprecipitation

The effect of pH of working media on the recoveries of chromium(III) and lead(II) ions on copper–5-chloro-2-hydroxyaniline precipitate were studied in the pH range of 2.0–10.0. Each pH was adjusted by using related buffer solutions given in Section 2. The results for this work are depicted in Fig. 1. The recoveries of analytes were increased with the increasing pH. The quantitative recovery values were obtained for chromium(III) and lead(II) ions in the pH range of 8–10. pH 8 was selected as working pH for all further coprecipitation works.

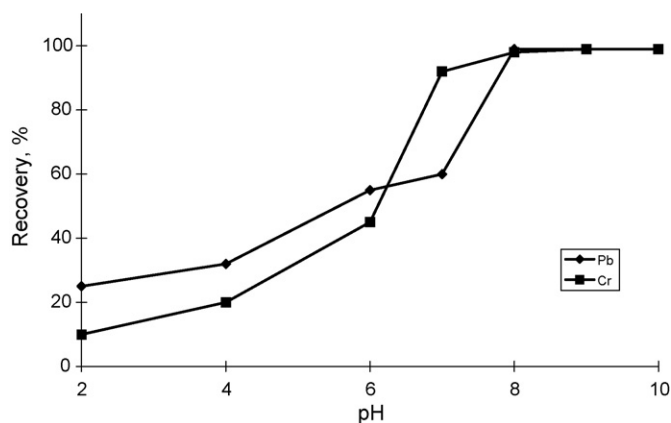


Fig. 1. Influences of pH on the recoveries of lead(II) and chromium(III) on the coprecipitation method ($N=3$).

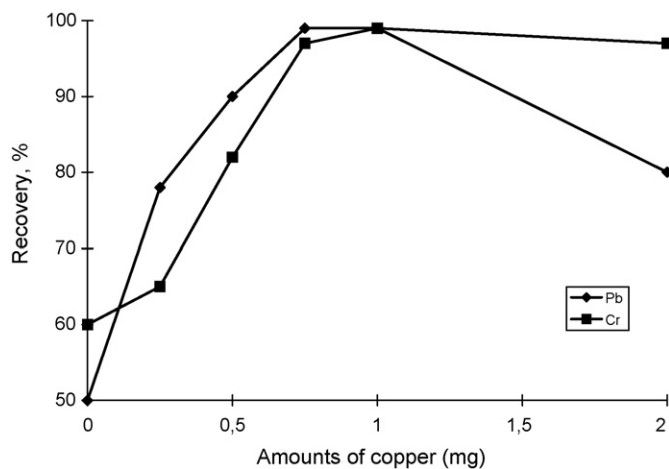


Fig. 2. Effects of amounts of copper on the recoveries of the analytes at pH 8 ($N=3$).

3.2. Effects of amounts of copper(II) as carrier element

The influences of amounts of copper(II) as carrier element were also investigated. The results are given in Fig. 2. Without copper, the recoveries for chromium(III) and lead(II) ions were not quantitative. Quantitative recovery values were obtained for the all analyte ions in 0.75–1.0 mg of copper. All further works were performed with 1 mg (1 mL of 1000 mg L⁻¹) of copper(II) ions as carrier element.

3.3. Effects of amount of 5-chloro-2-hydroxyaniline

The effects of amount of 5-chloro-2-hydroxyaniline on the recoveries of Pb(II) and Cr(III) ions on the coprecipitation system were also investigated. The results are given in Fig. 3. When the experiments were performed without 5-chloro-2-hydroxyaniline at pH 8, the recovery values were not quantitative. The recoveries of chromium(III) and lead(II) ions increased with increasing amounts of 5-chloro-2-hydroxyaniline; and reach to quantitative values at 10 mg of 5-chloro-2-hydroxyaniline. For the quantitative and simul-

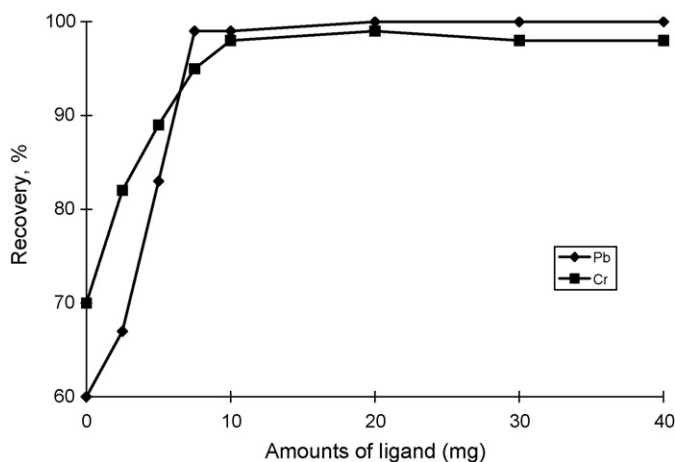


Fig. 3. Effects of amounts of 5-chloro-2-hydroxyaniline on the recoveries at pH 8 ($N=3$).

Table 1
Influences of some foreign ions on the recoveries of analytes ($N=3$)

Ion	Added as	Concentration (mg L ⁻¹)	Pb	Cr
Na ⁺	NaCl	20,000	97 ± 2	98 ± 3
K ⁺	KCl	3,000	95 ± 2	96 ± 2
Ca ²⁺	CaCl ₂	3,000	97 ± 3	98 ± 3
Mg ²⁺	MgCl ₂	5,000	95 ± 2	95 ± 2
Cl ⁻	NaCl	30,000	96 ± 3	98 ± 2
F ⁻	NaF	1,000	95 ± 2	95 ± 3
NO ₃ ⁻	KNO ₃	3,000	95 ± 2	97 ± 3
SO ₄ ²⁻	Na ₂ SO ₄	3,000	95 ± 2	96 ± 2
PO ₄ ³⁻	Na ₃ PO ₄	3,000	95 ± 2	97 ± 2
Al ³⁺	Al ₂ SO ₄	50	95 ± 2	98 ± 3
Cd ²⁺	Cd(NO ₃) ₂	50	96 ± 3	97 ± 3
Fe ³⁺	FeCl ₃	50	99 ± 2	98 ± 3
Zn ²⁺	ZnSO ₄	50	95 ± 3	98 ± 3
Mn ²⁺	MnSO ₄	50	95 ± 2	95 ± 2
Co ²⁺	CoSO ₄	50	95 ± 2	96 ± 3
Ni ²⁺	NiSO ₄	50	95 ± 2	97 ± 3

taneous recoveries of analyte ions, 5-chloro-2-hydroxyaniline is necessary. For all subsequent works, 10 mg (1.0 mL of 1.0% (w/v)) solution of 5-chloro-2-hydroxyaniline was used.

3.4. Interference studies

Interference effect of the matrix is a main problem on the flame atomic absorption spectrometric determination of metal ions [41–45]. The influences of ions given in Table 1 were investigated on the recoveries of the analyte ions. Various amounts of metal ions were added to a solution containing fixed amounts of analyte ions and the present procedure was followed. The results for this study are given in Table 1. The tolerance limit was defined as the ion concentration causing a relative error smaller than ±5% related to the coprecipitation and determination of the examined elements. The results are desired in view of applications to real samples including various salts at high-concentration levels.

3.5. Influences of sample volume on the recoveries

The effects of the sample volume on the coprecipitation efficiencies of the analytes were also examined in the sample volume range of 25–250 mL. The results are given in Table 2. Analyte ions were quantitatively recovered in the sample volume range of 25–100 mL. The precipitate of copper(II)–5-chloro-

Table 2
Effects of sample volume ($N=3$)

Volume (mL)	Recovery (%)	
	Pb	Cr
25	99 ± 2	98 ± 2
50	98 ± 3	97 ± 3
100	95 ± 2	95 ± 2
150	70 ± 3	80 ± 3
250	40 ± 2	65 ± 2

Table 3
Tests of addition/recovery for Pb and Cr determination in water samples (sample volume: 100 mL, final volume: 5 mL) ($N=4$)

Element	Added ($\mu\text{g L}^{-1}$)	Tap water		River water		Electro plating water	
		Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Pb	–	BDL ^a	–	BDL	–	BDL	–
	15	14.5 ± 0.6 ^b	97	14.6 ± 0.7	97	14.4 ± 0.9	96
	30	28.9 ± 1.3	96	29.1 ± 1.5	97	29.4 ± 1.8	98
	60	58.5 ± 2.9	98	57.6 ± 3.1	96	58.1 ± 2.6	97
Cr	–	6.3 ± 0.7	–	BDL	–	66.7 ± 3.5	–
	15	20.9 ± 0.8	98	14.3 ± 0.5	95	79.6 ± 2.8	97
	30	34.5 ± 2.2	95	28.5 ± 1.7	95	93.5 ± 3.9	97
	60	63.8 ± 3.5	96	58.1 ± 2.5	97	122.5 ± 6.3	97

^a Below detection limit.

^b Standard deviation.

2-hydroxyaniline that was including analytes was successfully dissolved in 500 μL of concentrated nitric acid. The volume was completed to 2.0 mL by distilled water. The analytes were quantitatively recovered in these studies. The preconcentration factor is calculated by the ratio of the highest sample volume (100 mL) and the lowest final volume (2 mL) for each analyte. The preconcentration factor was calculated as 50.

3.6. Figure of merits

The detection limits for analytes were calculated after presented preconcentration procedure applied to the blank solutions. The detection limits of the investigated elements based on three times the standard deviations of the blank ($k=3$, $N=11$) were 2.72 $\mu\text{g L}^{-1}$ for lead(II) and 1.20 $\mu\text{g L}^{-1}$ for chromium(III).

Tests of addition/recovery in the experiments for analyte ions were performed in water samples. The results are given in Table 3. A good agreement was obtained between the added and measured analyte amounts. The recovery values for the analyte ions were in the range of 95–100%. These values were quantitative and it shows that the presented method can be applied for the separation–preconcentration of analyte ions in real samples.

3.7. Applications

The validation of presented procedure was studied by the analysis of GBW 07309 stream sediment and NIST SRM 1633b coal fly ash certified reference materials. The results are given in Table 4. The results of our work and certified values for analytes are in good agreement. The coprecipitation procedure for analyte ions was applied to various environmental samples. The results

Table 4
The results for reference standard materials ($N=4$)

Element	GBW 07309 stream sediment ($\mu\text{g g}^{-1}$)		NIST SRM 1633b coal fly ash ($\mu\text{g g}^{-1}$)	
	Certified value	Our value	Certified value	Our value
Pb	23	22.1 ± 1.1 ^a	68.2	65.4 ± 3.2
Cr	85	82.5 ± 3.6	198.2	190.7 ± 10.5

^a Mean expressed as 95% tolerance limit.

Table 5
Concentration of analyte ions in microwave digested solid samples after application presented solid phase extraction procedure ($N=4$)

	Concentration ($\mu\text{g g}^{-1}$)	
	Pb	Cr
Soil from Tokat city	10.5 ± 0.7 ^a	30.2 ± 1.8
River sediment from Kızılırmak	15.1 ± 1.1	22.2 ± 1.5
Coal from Tokat city	7.5 ± 0.4	10.4 ± 0.6

^a Mean expressed as 95% tolerance limit.

are given in Table 5. The results have been calculated on the assumption of 100% recovery of analyte ions.

4. Conclusion

The coprecipitation method presented is simple, efficient and sensitive preconcentration in environmental samples. Under the optimum experimental conditions, quantitative recoveries were achieved for a preconcentration factor of 50. The developed method can be recommended for routine analysis of analyte ions in environmental samples like waters.

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