



Determination of Fe, Cr, Pb trace elements by atomic absorption spectrometry after co precipitation with Cadion

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ÖZET

Anahtar Kelimeler:
Kadyon, Birlikte Çöktürme, Atomik absorpsiyon spektroskopisi

Demir (III), Kurşun (II) ve Krom (III) eser miktardaki elementler için atomik absorpsiyon spektroskopisinde kadyon ile birlikte çöktürmeyle tayinleri için yeni bir metot geliştirildi. Kadyonun miktarı, örnek hacmi, matriks etkisi, santrifüjlemeden önce ve sonra bekleme süresi gibi bazı analitik parametreler tarandı. Hatta santrifüjleme süresi de incelendi. Tayin sınırı Pb, Fe ve Cr için sırasıyla 0.300, 0.090 ve 0.060 mgL⁻¹. Metodun geçerliliği standart referans madde analizleriyle test edildi. Aynı zamanda metot Kayseri, Sivas dan alınan musluk suları ile, bazı göl ve krater göllerden alınan örnek sular üzerinde de denendi. Oldukça iyi sonuçlar elde edildi (standart sapma < %5 ve geri kazanım > %95).

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ABSTRACT

Key Words:
Cadion, coprecipitation, atomic absorption spectrometry.

A method for the determination of trace amounts of iron(III), lead (II), chromium (III) is described, that combines atomic absorption spectrometry-cadion coprecipitation. The analytical parameters including amount of cadion, sample volume, matrix effects, waiting time after and before centrifuge, etc were investigated on the recoveries of analyte ions. The effects of centrifuge periods were also examined. The detection limits were for Pb, Fe, Cr; in order 0.300, 0.090, 0.060 mgL⁻¹. The validation of the presented coprecipitation method was performed by the analysis of standart referance material. The method was applied to the determination of analytes in real samples including some tap water in Kayseri and Sivas, lake and crater lake, barrage, etc. And good results were obtained. (relative standart deviations < 5%, recoveries > 95 %)

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1. Giriş

Heavy metals are environmental contaminants [1-3]. Industry, traffic, agriculture and other human factors are the main sources of metals in the environment; especially in drinking and utility water obtained from lakes and dams [3-5]. Both the positive and negative effects of these metals have been studied by researchers, and they are also important issues to the environment and environmental organizations [6-7]. Therefore, the detection of trace metal concentrations in water samples is of increasing importance in contamination monitoring studies. However, the main problem being faced in such studies is low detectability due to very low trace metal levels around $\mu\text{g L}^{-1}$ level. In order to overcome this phenomena, various preconcentrations or separation methods such as solvent extraction [8-9], ion exchange [10-11], sorbent extraction [12-13], resin chelation [14-16] and coprecipitation [17-18] have been developed and are widely used.

Coprecipitation is one of the most efficient preconcentration techniques for detecting trace of heavy metal ions [19]. In spite of the decrease on the amount of recoveries, it has several advantages: it is simple and fast, several analyte ions can be preconcentrated and separated from the matrix, as well as both inorganic or organic coprecipitants can be used as efficient collectors of trace elements [20-24]. Various carrier element-organic ligand combinations have been used in the coprecipitation of trace heavy metal ions in environmental samples, including natural water and food samples [25-30].

This work presents a coprecipitation system for the preconcentration of lead (II), iron (III) and chromium (III) ions using cadion as ligand (Fig. 1). We investigated the experimental conditions for coprecipitation of analyte ions such as pH value, cadion concentration, sample volume, etc.

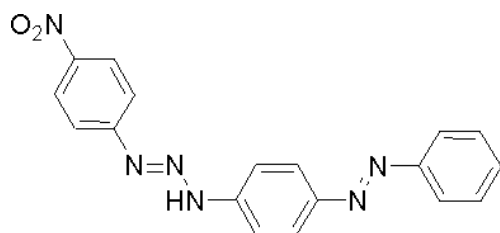


Fig. 1. Structure of cadion

1. Experimental design

1.1 Reagents and solutions

High purity reagents were used for the preparations of all standard and sample solution. Stock metal solution with a concentration of 1000 mg L^{-1} (Sigma, St. Louis) were diluted in daily base to obtain reference and working solutions. Standard solutions used for calibration procedures were prepared by diluting stock solution with 1

$\text{mol L}^{-1} \text{HNO}_3$ prior to usage. Stock solutions of diverse elements were prepared from high purity compounds (99.9%, E. Merck, Darmstadt).

1% cadion solution was prepared by dissolving cadion (Fluka, STEINHEIM) in methyl alcohol, then diluting an amount of 25 ml with methyl alcohol (99.9%), which was absolute grade from Merck.

1.1 Apparatus

To detect the existence of metal ions PerkinElmer Model 3110 atomic absorption spectrometer equipped with PerkinElmer single-element hollow cathode lamps and 10-cm air-acetylene burner were used. The Analytical parameters for PerkinElmer 3110 AAS were 283.3 nm wavelength, 0.7 mm slit width and 15 mA lamp current for Pb element; 248.3 nm wavelength, 0.2 mm slit width and 20 mA lamp current for Fe element; 357.9 nm wavelength, 0.7 mm slit width and 12 mA lamp current for Pb element. A pH meter with a Sartorius PT-10 Model glass-electrode was utilized for measuring pH values during aqueous phase. Solutions were centrifuged using a ALC PK 120 model centrifuge. Water was purified in a Human model RO 180, resulting in a conductivity of $1 \mu\text{S cm}^{-1}$.

1.1 Model working

Before the coprecipitation of analyte ions on a real sample, some test has been performed for optimization. For that purpose, 1.0 mL of 1.0 % cadion solution was added to 10.0mL solution containing 10–20 mg of analyte ions. The pH of this solution was adjusted to 8 by adding $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer. After waiting 25 mins, the solution was centrifuged at 3500 rpm for 25 min, and then the supernatant was removed. The remaining precipitate adhered to the tube was dissolved with 1 mL of $1 \text{ mol L}^{-1} \text{HNO}_3$. $1 \text{ mol L}^{-1} \text{HNO}_3$ was added to the obtained solution until it reached 2.0 or 5.0 mL. The concentration of analyte ions to be investigated was determined by flame atomic absorption spectrometry.

1.2 Analysis of real samples

50 milliliters of water was poured into a centrifugation tube. 1 ml of 1.0 % cadion solution was added to the sample to form a cadion precipitate for coprecipitation. pH of this solution was adjusted to 8 by adding NH_4Cl buffer. After waiting 25 mins, the precipitate was centrifuged at 3500 rpm for 25 mins and the supernatant was discarded. As the results, a small amount of precipitate adhered to the bottom of the tube. Then, 1mL of $1 \text{ mol L}^{-1} \text{HNO}_3$ was added to dissolve the precipitate. $1 \text{ mol L}^{-1} \text{HNO}_3$ was added to the obtained solution until it reached 2.0 or 5.0 mL. The analyte ions in this solution were detected by flame atomic absorption spectrometry.

3. Results and discussion

3.1. Optimization stage

Due to the matrix of cadion, its effect on the detection of analyte ions was initially examined by flame atomic absorption spectrometry. Cadion was added to the aqueous solution containing analytes in increasing concentrations. These solutions were analyzed by FAAS without any

pretreatment. The concentration of cation in the final solution, which would be used in the combined method using coprecipitation and FAAS, must exceed 500 mg L^{-1} . Cation was formed at basic pH values. The influence of aqueous solution's pH on the recovery values of analytes has been investigated at range of 2–10. Results are depicted in Fig. 2. Recoveries of lead (II), iron (III) (100%) and chromium (III) ions were quantitative (95%) at 7–10 and 8–10 pH range. All subsequent works were performed at pH 8, obtained by adding NH_4Cl buffer. The effect of the quantity of cation, on the coprecipitation of analytes were also examined in the range of 0–20 mg. Results are given in Fig. 3. Recoveries of analyte ions were not quantitative (below 95%) without cation.

factors were 25 for iron and lead whereas it was 20 for chromium for 2.0 mL.

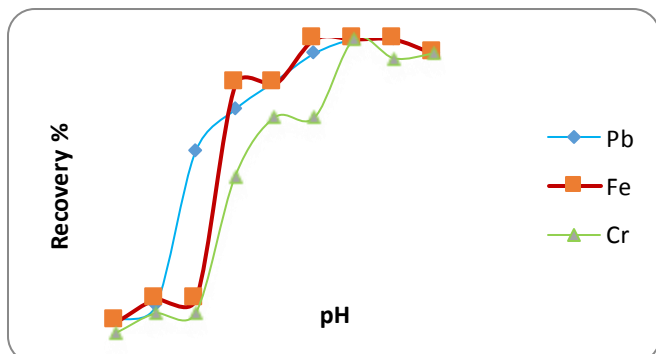


Fig. 2. Effects of pH on the recoveries of analyte ($N= 3$).

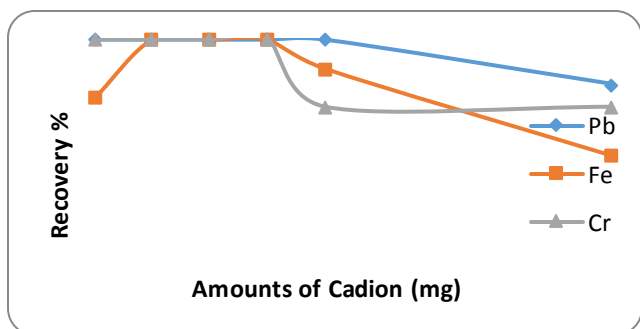


Fig. 3. Influences of cation amounts on the recoveries ($N= 3$).

Quantitative recovery values for all analytes were obtained in the range of 4.0–8.0 mg cation. The optimal amount of cation for all subsequent works was considered as 8.0 mg.

The effect of sample volume on the recoveries of lead (II), chromium (III) and iron (III) ions were examined in the range of 10–300 mL by using model solutions. Results are displayed in Fig. 4. Although Chromium (II) was recovered quantitatively in the range of 10–40 mL (100), the optimal value was found to be 50 mL. The other analytes were quantitatively (100%) recovered in the sample volume range of 10–50 mL. The final volume of the coprecipitation work varied between 2.0–10.0 mL whereas 2 mL was too small to measure the analytes by flame atomic absorption spectrometry. Three different final solutions were prepared for each element to determine analyte ions. Moreover, the existence analyte ion in each solution was determined by flame atomic absorption spectrometry. The preconcentration

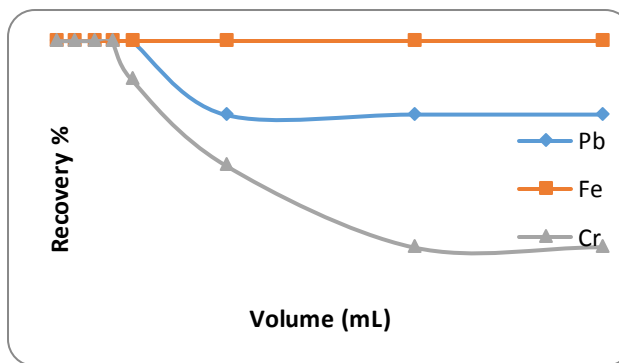


Fig. 4. Effects of volume on the recoveries ($N=3$).

The effect of standing time for cation precipitate on the recovery of analytes was also examined. Results are shown in Table 1. Analyte ions were quantitatively recovered between 25 to 30 mins. After 10 mL, the recovery values were not quantitative. For subsequent works, 25 mins was selected as the optimal standing time for cation precipitate.

Table 1. Effects of standing time for precipitate on the recoveries ($N=3$).

Standing time (min.)	Recovery (%)		
	Fe	Pb	Cr
5	0	11 (± 1)	0
10	5 (± 2)	11 (± 1)	0
15	10 (± 2)	11 (± 1)	15 (± 2)
20	100 (± 3)	100 (± 2)	85 (± 2)
25	100 (± 3)	100 (± 2)	100 (± 2)
30	100 (± 3)	95 (± 2)	95 (± 2)

The effect of centrifugation time on the recovery of analyte ions was examined in the range of 5–30 mins at 3500 rpm. Results are displayed in Fig. 5. For all analytes, quantitative recoveries were observed in the range of 25–30 mins. For further works 25 mins was taken as the optimal centrifugation time.

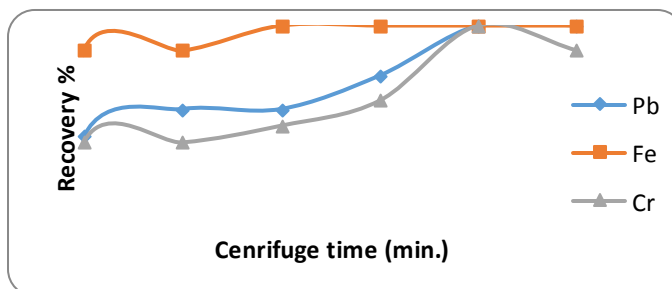


Fig. 5. Centrifuge time.

Centrifuge velocity was also investigated and (Fig. 6) for all analytes, quantitative recoveries were obtained in the range of 3500-4000 rpm. For subsequent works 3500 rpm was taken as the optimal centrifuge velocity.

The effect of concomitant ions on the coprecipitation efficiency of the analyte ions was examined. The coprecipitation procedure given in the experimental design was separately applied to each concomitant ion. Results are summarized in Table 2. The ions, which normally exist in water, didn't interact with experimental conditions. Also, some of the transition metals at mg L^{-1} levels were not detected in the recoveries of analyte ions.

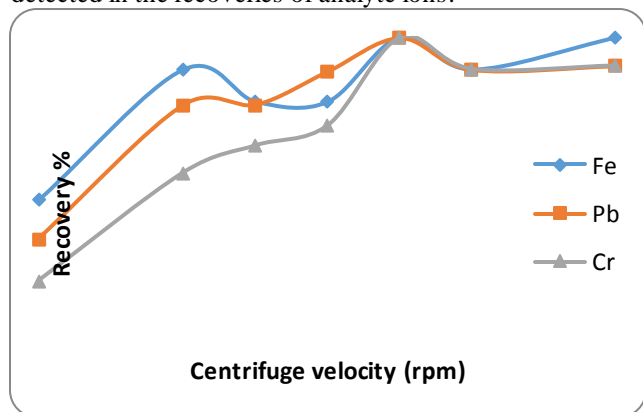


Fig. 6. Centrifuge velocity.

Table 2. Tolerance levels of the concomitant ions on the recoveries of analyte ions (N=3).

Ion	Added salt	Concentration (mg L^{-1})	Recovery %		
			Pb	Fe	Cr
NO_3^-	Na_2NO_3	1000	100(±3)	100(±3)	95(±0)
Na^+	NaCl	10000	100(±4)	100(±2)	97(±2)
Al^{3+}	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	50	100(±3)	100(±4)	95(±2)
Cl^-	NaCl	8000	100(±0)	100(±2)	97(±0)
SO_4^{2-}	Na_2SO_4	1000	100(±0)	95(±2)	95(±0)
Mg^{2+}	MgCl_2	800	100(±1)	100(±0)	95(±0)
Ni^{2+}	NiSO_4	20	95(±3)	100(±4)	95(±0)
K^+	KCl	2000	100(±2)	100(±2)	97(±0)
PO_4^{2-}	Na_2PO_4	800	100(±2)	100(±2)	95(±0)
Fe^{2+}	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	15	100(±1)	100(±1)	95(±1)
Cr^{3+}	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	20	100(±3)	100(±3)	95(±1)
Zn^{2+}	ZnCl_2	10	95(±2)	100(±0)	95(±2)
Ca^{2+}	CaCl_2	2000	100(±1)	100(±1)	95(±0)
Cu^{2+}	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	20	95(±3)	100(±1)	95(±3)
Pb^{2+}	$\text{Pb}(\text{NO}_3)_2$	10	95(±3)	100(±3)	97(±1)

3.2. Analytical performance

The standard deviations of analyte ions at the end of atomic absorption spectrometric measurements were between 1 and 10 % in model solutions. The detection limits for the concentration were defined as three times the standard deviation ($n = 10$) of the blank sample, which are displayed in Table 3.

Table 3. Limit of detection values for the analytes.

Analytes	Limit of detection (mg L^{-1})
Pb	0.300
Fe	0.090
Cr	0.060

3.3. Application of the proposed method

The aim of this paper was to investigate the feasibility of the proposed methodology in experimental design, using preconcentration for the detection of Pb(II), Cr(III) and Fe(III) in different environmental matrices by standard addition method. Reliability was checked by spiking experiments and by independent analysis. The results of this study for three different tap water samples collected from central Anatolian cities are displayed in Table 4 whereas sodium chloride and potassium chloride samples are shown in Table 5. The recovery of analytes from spiked samples is found to be reasonably satisfactory. Added and measured analyte amounts matched well. The recovery values, calculated for the added standards, were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

Table 4. Application of the presented procedure on water samples (N=3).

Analyte	Added(μg)	Kayseri tap water		Isparta tap water		Eskişehir tap water	
		Found(μg)	Recovery%	Found(μg)	Recovery%	Found(μg)	Recovery%
Fe	0	BDL	-	0.201	-	0.575	-
	2	1.96	98(±0)	2.10	95(±0.5)	2.57	100(±1.1)
	4	4.22	105(±0.7)	4.10	98(±0.6)	4.578	100(±1.1)
	0	BDL	-	0.201	-	0.575	-
Pb	0	0.121	-	BDL	-	0.200	-
	2	2.005	95(±0.6)	1.90	95(±0.7)	2.20	100(±1.5)
	4	4.00	97(±0.7)	3.92	98(±0.6)	4.20	100(±1.5)
	0	BDL	-	BDL	-	BDL	-
Cr	2	2.002	100(±0)	1.90	95(±0)	1.98	99(±3.0)
	4	3.95	99(±0)	3.90	98(±1.4)	3.96	99(±1.5)

Table 5. Levels of analyte ions in various sample after application of coprecipitation procedure (N=5).

Sample	Concentration (µg/g)		
	Fe	Pb	Cr
Gölcük(Creater lake)	0.30(±0.1)*	0.73(±0)	0.55(±0.1)
Beypınarı(Spring water)	0.20(±0.1)	0.81(±0.2)	BDL
Apaşziti(Spring water)	0.20(±0.1)	BDL	BDL
Kuşkavası(Spring water)	0.20(±0.1)	BDL	BDL
Çayralan(Spring water)	0.22(±0.1)	0.73 (±0.2)	BDL
İncesu(Barrage)	BDL	0.33(±0.1)	BDL

BDL: below the detection limit.

* Mean ± S.D.

The developed coprecipitation method was applied to Standard Reference Materials (Bovine Liver 1577-b) for the detection of analyte metals. Results are given in Table 6. The results were based on the average of three replicates for analytes, and they were quite consistent with certified values.

Table 6. Application of the method to the standard reference materials (N=3).

Element	Bovine Liver 1577-b	
	Certified value (µg/g)	Observed value (µg/g)
Pb	0.129 ± 0.004	BDL
Fe	184 ± 15	187 ± 25
Cr	-	BDL

BDL: below the detection limit.

* $\chi \pm t_{s, \alpha/5}, p = 0.95$.

4. Conclusion

Coprecipitation with cation could be a useful preconcentration technique in trace metal analysis. This is a sensitive method to detect coprecipitated analyte ions since cation doesn't have any effect by atomic absorption spectrometry.

After a successful validation process, the developed method was successfully utilized in the analysis of agricultural and geological materials. The advantages of the proposed method are: 1) the use of cation as a coprecipitant is new; 2) the method is fast, the time required for coprecipitation and determination is about 50 min; 3) the method is also economic, the amount of cation used in all the experiments during our study was 8.0 mg; 4) the detection limits of investigated analyte ions are superior to those of other preconcentration techniques

[21,22,27,28,32,33,34]. The characteristics of the proposed coprecipitation method show that it is both convenient and simple. In addition, the presented method is relatively quick compared to previously reported procedures used to enrich analytes of trace heavy metal ions in real samples.

Even though this method is fast and economical, recoveries are the same and the preconcentration factor is lower than the ones previously recorded [33-35].

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