Technical paper

Solid-phase Chelate Extractive Preconcentration of Heavy Metal Ions Prior to Their Ultratrace Determination by Microsample Injection System Coupled Flame Atomic Absorption Spectrometry

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Abstract

A Chromosorb-105 resin/1-(2-pyridylazo)-2-naphthol (PAN) system was developed for solid phase chelate extractive preconcentration of heavy metal ions. The metal ions on Chromosorb-105 resin column were eluted with 3.0 mL of 2.0 mol L^{-1} HNO_3 and determined by microsample injection system coupled flame atomic spectrometry (MIS-FAAS) using 75.0 µL of sample solution for single element determination. The influence of pH, resin amount, reagent amount, flow rate and volume of eluent and sample solution was optimized. The quantitative recoveries (≥95%) of Fe(III), Zn(II), Cu(II) and Pb(II) ions were achieved at pH 9; resin amount, 700 mg; reagent amount, 6.0 µmol; flow rate of eluent and sample solution, 1.0 mL min^{-1} and 5.0 mL min^{-1}, respectively. The limit of detection and limit of quantification of understudied analytes were found to be 0.17–1.74 µg L^{-1} and 0.40–2.98 µg L^{-1}, respectively with preconcentration factor of 150–300. The proposed method was validated by analysis of waste water (BCR–715) as a certified reference material. The method was applied successfully for ultratrace determination of studied metal ions in tap water and hot spring water samples.

Keyword: PAN; Chromosorb-105; Preconcentration; Trace metal; Microsample injection; MIS-FAAS

1. Introduction

Heavy metals are important group of toxic pollutants which exist in environmental samples. Some heavy metal ions such as Fe(III), Zn(II) and Cu(II) are essential for maintaining the health throughout the life at reasonable levels,[1–3] and Pb(II) is non essential at all levels.[4] Usually, Fe(III), Zn(II), Cu(II) and Pb(II) occur together in many samples such as water and soil. These metals ions are taken up by plants from water, soil, and subsequently transfer into the food chain. Thus, the development of rapid and highly sensitive analytical methods for the trace determination of heavy metal ions in environmental samples is a subject of the great concern for the analytical chemists.[5,6] The direct ultratrace determination of heavy metal ions by flame atomic absorption spectrometry (FAAS) is limited due their lower sensitivity and interference of possible matrices.[7,8] Therefore, preconcentratation procedure is required prior to the ultratrace determination of heavy metal ions.[9] Several preconcentration methods based on coprecipitation,[10,11] dispersive liquid–liquid microextraction,[12] liquid-liquid extraction,[13] and solid phase extraction (SPE)[14–17] have been reported. Among these methods, SPE is preferable due its selectivity, high preconcentration factor, flexibility, ecofriendliness, reusability, speed and simplicity.[18] For SPE, various solid phase materials such as silica gel, polyurethane foam, activated carbon, naphthalene, Amberlite-XAD and Chromosorb resins have been employed.[19] So far, amonnium pyrolidine dithiocarbamate (APDC),[20] sodium diethyldithiocarbamate (NaDDTC),[21,22] 8-hydroxyquinoline,[23–25] 4-(2-thiazolylazo)resorcinol (TAR)[26,27] and 1-(2-pyridylazo)-2-naphthol (PAN),[28] etc. have been used for chelate extractive preconcentration of heavy metal ions. Among these reagents, PAN selectively reacts with Fe(III), Zn(II), Cu(II) and Pb(II) at room temperature to form their chelates.[29] To the best of our knowledge, there is no report in the literature for chelate extractive preconcentration of metal ions by use of PAN as a chelating reagent on the Chromosorb-105 resin column. Chromosorb porous polymers are composed of polyaromatic cross-linked resin with uniform and rigid structure which are infusible and insoluble in the most of solvents.[30]

In this current study, we focus on the simultaneous ultratrace chelate extractive preconcentration of Fe(III), Zn(II), Cu(II) and Pb(II) ions on Chromosorb-105 resin mini-column. The preconcentrated metal ions were determined by microsample injection system coupled flame atomic absorption spectrometry (MIS-FAAS) using 75.0 μL of sample solution for single metal determination. The proposed method was validated by analysis of waste water (BCR-715) as a certified reference material. Finally, the method was applied successfully for ultratrace determination of Fe(III), Zn(II), Cu(II) and Pb(II) in water samples.

2. Experimental

2. 1. Apparatus

The determination of studied metal ions were performed by PerkinElmer FAAS (AAnalyst 200) equipped with hollow cathode lamp. The operating parameters for the studied elements were set as recommended by the manufacturer. A Hanna pH 211 Model (Germany) digital pH meter with a combined glass electrode was used for pH measurements.

2. 2. Reagents and Solutions

The analytical-grades chemicals were purchased from Fluka and Merck and employed through the experiments. Ultrapure quality water (resistivity 18.2 MΩcm^{-1}) was obtained by reverse osmosis system (Human Corp., Seoul, Korea), and used throughout the experiments. Stock solutions (1000±4 mg L^{-1}) of Fe(III), Zn(II), Cu(II) and Pb(II) ions were purchased from Merck (Darmstad and Germany).

The standards and working solutions were prepared daily by suitable dilution of stock solutions by addition of water. The buffer solutions, hydrochloric acid/potassium chloride, acetic acid/ammonium acetate, carbonic acid/sodium bicarbonate, and ammonia/ammonium nitrate solutions were used for pH 2, 4–6, 7 and 8–10, respectively. Chelating reagent solution was prepared by dissolving 10 mg of PAN in 10 mL of ethanol. Certified reference material, waste water (BCR-715) was furnished by European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (EC-JRC-IRMM), Geel, Belgium.

2. 3. Sample Collection

Polyethylene bottles were used for water samples storage. The bottles were successively pre-cleaned with water, detergent, water, dilute nitric acid and water. Karahayıt hot spring water sample was collected from a famous source of hot spring water known as red water in Karahayıt district, Denizli, Turkey. Red hot (at about 60 °C) spring water contain; sodium,114.9 mg L^{-1}; potassium, 32.9 mg L^{-1}; calcium, 466.0 mg L^{-1}; magnesium, 131.0 mg L^{-1}; bicarbonate, 1329.6 mg L^{-1}; sulphate, 830.0 mg L^{-1}; chloride, 130.0 mg L^{-1}; iron, 2.5 mg L^{-1} and aluminum, 0.85 mg L^{-1}. Pamukkale hot spring water sample was collected from one of terrace series in Pamukkale (Cotton Castle), Denizli, Turkey. Pamukkale hot (at almost 33–36 °C) spring water contain; sodium, 332.3 mg L^{-1}; potassium, 13.5 mg L^{-1}; calcium, 464.5 mg L^{-1}; magnesium, 911.0. mg L^{-1}; bicarbonate, 1045.3 mg L^{-1}; sulphate, 675.5 mg L^{-1}; chloride, 53.0 mg L^{-1}; iron, 0.036 mg L^{-1} and aluminum, 2.3 mg L^{-1}. The samples were filtered through cellulose nitrate membrane (pore size, 0.45 μm and diameter, 47.0 mm), buffered to pH 9, and stored for analysis. Both Karahayıt and Pamukkale hot spring water samples have complex matrices. Tap water sample was collected freshly from Research Laboratory, Department of Chemistry, Pamukkale University, Turkey.

2. 4. Column Preparation

The glass column (100 mm in length and 10 mm in diameter) with stopcock was packed with 700 mg of Chromosorb-105 resin. The small amount of glass wool was placed on the disc of both end of the column to prevent the loss of the resin particles during sample loading and elution. The resin packed in the column was decontaminated by successive washing with water, 1.0 mol L^{-1} HCl, water, 1.0 mol L^{-1} NaOH, water, 2.0 mol L^{-1} HNO_3, and finally with water. The column was pre-conditioned to the desired pH before passing the sample. After each use, the resin packed in the column was washed thoroughly with water and then stored in water for reuses.

2. 5. Preconcentration Procedure

100 mL of model solution containing 5–10 μg of Fe(III), Zn(II), Cu(II) and Pb(II) was adjusted to pH 9 and 6.0 μmol of PAN was added into it. The system was sha-

ken at room temperature for 5.0 min and passed through the column at flow rate of 5.0 mL min^{-1}. The adsorbed analytes were eluted with 3.0 mL of 2.0 mol L^{-1} HNO_3 at flow rate of 1.0 mL min^{-1}. The eluate was evaporated almost to dryness on hot plate at ~40 °C and the remaining material was dissolved in 1.0 mL with 2.0 mol L^{-1} HNO_3. The analytes in final solution were determined by MIS-FAAS using 75 µL of sample solution for single element determination.

2. 6. Microsample Injection Coupled Flame Atomic Absorption Spectrometry

In general, 2.0–4.0 mL is required for single element determination by FAAS. Multi element determinations require larger volume which lead lower preconcentration factor. Therefore, microsample injection coupled flame atomic absorption spectrometry (MIS-FAAS) was employed to solve this problem. For this purpose, nebulizer needle of FAAS was coupled with the disposable-tip of micropipette (capacity 20–200 µL) using PTFE capillary tube (length of 10.0 cm). The flow rates of air and acetylene were 10 and 2.5 Lmin^{-1}, respectively. A micropipette was used for microsample injection and absorbance was recorded as peak height within 5.0 to 10.0 seconds. MIS-FAAS offers 75.0 µL of sample solution for single element determination with maximum absorbance signal, high accuracy, and reproducibility.[31]

2. 7. Analysis of Certified Reference Materials

The proposed method was applied for trace determination of studied metal ions in certified reference material. For this, 1.0 mL of wastewater (BCR-715) was diluted to 100 mL by addition of water and then subjected according to the proposed method.

3. Results and Discussion

3. 1. Effect of pH

pH is one of the most important analytical parameter that influnces the preconcentration procedure, because the formation of metal chelates and their stabilitiy, solubility, and surface activity of resin are strongly pH dependent. The effect of pH on the retention of metal-PAN (M-PAN) chelate on the Chromosorb-105 resin column was studied. For this, model solutions were adjusted to pH 2–10 and passed through the column according to the proposed procedure. The recoveries of Zn(II) and Pb (II), Fe(III) and Cu(II) were quantitative (≥95%) at pHs 7–9.5, 6–10 and 4–9.5, respectively as shown in Figure 1. Because of the protonation of PAN at lower pHs, the formation of chelate is prevented. Hence, the sorption decreases with decrease in pH 6–2 (except copper) while increases with increase in pH 7–9.5. At pH > 9.5, formation of precipitates and/or anionic hydroxide complexes of metals may decrease the sorption. Therefore, pH 9 was chosen as working pH for the further experiments.

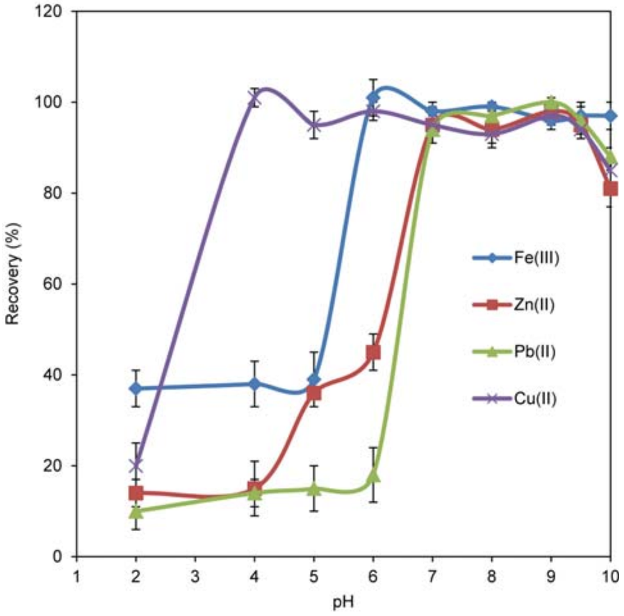

Figure 1. Effect of pH on the recovery of studied metal ions (volume = 100 mL, n = 4)

In light of these findings above, the quantitative recoveries of studied analytes can be explained with the formation of neutral-hydrophobic M-PAN chelates in alkaline solution,[28,29] which can be adsorbed by the hydrophobic Chromosorb 105 resin. Because of both polyaromatic Chromosorb 105 resin and M-PAN chelate having π-electrons, also, it may be concluded that additional π–π interaction was responsible for adsorption of studied metals onto Chromosorb 105 resin. Thus, it might be concluded that the adsorbed analytes were desorbed by an acidic solution due to the decomposition of M-PAN chelates.

3. 2. Effect of PAN Amount

The amount of PAN plays an important role to achieve the quantitative recoveries of studied metal ions. The excess amounts of PAN prevent the retention of M-PAN chelates due to sorption competitions between M-PAN and PAN. Thus, the effect of PAN amount on the retention of M-PAN chelates was investigated in the range of 0.0–8.0 µmol. The recoveries of the metal ions increased with increase of PAN amount, 1.5–6.0 µmol and decreased with further increase in amount, 6.0–8.0 µmol, because of sorption competitions between M-PAN and PAN as shown in Figure 2. Therfore, 6.0 µmol was chosed as best amount of PAN for the further experiments.

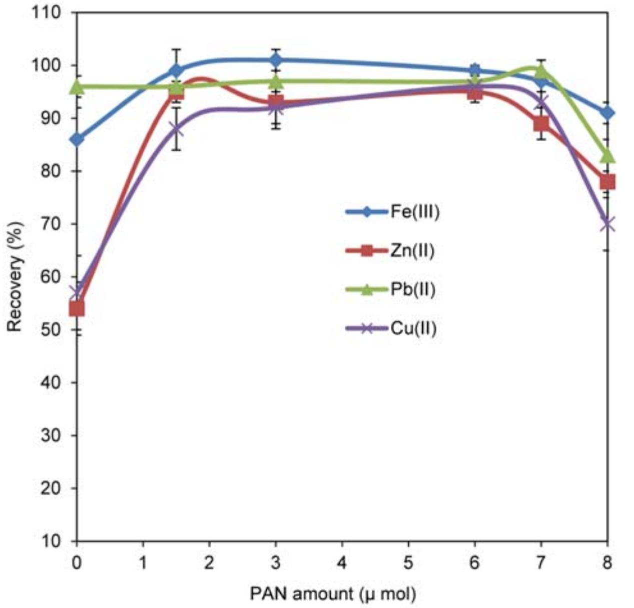

Figure 2. Effect of PAN amount on the recovery of studied metal ions (volume = 100 mL, n = 4).

3. 3. Effect of Eluent

The effect of eluent solvents on the recoveries of studied metal ions was investigated. For this, 3–5 mL of 1–3 mol L^{-1} HNO$_3$ and nitric acid/acetone pair were tested as eluent solvents. The quantitative recoveries (≥95%) of studied metal ions were achieved with 3–5 mL of 2.0 mol L^{-1} HNO$_3$ (Table 1). Thus, 3.0 mL of 2.0 mol L^{-1} HNO$_3$ was chosen as the best eluent.

Table 1: Effect of eluents on the recoveries of studied metal ions (volume = 3.0 mL, n = 3, s: standard deviation).

	Recovery±s (%)			
Eluent types	**Fe(III)**	**Zn(II)**	**Cu(II)**	**Pb(II)**
1.0 mol L^{-1} HNO$_3$	31±4	65±3	84±2	80±4
2.0 mol L^{-1} HNO$_3$	100±2	96±3	97±2	101±2
3.0 mol L^{-1} HNO$_3$	98±3	97±2	96±4	100±2
Acetone	19±2	66±4	39±3	13±2
1.0 mol L^{-1} HNO$_3$/Acetone	94±3	85±4	62±2	70±1
2.0 mol L^{-1} HNO$_3$/Acetone	104±1	81±5	89±4	86±3
3.0 mol L^{-1} HNO$_3$/Acetone	97±2	87±3	90±3	85±4

3. 4. Effect of Sample Volume and Preconcentration Factor

The effect of sample volume on the recoveries of the studied metal ions were investigated. For this, 25–350 mL of model solution was adjusted to pH 9 and passed through Chromosorb-105 column. The retained metal ions were eluted with 3.0 mL of 2.0 mol L^{-1} HNO$_3$, the eluate was evaporated to dryness on hot plate at ~40 °C and quantitatively completed to 1.0 mL with 2.0 mol L^{-1} HNO$_3$. The recoveries of Fe(III), Zn(II), Cu(II) and Pb(II) were quantitative (≥95%) until 300, 250, 150 and 150 mL, respectively of sample solution as shown in Figure 3. Thus, the preconcentration factors for Fe(III), Zn(II), Cu(II) and Pb(II) were calculated; 300, 250, 150 and 150, respectively.

3. 5. Effect of Flow Rate

Effect of flow rates of eluent and sample solution on the recoveries of studied metal ions was investigated. For this, 100 mL of model solution was passed through the column at flow rate of 2–10 mL min^{-1}, the retained metal ions were eluted with 3.0 mL of 2.0 mol L^{-1} HNO$_3$ at flow rate of 1.0–3.0 mL min^{-1}. The recoveries of studied metal ions were obtained quantitative (≥95%) at flow rate of 1.0 and 5.0 mL min^{-1} of eluent and sample solution, respectively. Therefore, 1.0 and 5.0 mL min^{-1} were chosen as optimum flow rates of eluent and sample solution, respectively.

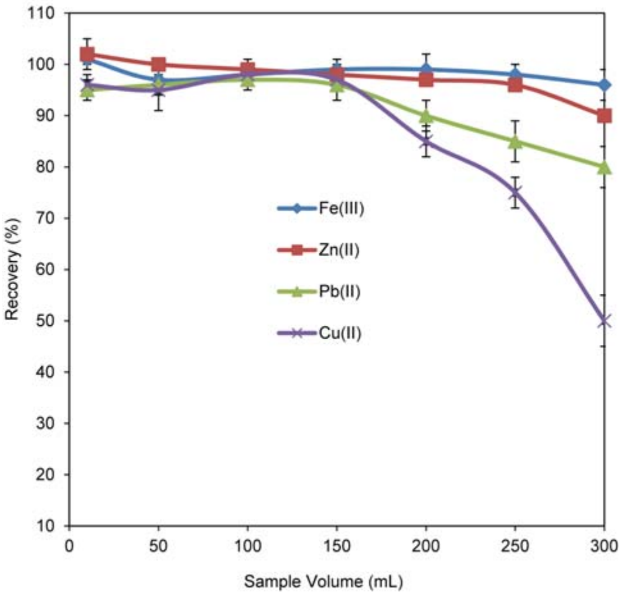

Figure 3. Effect of sample volume on the recovery of studied metal ions (n = 4).

3. 6. Effect of Resin Amount

The effect of resin amount on the quantitative recoveries of studied metal ions was investigated. For this, 100 mL of model solution was adjusted to pH 9 and passed through the column packed with 200–1000 mg of Chromosorb-105 resin at flow rate of 5.0 mL min^{-1}. The retained metal ions were eluted with 3.0 mL of 2.0 mol L^{-1} HNO$_3$ at flow of 1.0 mL min^{-1}. The quantitative recoveries (≥95%) of studied metal ions were obtained with 700–1000 mg of the resin. Therefore, 700 mg was chosen as best resin amount for the further experiments.

3. 7. Effect of Foreign Ions

Interference is the main problem in the determination of heavy metal ion by FAAS. The effect of matrices such as alkali and alkaline earth metal ions, heavy metal ions which probably form chelate with PAN, and commonly existing anions in natural waters on the recoveries of studied metal ions was investigated. For this, 100 mL of model solution was spiked with the foreign ions and passed through the column according to the proposed procedure. The tolerable limit was accepted as recoveries of studied metal ions were achieved quantitative with reative error < ±5% as shown in Table 2.

3. 8. Analytical Performance of the Method

The analytical performance of the proposed method was evaluated with the analytical figures of merit including limit of detection (LOD), limit of quantification (LOQ), precision as RSD, and accuracy. The LOD (blank+3σ) and LOQ were (blank+10 σ, where σ is standard deviation of blank analysis, *n* = 20) were defined by IUPAC.[32] The LOD and LOQ of Fe(III), Zn(II), Cu(II) and Pb(II) were found to be 1.74, 0.85, 0.17, 0.70 μg L^{-1} and 2.98, 1.49, 0.40 and 1.32 μg L^{-1}, respectively. The validation and accuracy of the proposed method were evaluated by analysis of waste water (BCR-715) as certified reference material. All studied metal ions were found to be in good agreement with certified values as shown in Table 3. The validation and high accuracy of the proposed method was confirmed with *t*-test[33] at confidence level of 95% with RSD ≤ 7.2% (*n* = 4).

Table 2: Tolerable ion concentration limits for foreign ions to the proposed procedure (volume = 100 mL, n = 4).

Foreign ions	Added salt	Tolerable concentration limits (mg L^{-1})
Na^+	NaCl	30000
K^+	KCl	20000
Ba^{2+}	$Ba(NO_3)_2$	15000
Ca^{2+}	$CaCl_2$	15000
Mg^{2+}	$MgCl_2$	10000
Ni^{2+}	$Ni(NO_3)_2$	50
Cd^{2+}	$Cd(NO_3)_2$	50
Mn^{2+}	$MnSO_4$	50
Cr^{3+}	$Cr(NO_3)_3$	50
Al^{3+}	$Al(NO_3)_3$	50
Cl^-	NaCl	30000
NO^-_3	KNO_3	20000
CO^{2-}_3	Na_2CO_3	20000
SO^{2-}_4	Na_2SO_4	10000
PO^{3-}_4	K_3PO_4	5000

The reusability and stability of the resin were checked by passing 100 mL of the model solution through the column packed with 700 mg of the resin at optimum conditions. The resin was recycled more than 400 times, the recoveries were achieved to be quantitative (≥95%) which shows high reusability and stability of Chromosorb-105 resin.

Table 3: Determination of studied metal ions in certified reference material (volume = 100 mL, n = 4, P = 0.95).

Analytes	Concentration (μg L^{-1}) Certified	Found, x ± ts/√n, (RSD %)	Relative error (%)
Fe(III)	3000	3030±111 (2.3)	+1.0
Zn(II)	4000	4100±127 (2.0)	+2.5
Cu(II)	900	830±95 (7.2)	–7.8
Pb(II)	490	505±35 (4.4)	+3.1

3. 9. Applications of The Proposed Method

The proposed method was applied successfuly for the preconcentration and ultratrace determination of studied metal ions in tap water and spring hot water samples. The spring hot water samples are found to be contaminated with studied metal ions as shown in Table 4.

3. 10. Comparison With Reported Methods

Various methods have been reported for the preconcentration and trace determination of heavy metal ions.[28, 34–38] In this method, Chromosorb-105 resin/PAN system has been used for solid-phase chelate extractive preconcentration of Fe(III), Zn(II), Cu(II) and Pb(II) ions. This method is more accurate with comparatively

Table 4: Determination of studied metal ions in real samples by proposed method (volume = 100 mL, n = 4, P = 0.95).

Samples	Concentration (μg L^{-1}), x ± ts/√n , (RSD %) Fe(III)	Zn(II)	Cu(II)	Pb(II)
Tap water	27.4±1.9 (4.4)	not detected	9.6±0.8 (5.2)	5.2±0.3 (3.8)
Hot spring red water (Karahayıt)	28.9±1.3 (2.8)	13.3±0.6 (3.0)	not detected	60.1±11.2 (11.8)
Hot spring water (Pamukkale)	57.4±6.7 (7.3)	15.9±1.7 (6.9)	6.8±0.5 (4.4)	31.9±1.9 (3.8)

RSD: Relative standard deviation

Table 5: Comparison of analytical parameters for the trace determinations of metal ions by FAAS using different resins/ligands.

Resin	Metal Ions	Sample vol. (mL)	PF	LOD ($\mu g\ L^{-1}$)	RSD	Ref. (%)
XAD-4 loaded PAN	Cd(II), Co(II), Ni(II), Mn(II), Zn(II),	800–1000	160–400	0.09–1.30	2.2–4.8	28
XAD-1180 coated PAN	Cd(II), Mn(II), Ni(II), Pb(II), Zn(II)	50–150	10–30	0.7–3.1	<11	34
XAD-16 immolized PAN	Ni(II), Cd(II), Co(II), Cu(II), Pb(II), Cr(III)	1000	200	0.056–0.268	<8.0	35
XAD-1180 functionalized PAN	Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II), Pb(II)	400–750	≥80	0.06–4.1	<8.5	36
XAD-4/PAN	Pb(II), Cd(II), Cr(III), Ni(II), Mn(II), Cu(II)	1000	200	0.16–0.45	<10	37
XAD-2 loaded PAN	Cu(II), Cd(II), Pb(II)	100	50	0.8–23.2	<5.0	38
Chromosorb-105/PAN	Pb(II), Zn(II), Cu(II), Fe(III)	150–300	150–300	0.17–1.74	2.8–7.3	This work

LOD: Limit of detection; PF: Preconcentration factor, RSD: Relative standard deviation

high precontration factor and lower LOD values as shown in Table 5.

4. Conclusion

A novel solid-phase chelate extractive preconcentration method was developed for ultratrace determination of Fe(III), Zn(II), Cu(II) and Pb(II) ions in different water samples by MIS-FAAS using Chromosorb-105 resin/PAN system. The analytical performance of method was evaluated by analysis of waste water (BCR-715) as certified reference material for preconcentration and ultratrace determination of studied metal ions. The validation and high accuracy of the proposed method was confirmed with *t*-test at confidance level of 95% with RSD ≤ 7.2% ($n = 4$). The interference study demonstrated that the proposed method is applicable to water samples containing alkali metal and alkaline earth metal ions, heavy metal ions, and commonly existing anions. The resin was successfully recycled more than 400 times in different interval of times without significant loss in recoveries (%) of studied metal ions. The innovative MIS-FAAS offers, 75.0 µL of sample for single element determination with maximum absorbance signal, high accuracy, reproducibility with high preconcentration factor.

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Povzetek

Za predkoncentracijo kelatov ionov težkih kovin z ekstrakcijo na trdno fazo smo razvili sistem s polimerom Chromosorb-105 in 1-(2-piridilazo)-2-naftolom (PAN). Kovinske ione smo s kolone s Chromosorb-105 polimerom eluirali s 3,0 mL 2,0 mol L^{-1} HNO_3 in določili s sistemom za injiciranje mikrovzorcev, sklopljenim z plamensko atomsko spektrometrijo (MIS-FAAS) ob uporabi samo 75,0 µL raztopine vzorca za določitev enega elementa. Optimizirali smo vpliv pH, količine polimera, količine reagenta, pretoka in volumna eluenta ter raztopine vzorca. Kvantitativne izkoristke (≥95 %) za Fe(III), Zn(II), Cu(II) in Pb(II) ione smo dosegli pri pH 9; količini polimera 700 mg; količini reagenta 6,0 µmol; pretoku eluenta 1,0 mL min^{-1} in pretoku raztopine vzorca 5,0 mL min^{-1}. Meje zaznave za preučevane analite so bile 0,17–1,74 µg L^{-1}, meje določitve 0,40–2,98 µg L^{-1}, predkoncentracijski faktor pa 150–300. Predlagano metodo smo validirali z analizo odpadne vode (BCR-715) kot certificiranega referenčnega materiala. Metodo smo uspešno uporabili za določitev ultrasledov preiskovanih kovinskih ionov v vzorcih vodovodne vode in termalne vode.