



Heavy metals separation and determination in waters using MIS-FAAS by bismuth(III) hydroxide co-precipitation method

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ABSTRACT

Potable and urban waters, which is a vital resource, constitute the most basic research area of today. In the current study, a newly optimized co-precipitation method using bismuth(III) hydroxide has been examined for quantitative separation and preconcentration of iron(III), chromium(III), copper(II), cobalt(II), manganese(II), nickel(II), and cadmium(II) ions from water samples. Analytes were co-precipitated and after dissolving analyzed by micro-sample injection system flame atomic absorption spectrophotometry. The influence of variables such as sample volume, sodium hydroxide concentration, bismuth(III) concentration, matrix effects, etc. were investigated. The theoretical enrichment factor of the optimized method is 50. The precisions of within-day and intra-day for the analyte elements working real water samples were found in the range of 4.1–4.5. The limit of detections for the analyte elements were in the range of 0.8–9.5 µg/L. The limit of quantification of iron(III), chromium(III), copper(II), cobalt(II), manganese(II), nickel(II), and cadmium(II) ions were calculated to be 18.0, 21.0, 7.6, 6.8, 13.0, 27.0, and 1.1 µg/L, respectively. The analysis of the BCR-715 standard reference water sample demonstrated the procedure's accuracy, and the method was successfully applied to two different water samples and nine different plants as a real sample.

Keywords: Heavy metals; Co-precipitation; Bismuth(III) hydroxide; Waters; Atomic absorption spectrometry

1. Introduction

Heavy metal pollution is one of the world's most serious environmental problems and the determination of these elements especially in drinking water, urban and industrial wastewater is extremely important due to public health studies. The interaction and accumulation of heavy metals are harmful to plants and animals, that creates a risk factor for humans with their transfer and accumulation in the food chain [1–3]. While iron, copper, and zinc occur together in water and soil samples. These trace metals are absorbed by plants from the soil and water [4]. Plants have been used by humans to prevent diseases, maintain health or cure diseases since ages [5,6]. The essential elemental content of

herbals depends on the properties of the soil and their ability of accumulation elements. However, atmospheric dusts, rainfall, fertilizers and wastewater can cause contamination in plants [7,8]. Heavy metals are plant component molecules that have biological activity in human metabolism as either essential or harmful agents [8–10]. Low levels of iron, zinc, copper, and manganese are essential for good health, but some metal ions, such as cadmium, lead, arsenic, and mercury, have hazardous effects on our bodies' biochemical responses [11–14]. The restricted limit concentrations for Cr, Cd and Pb in drinking water are 0.1, 5 and 10 µg/L, respectively [14]. According to Commission Regulation [15] No 1881/2006 and No 629/2008, maximum allowable levels of lead and cadmium in leafy vegetables are 0.3 and 0.05 mg/kg.

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Water and plants contain heavy metal ions in a wide range of concentration, the determination of these ions is important for the control of human health [12,13,16]. Flame atomic absorption spectrometry (FAAS) is greatly employed for the determination of trace metals owing to its high analytical performance and low cost [17–20]. Most of the AAS combined analytical techniques are recommended to expand the problems caused by high concentrations of interfering matrix components in real samples and the requirement for high instrument detection limits [4,20,21]. For this purpose an effective separation and enrichment have been frequently carried out using liquid phase extraction [1,22,23], solid phase extraction [24–33], membrane filtration [17,34], and cloud point extraction [35–38].

Another important separation-preconcentration method that draws attention as it is a simple, fast and green technique is co-precipitation. In trace metal ion co-precipitation experiments, both organic and inorganic precipitants can be utilized [39–43]. Metal hydroxides are the preferred choice for co-precipitation of trace metal ions due to their high recovery and separation. Various metal hydroxides including lutetium, praseodymium, holmium, aluminum, cerium, dysprosium, europium, magnesium, erbium, samarium, scandium and zirconium have been used to separate and preconcentrate trace elements from water, food, plant and environmental samples previous to their determinations [44–57].

Bismuth(III) hydroxide is another important metal hydroxide co-precipitant. However using as co-precipitant is limited to a few works like determination of trace metals in vanadium-aluminium alloy and vanadium metal [58], lead and iron in high-purity zinc metal [59], mercury(II) from an aquatic environment [60] and soils and sediments [61].

A developed co-precipitation method using Bi(III) hydroxide was applied for the separation/enrichment and determination of iron(III), copper(II), chromium(III), cobalt(II), manganese(II), cadmium(II) and nickel(II) ions in water samples. In addition, it was also tested for some plant samples. The parameters such as bismuth(III) concentration, matrix effects, NaOH concentration, and sample volume have been optimized for the quantitative co-precipitation method. The microsample injection system-flame atomic absorption spectrophotometry (MIS-FAAS) method, which employs bismuth as a precipitating reagent, is notable for its suitability for multi-element determination, low cost for routine and large-scale analysis, and speed and simplicity of use.

2. Materials and methods

2.1. Apparatus

Throughout this research, Perkin Elmer AAnalyst 700 trademark FAAS with an air-acetylene burner and a deuterium lamp background corrector was utilized. The flame was created with air with a flow rate of 10 L/min and acetylene with a flow rate of 2.5 L/min. Absorbances were measured as the peak height by a microsample injection system (MIS) coupled with FAAS at 324.8, 248.3, 232.0, 240.7, 279.5, 228.8 and 357.9 nm, using a spectral bandwidth of 0.7, 0.2, 0.2, 0.2, 0.4, 0.7 and 0.7 for copper, iron, nickel, cobalt, manganese,

cadmium and chromium, respectively. For all samples and calibration solutions, 100 μ L aliquots were used and injected directly into the MIS. As previously reported, the injection system was connected to the nebulizer needle through a PTFE capillary tube with a micropipette tip [62]. WTW 720 Digital pH Meter (Weilheim, Germany) was used to determine the pH of the aqueous phase. A centrifuge Nuve NF 400 (Ankara, Turkey) was used to hasten the process of phase separation. A vortex mixer from Velp Scientifica (Milan, Italy) was used to dissolve the precipitate that remained adhered to the tube. All weighing were made with a Precisa XB 220 A analytical scales (± 0.0001 g, Dietikon, Switzerland). The ultrapure water used in the studies was obtained in the laboratory with the reverse osmosis system Human Corporation Device (Seoul, Korea).

2.2. Reagents and solutions

All solutions were prepared using analytical grade chemicals. Ultrapure grade water with a resistivity of 18.2 M/cm was used for prepared solutions and experiments. The calibration standard and diluted model solutions of Fe(III), Cu(II), Cr(III), Co(III), Mn(II), Ni(II), and Cd(II) were prepared daily by appropriate dilutions of 1,000 mg/L stock solution of the respective analytes (Merck, Darmstadt, Germany). A Bi(III) solution (2,000 mg/L) was freshly prepared by dissolving Bi(NO₃)₃ (Merck, Darmstadt, Germany) 0.095 g in 2 mL of HNO₃ (Merck, Darmstadt, Germany) and diluting to 25 mL with water. Sodium hydroxide (Sigma-Aldrich, Steinheim, Germany) was utilized for preparation of 1 mol/L NaOH. BCR-715 wastewater certified reference material was furnished by European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (EC-JRC-IRMM), Geel, Belgium.

2.3. Co-precipitation procedure

The process was optimized with model solutions before co-precipitation of analyte ions from real samples. For that purpose, 250 μ L of 2,000 mg/L bismuth(III) solution was added to 10.0 mL of solution containing 5 μ g Cd(II), 10 μ g Fe(III), Cu(II), Co(III), Mn(II), Ni(II), and 20 μ g Cr(III) ions. The NaOH concentration was then adjusted to 0.1 mol/L with the addition of 1.0 mol/L NaOH for the purpose of collect the analytes on bismuth(III) hydroxide. The tube was left for a few seconds and the precipitate was centrifuged at 4,000 rpm for 3 min. The supernatant was eliminated completely. 1 mL of 2 mol/L HNO₃ was used to dissolve the precipitate that remained stuck to the tube. A microsample injection technique combined with FAAS was used to quantify the analyte ions in this solution.

2.4. Real samples analysis

The co-precipitation technique was implemented for determination of copper, iron, nickel, cobalt, manganese, cadmium and chromium in the followings samples: drinking water from Pamukkale University, with the assistance of the Denizli environment quality laboratory, industrial effluent was sampled from an organized industrial zone in Denizli, and herbs were obtained in Denizli, Turkey, from

several gardens. The herbal samples were dried for 6 h at 110°C. The dried samples were homogenized with an agate homogenizer and stored in plastic bottles at room temperature until analysis. The application of the optimized procedure is demonstrated using BCR-715 wastewater certified reference material.

For analysis of liquid samples, a fifty millilitre of water samples was filtered through a 0.45 mm cellulose nitrate membrane, then were placed into a centrifugation tube and co-precipitation method was applied. Plant samples were dissolved by adding 15 mL of aqua regia to 0.5 g sample according to the procedure suggested by Divrikli et al. [8], and the solution was evaporated until dryness was twice. The residue was diluted with 45 mL of ultrapure water. The enrichment technique was used on the 50 mL final solution after the suspension had been filtered through blue band filter paper and washed with ultrapure water. Analytes taken to a final volume of 1.0 mL were determined by MIS-FAAS.

3. Results and discussion

In real samples, it is difficult to precipitate elements in trace concentrations by conventional methods because they form colloidal or small amounts of the precipitate. The developed method is based on the co-precipitation of trace elements with bismuth hydroxide. The influence of analytical parameters such as bismuth(III) concentration and NaOH concentration on the co-precipitation efficiency of analyte ions were investigated by preparing model solutions. In order to prevent the matrix effect that may occur in FAAS, studies were started with a low amount of Bi(III) and continued by increasing it. Analyte absorbances were obtained close to each other and at approximate values up to 1.5 mg Bi³⁺.

3.1. Effect of NaOH concentration

The target trace metal ions were enriched using bismuth hydroxides as a co-precipitant. Since the precipitation of bismuth(III) ion and together trace elements as hydroxides

depends on the base concentration of the aquatic medium, the quantitative recovery values for the co-precipitation of the analytes were investigated by studying different sodium hydroxide concentrations. The amount of Bi(III) added to the model solutions was 2 mg. The effect of NaOH was worked by varying it in the range of 0.0025–1.0 mol/L in a 10 mL model solution containing 5–20 µg of trace metal ions. The recovery values obtained for analytes without using NaOH were below 40%. In the NaOH concentration range of 0.1–1.0 mol/L, the recoveries of the investigated metals were greater than 90% (Fig. 1). All further works were performed at NaOH 0.1 mol/L.

3.2. Effect of Bi(III) amount as carrier element

The effect of bismuth amount on the quantitative precipitation of analytes at 0.1 mol/L NaOH was evaluated in the range 0.0025–4 mg on the spiked sample. Without bismuth(III), analyte ion recoveries were less than 44%. The recoveries for analyte ions were over 95% in the 0.25–1.5 mg bismuth(III) amount range (Fig. 2). It was thought that chromium(III), manganese(II), nickel(II) and cadmium(II) ions form a stable second solid phase after the addition of 2 mg and more of bismuth, but cannot hold on to the bismuth hydroxides precipitate. For this reason, there were co-precipitation losses and the recovery decreased. In all subsequent experiments, 0.5 mg of bismuth(III) was used as a carrier element.

3.3. Effect of precipitate formation time

The duration of waiting is an important parameter for the formation of the bismuth hydroxide precipitate and the completion of the co-precipitation of the analytes. The effect of precipitate formation time was tested for 0, 5, 10, 20 and 30 min (Table 1). No significant changes were observed in the range studied and all analytes were obtained with quantitative recoveries. The results showed that the co-precipitation can be done without any precipitate formation time (at 0 min).

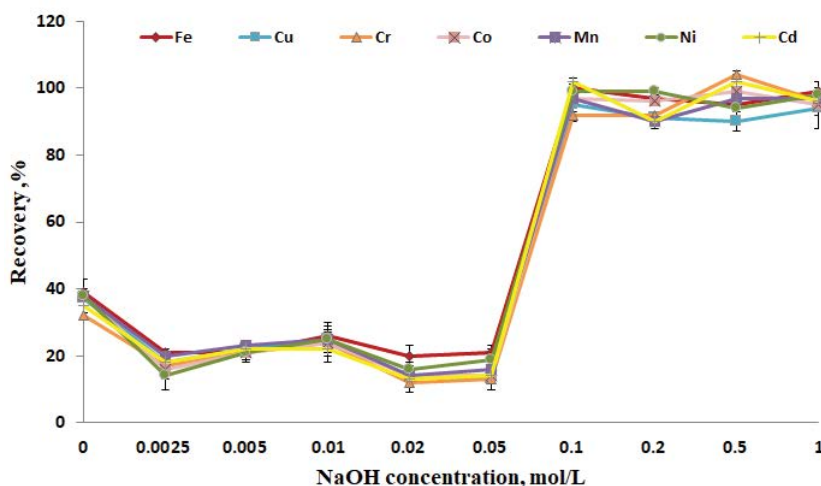


Fig. 1. Effect of NaOH concentration on the recoveries of analytes ($n = 4$).

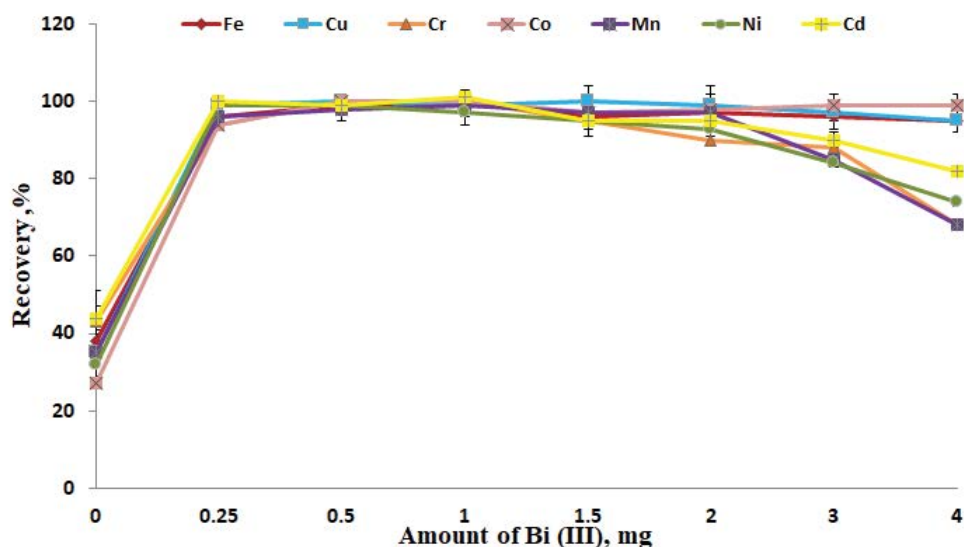


Fig. 2. Effect of bismuth(III) amount on the recoveries of analytes ($n = 3$).

Table 1
Effects of precipitate formation time for bismuth hydroxide precipitate ($n = 4$)

Analyte	Recovery %				
	0 min	5 min	10 min	20 min	30 min
Fe	99 ± 1	101 ± 1	100 ± 1	100 ± 1	99 ± 1
Cu	100 ± 1	97 ± 2	99 ± 1	98 ± 2	100 ± 1
Cr	98 ± 1	96 ± 5	98 ± 4	97 ± 1	95 ± 5
Co	99 ± 1	97 ± 3	99 ± 2	92 ± 1	99 ± 2
Mn	100 ± 1	100 ± 1	99 ± 1	101 ± 1	100 ± 1
Ni	100 ± 1	100 ± 1	100 ± 1	100 ± 1	101 ± 1
Cd	99 ± 1	95 ± 1	99 ± 1	97 ± 1	96 ± 3

Table 2
Centrifugation time effect ($n = 4$)

Analyte	Recovery %		
	3 min	5 min	10 min
Fe	95 ± 3	92 ± 2	94 ± 2
Cu	96 ± 3	93 ± 1	95 ± 2
Cr	96 ± 1	92 ± 2	97 ± 2
Co	97 ± 1	97 ± 1	97 ± 4
Mn	94 ± 3	96 ± 1	97 ± 2
Ni	94 ± 1	99 ± 1	100 ± 1
Cd	100 ± 1	99 ± 1	99 ± 1

3.4. Effect of the centrifugation time

The effects of centrifugation time on analyte ion recovery were studied in the range of 3–10 min at 4,000 rpm. The percent recovery values of the analytes were found in the range of 92–100 (Table 2). All subsequent work was performed with a 3 min centrifugation time.

3.5. Effect of sample volume

The sample volume is a critical parameter for co-precipitation methods because it influences the preconcentration factor value showing one of the method performance. So, model solutions with sample volumes ranging from 10 to 50 mL were used to investigate the effect of sample volume on analyte ion recoveries under the optimal conditions. Iron(III), chromium(III), and cadmium(II) ions were quantitatively (95%) recovered and copper(II), cobalt(II), manganese(II), and nickel(II) ions were obtained over 90% recovery in the studied sample volume range (Fig. 3). When

the final volume was 1.0 mL, the preconcentration factor for the analytes could be achieved 50 with an initial sample volume of 50 mL.

3.6. Effect of matrix ions

In the extraction processes, the ions that make up the aquatic media components and the salt effect are important parameters that affect the extraction efficiency. Addition of salt causes an increase in the ionic strength of the solution and poor solubility of polar analytes in water. This occurs when matrix (salt) ions surround the hydration layer, reducing the solubility of the analyte in water. In the methods where separation is made by precipitation, the ionic strength of the analyzed medium or the increase of the matrix ions (salt effect) can facilitate the precipitation and co-precipitation processes. However, interferences from matrix components are one of the most significant restrictions in AAS detection of heavy metals. The impacts of various matrix ions on the co-precipitation efficiency of iron(III), copper(II), chromium(III), cobalt(II), manganese(II), nickel(II),

and cadmium(II) ions were studied by adding known concentrations of these ions. The co-precipitation technique was then used on each of the different ions independently. The recovery values of the analytes ranged from 90% to 100% (Table 3). Under the conditions utilized in the experiment, target matrix components have not interfered with the recoveries of the analyte ions. The proposed co-precipitation method could be applied to the highly saline samples.

3.7. Analytical performance of the procedure

The suggested method's analytical performance was assessed using limit of detection (LOD), limit of quantification (LOQ), precision, accuracy, and preconcentration factor (PF). The calibration graphs were obtained for all target analytes, determined by MIS-FAAS. The LOD and LOQ were calculated as $3 \times S_b/m$ and $10 \times S_b/m$, respectively [62]. Where S_b is the standard deviation of the blank ($n = 20$) and m is the slope of the linear section of the calibration graph. The LOD of Fe(III), Ni(II), Cr(III), Cu(II), Mn(II), Co(III), and Cd(II) were found to be 9.5, 9.2, 6.8, 3.8, 1.9, 1.4, and 0.8 $\mu\text{g/L}$, respectively. The precisions of within-day and intra-day for the analyte elements were calculated in the range of 4.1 to 4.5 with analysis of variance (ANOVA) test from the real water samples (Table 4). The ratios of the slopes of the calibration curves with preconcentration

of 1.0 mL and without preconcentration solution were used to calculate the experimental preconcentration factor (Table 4). The theoretical preconcentration factor is 50, which was obtained by dividing the sample volume (50 mL) by the final solution volume (1.0 mL).

3.8. Applications

Different concentrations of analytes were spiked in tap and wastewater to validate the accuracy of the current co-precipitation technique for metal ions. Table 5 summarizes the findings. The content of the added and found analytes was determined to be in good agreement. With a few exceptions, the relative recovery values estimated for the standard additions were greater than 90%, indicating the procedure's accuracy and the absence of matrix effects.

The developed co-precipitation method was applied to BCR-715 wastewater standard reference material for the determination of analytes. The mean results of the triplicate experiments are good congruent for all analytes given a certified value (Table 6).

Analytes of 2 mg Mn and Cd, 4 mg Co, Cu, Ni, and Cr, and 8 mg Fe ions were added to the dissolved dried mint sample to assess the method's applicability in plant samples. The relative recovery percentage of Mn(II), and Fe(III) were found to be 93 ± 4 , and 94 ± 6 , respectively. The other elements have less than 60% recovery.

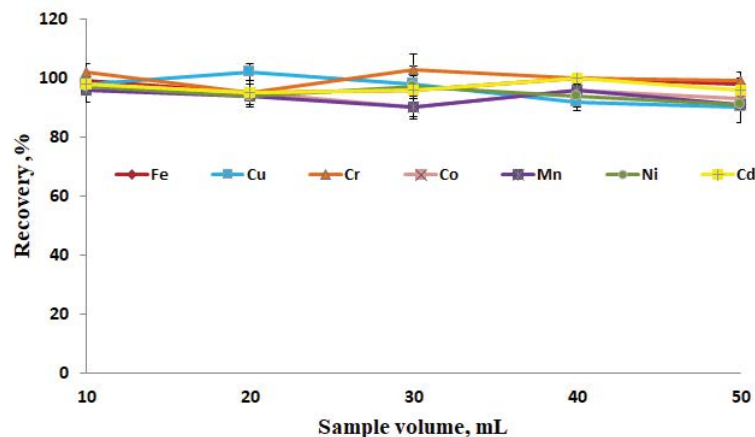


Fig. 3. Effect of sample volume on the recoveries of analytes ($n = 4$).

Table 3
Tolerance levels of the matrix ions ($n = 4$)

Ion	Added as	Concentration (mg/L)	Recovery %						
			Fe	Cu	Cr	Co	Mn	Ni	Cd
Na ⁺	NaCl	20,000	97 ± 3	95 ± 7	92 ± 7	94 ± 4	96 ± 5	95 ± 6	100 ± 6
K ⁺	KCl	2,500	98 ± 2	99 ± 1	97 ± 2	97 ± 2	90 ± 1	97 ± 2	98 ± 2
Ca ²⁺	CaCl ₂	2,000	100 ± 1	97 ± 1	91 ± 4	96 ± 1	100 ± 2	97 ± 2	95 ± 5
Mg ²⁺	MgCl ₂	2,500	99 ± 1	99 ± 1	91 ± 1	99 ± 1	93 ± 2	97 ± 3	96 ± 1
SO ₄ ²⁻	Na ₂ SO ₄	2,500	98 ± 7	97 ± 4	95 ± 4	97 ± 4	90 ± 8	97 ± 7	97 ± 4
PO ₄ ³⁻	Na ₃ PO ₄	2,500	96 ± 2	97 ± 2	98 ± 2	94 ± 2	92 ± 2	95 ± 5	98 ± 2
HCO ₃ ⁻	NaHCO ₃	5,000	100 ± 1	96 ± 2	95 ± 1	96 ± 2	97 ± 2	96 ± 3	95 ± 2

Table 4
Analytical figures of merit of the proposed method

Analyte	Linear range (mg/L)	Calibration equation						
		Without preconcentration	With preconcentration	PF	Precision (%) ANOVA		LOD (µg/L)	LOQ (µg/L)
					Within-day	Intra-day		
Fe	1–8	$y = 0.009x + 0.002$ ($r^2: 0.999$)	$y = 0.430x$ ($r^2: 0.998$)	47.8	4.5	4.3	9.5	18.0
Cu	0.5–8	$y = 0.049x + 0.001$ ($r^2: 0.999$)	$y = 2.416x - 0.001$ ($r^2: 0.999$)	49.3	4.5	4.2	3.8	7.6
Cr	1–20	$y = 0.007x + 0.003$ ($r^2: 0.998$)	$y = 0.322x + 0.001$ ($r^2: 0.999$)	46.0	4.5	4.3	6.8	21.0
Co	0.5–10	$y = 0.022x + 0.005$ ($r^2: 0.997$)	$y = 1.144x + 0.005$ ($r^2: 0.998$)	52.0	4.4	4.2	1.4	6.8
Mn	0.5–8	$y = 0.053x + 0.001$ ($r^2: 0.999$)	$y = 2.503x + 0.012$ ($r^2: 0.999$)	47.2	4.4	4.1	1.9	13.0
Ni	1–8	$y = 0.013x + 0.003$ ($r^2: 0.998$)	$y = 0.694x + 0.013$ ($r^2: 0.998$)	46.3	4.3	4.1	9.2	27.0
Cd	0.1–4	$y = 0.241x + 0.012$ ($r^2: 0.998$)	$y = 12.96x + 0.002$ ($r^2: 0.999$)	53.8	4.3	4.1	0.8	1.1

PF: Preconcentration factor, LOD: Limit of detection, LOQ: Limit of quantification

Table 5
Application of the presented procedure for some water samples ($n = 3$)

Analyte	Added (µg/L)	Tap water			Wastewater		
		Found (µg/L)	R %	RSD %	Found (µg/L)	R %	RSD %
Fe	0	36.3 ± 4.0	–	11.0	31.2 ± 2.4	–	7.7
	40	72.1 ± 2.1	90 ± 1	2.9	70.1 ± 0.1	97 ± 1	0.1
	80	118.3 ± 4.8	102 ± 2	4.0	114.6 ± 1.6	104 ± 2	1.4
Cu	0	33.8 ± 1.4	–	4.1	37.5 ± 1.4	–	3.7
	40	71.7 ± 0.4	95 ± 1	0.6	74.7 ± 0.9	93 ± 2	1.2
	80	113.5 ± 1.8	100 ± 1	1.6	110.3 ± 1.3	91 ± 1	1.2
Cr	0	BDL	–	–	BDL	–	–
	80	78.1 ± 0.1	98 ± 1	0.1	75.1 ± 0.1	94 ± 2	0.1
	160	157.2 ± 0.2	98 ± 1	0.1	162.1 ± 2.2	101 ± 1	1.4
Co	0	BDL	–	–	BDL	–	–
	80	79.1 ± 5.8	99 ± 1	7.3	72.1 ± 1.1	90 ± 1	1.5
	160	156.8 ± 1.0	98 ± 2	0.6	146.1 ± 0.1	91 ± 2	0.1
Mn	0	BDL	–	–	17.0 ± 1.4	–	8.2
	80	80.6 ± 7.4	101 ± 1	9.2	93.1 ± 0.1	95 ± 1	0.1
	160	159.3 ± 16.5	100 ± 2	10.4	171.4 ± 11.0	97 ± 3	6.4
Ni	0	BDL	–	–	BDL	–	–
	80	84.0 ± 8.0	105 ± 2	9.5	72.0 ± 0.1	90 ± 2	0.1
	160	145.8 ± 6.2	91 ± 1	4.3	158.5 ± 5.7	99 ± 1	3.6
Cd	0	BDL	–	–	4.0 ± 0.4	–	10
	40	42.0 ± 0.8	105 ± 3	1.9	40.8 ± 0.1	92 ± 1	0.3
	80	75.6 ± 0.9	95 ± 1	1.2	80.8 ± 0.1	96 ± 1	0.1

BDL: Below the detection limit, R: Recovery, RSD: Relative standard deviation

Despite the limitations, the co-precipitation method was applied to the determination of iron(III), copper(II), chromium(III), cobalt(II), manganese(II), nickel(II), and cadmium(II) ions in some herbal samples. Table 7 summarizes

the results, which were calculated with the assumption of 100% analyte relative recovery. The metal concentration of the herbal plant samples was found to be in the following ranges: 22.3–157.4 µg/g for iron, 1.6–7.3 µg/g for copper,

Table 6
Results for wastewater BCR-715 reference standard materials (mg/L)

Analyte	Fe	Cu	Cr	Co	Mn (µg/L)	Ni	Cd (µg/L)
Certified value	3	0.90	1.00	**	248	1.20	40
Found value	2.9 ± 0.3	0.87 ± 0.09	1.14 ± 0.04	**	247 ± 14	1.28 ± 0.10	38 ± 3

* $P = 0.95$; $x \pm t_s/\sqrt{N}$; **Not certificated.

Table 7
Analysis of real herbal samples ($n = 3$)

Sample	Concentration, µg/g ^a						
	Fe	Cu	Cr	Co	Mn	Ni	Cd
Black cumin	122.2 ± 11.1	6.8 ± 0.6	3.4 ± 0.3	BDL	54.3 ± 5.3	1.9 ± 0.2	0.97 ± 0.11
Thyme	80.4 ± 8.2	4.7 ± 0.5	3.1 ± 0.2	BDL	12.5 ± 1.1	7.4 ± 0.1	0.81 ± 0.06
Basil	129.0 ± 16.6	7.1 ± 0.2	5.2 ± 0.2	0.91 ± 0.01	38.9 ± 4.0	1.5 ± 0.2	0.64 ± 0.07
Garden sorrel	154.7 ± 20.4	2.7 ± 0.4	2.6 ± 0.2	0.67 ± 0.01	17.3 ± 1.6	2.6 ± 0.2	1.17 ± 0.07
Mint	42.8 ± 4.8	3.9 ± 0.5	3.5 ± 0.2	0.75 ± 0.10	30.7 ± 2.0	1.5 ± 0.2	1.03 ± 0.10
Red pepper	84.4 ± 2.5	1.6 ± 0.1	2.9 ± 0.1	BDL	8.0 ± 0.4	9.8 ± 0.2	2.3 ± 0.1
Mallow	118.0 ± 1.6	7.3 ± 0.4	5.1 ± 0.2	0.56 ± 0.06	12.4 ± 1.0	1.05 ± 0.01	5.1 ± 0.1
Rosemary	27.1 ± 1.0	BDL	1.1 ± 0.1	BDL	2.3 ± 0.2	1.5 ± 0.1	7.4 ± 0.6
Sweet basil	22.3 ± 1.1	5.6 ± 0.6	1.4 ± 0.2	BDL	17.5 ± 2.5	1.8 ± 0.2	14.4 ± 0.2

^aMean ± standard deviations, BDL: Below the detection limit

1.1–5.2 µg/g for chromium, 0.56–0.91 µg/g for cobalt, 2.3–54.3 µg/g for manganese, 1.05–9.8 µg/g for nickel and 0.64–14.4 µg/g for cadmium. The acquired results are consistent with those given in the literature [8,56].

3.9. Comparison with previous methods

The determined element and sample type, instruments and analytical performance of the method and other selected co-precipitation methods are summarized in Table 8. Except for the method in which zirconium and aluminum [57] are used, determinations in all other methods were carried out by atomic absorption spectrometry. However, graphite furnace AAS is a more costly equipment, which is difficult to implement compared to flame AAS. Co-precipitation with bismuth allows multiple trace element determination like some other methods (outside of zirconium, magnesium, cerium, aluminum [53] and praseodymium). The amount of co-precipitant is 1.2 to 18 times lower than other methods described (excluding Saracoglu et al. [54]) and the same as Soylak et al. (2005, 2006). The preconcentration factor is generally obtained with a sample volume ratio of the final volume. Apart from the methods using lutetium, praseodymium, and dysprosium as metal hydroxide, the analytes' preconcentration factor is 2 to 50 times higher than the other compared methods. The limit of detections of the analytes are comparable to some of the reported methods [54,56] and better than others [47,49,51].

When the methods are compared in terms of the cost of implementation, the price of the precipitating reagent salts used should also be evaluated. When the catalog prices

of the nitrate salts of the elements shown in the table are examined, the cheapest ones per gram are aluminum, bismuth, magnesium, and cerium, respectively (<https://www.sigmaaldrich.com>). Others are about 10–400 times more expensive. This FAAS method, in which 500 mg of bismuth is presented as a precipitating reagent; it stands out in terms of being suitable for multi-element determination, low cost in routine analysis processes, easy and fast application.

4. Conclusions

The proposed method, which uses bismuth(III) ion as a precipitating reagent has been optimized in all conditions and applied to real samples is the first technique in this working area. Bismuth hydroxide precipitate to coprecipitate iron(III), copper(II), chromium(III), cobalt(II), manganese(II), nickel(II), and cadmium(II) ions, is simple and accurate. The method combined with MIS-FAAS allows to work in a sample volume of 10 mL at low amount sodium hydroxide. For flame atomic absorption spectrophotometry, the matrix ion effects are permissible. At the best working conditions, analytes were relative recovered at a rate of more than 95%. The developed method has been successfully applied to the analysis of tap water and wastewater after validation. Furthermore, it was studied for the determination of metals (especially for Mn(II) and Fe(III) ions) in some plant samples. The total analysis time spent for the co-precipitation and determination was only about 20 min. Moreover the amount of bismuth(III) used for all experiments is 0.50 g. The proposed method with optimized all analysis parameters is new, very fast, economical, and eco-friendly for multi-element determination.

Table 8
Comparison of co-precipitation methods with hydroxide precipitates

Type of metal hydroxide	Determined element	Sample type	Method of analysis	Range of detection limit, µg/L	Coprecipitant amount, µg	Preconcentration factor	References
Zirconium ^a	Bi	Natural water	DPASV	–	–	–	44
Scandium ^b	Cu, Sn, Pb, Sb, Bi, Cd, Cr, Co, and Ni	Water	GFAAS	–	–	–	45
Magnesium	Cd, Cr, Pb, and Mn	Urine	GFAAS	0.08–0.15	600	10	46
Samarium	Cu, Fe, Ni, Co, Pb, Cd, Mn, and Cr	Urine and dialysis solutions	FAAS	0.99–24.0	1,000	10	47
Erbium	Cu, Mn, Co, Cr, Fe, and Pb	Urine, soil and sediment, natural water	FAAS	0.04–0.87	500	10	48
Europium	Cr, Fe, Pb, and Mn	Waters and some food, soil and fertilizer samples	FAAS	1.7–17.1	500	10	49
Magnesium	Se	Food and water samples	GFAAS	0.030	1,000	25	50
Dysprosium	Pb, Cu, Ni, Co, Cd, and Mn	Table salts and natural waters	FAAS	14.1–25.3	2,000	250	51
Cerium	Cr	Drinking and wastewaters	FAAS	0.18	9,000	25	52
Aluminum	As	Natural water samples	HG-AAS	0.012	1,000	25	53
Holmium	Cu, Mn, Co, Ni, Cr, Fe, Cd, and Pb	Food and soil samples	FAAS	0.48–58.4	400	1	54
Praseodymium	Cr	Water samples	FAAS	0.25	1,000	180	55
Lutetium	Cu, Pb, Mn, Co, Cd, Fe, and Ni	Water and herbal plant samples	FAAS	1.6–7.2	1,000	100	56
Aluminum	V, Cr, Mn, Ni, Co, Cu, Zn, As, Se, Cd, Pb, and U	Sea water	ICP-MS	0.0023–1.5046	5,000	2	57
Bismuth	Fe, Cu, Cr, Co, Mn, Ni, and Cd	Water and herbal samples	MIS-FAAS	0.8–9.5	500	50	Present work

^aArticle data not available;

DPASV: Differential pulse anodic stripping voltammetry, GFAAS: Graphite furnace atomic absorption spectrometry, FAAS: Flame atomic absorption spectrometry, MIS-FAAS: Micro-sample injection system-flame atomic absorption spectrophotometry, ICP-MS: Inductively coupled plasma-mass spectrometry

Compliance with ethical standards

Authors of this manuscript declared that there has no conflict of interest.

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References

- [1] A.N. Siyal, S.Q. Memon, A. Elçi, A. Akdogan, A. Hol, A.A. Kartal, L. Elci, Schiff base-functionalised styrofoam resin for preconcentration of metal ions in wastewater and wastewater-irrigated vegetables samples, *Int. J. Environ. Anal. Chem.*, 94 (2014) 1463–1477.
- [2] E. Yilmaz, R.M. Alosmanov, M. Soylak, Magnetic solid phase extraction of lead(II) and cadmium(II) on a magnetic phosphorus-containing polymer (M-PHCP) for their microsampling flame atomic absorption spectrometric determinations, *RSC Adv.*, 5 (2015) 33801–33808.
- [3] K.H. Kim, A.A. Keller, J.K. Yang, Removal of heavy metals from aqueous solution using a novel composite of recycled materials, *Colloids Surf., A*, 425 (2013) 6–14.
- [4] S. Sari, A.A. Kartal, A. Elci, A. Akdogan, A. Hol, A.N. Siyal, L. Elci, Solid-phase chelate extractive preconcentration of heavy metal ions prior to their ultratrace determination by microsample injection system coupled flame atomic absorption spectrometry, *Acta Chim. Slov.*, 60 (2013) 901–907.
- [5] S. Kilic, M. Soylak, Determination of trace element contaminants in herbal teas using ICP-MS by different sample preparation method, *J. Food Sci. Technol.*, 57 (2020) 927–933.

- [6] M. Moghaddam, L. Mehdizadeh, Z. Sharifi, Macro and microelement content and health risk assessment of heavy metals in various herbs of Iran, *Environ. Sci. Pollut. Res.*, 27 (2020) 12320–12331.
- [7] A. Celik, A.A. Kartal, A. Akdoğan, Y. Kaska, Determining the heavy metal pollution in Denizli (Turkey) by using *Robinia pseudo-acacia* L, *Environ. Int.*, 31 (2005) 105–112.
- [8] U. Divrikli, N. Horzum, M. Soylak, L. Elci, Trace heavy metal contents of some spices and herbal plants from Western Anatolia-Turkey, *Int. J. Food Sci. Technol.*, 41 (2006) 712–716.
- [9] M.R. Gomez, S. Cerutti, L.L. Sombra, M.F. Silva, L.D. Martinez, Determination of heavy metals for the quality control in Argentinian herbal medicines by ETAAS and ICP-OES, *Food Chem. Toxicol.*, 45 (2007) 1060–1064.
- [10] M. Soylak, M. Koksall, Deep eutectic solvent microextraction of lead(II), cobalt(II), nickel(II) and manganese(II) ions for the separation and preconcentration in some oil samples from Turkey prior to their microsampling flame atomic absorption spectrometric determination, *Microchem. J.*, 147 (2019) 832–837.
- [11] M. Soylak, Z. Cihan, E. Yilmaz, Evaluation of trace element contents of some herbal plants and spices retailed in Kayseri, Turkey, *Environ. Monit. Assess.*, 184 (2012) 3455–3461.
- [12] K. Jurowski, M. Krośniak, M. Folta, B. Tatar, M. Cole, W. Piekoszewski, The toxicological analysis of Cu, Mn and Zn as elemental impurities in pharmaceutical herbal products for teething available in pharmacies in Poland, *J. Trace Elem. Med. Biol.*, 53 (2019) 109–112.
- [13] D. Mendil, O.D. Uluozlu, M. Tuzen, M. Soylak, Multi-element determination in some foods and beverages using silica gel modified with 1-phenylthiosemicarbazide, *Food Addit. Contam., Part A*, 36 (2019) 1667–1676.
- [14] Y. Vasseghian, F. Almomani, E.N. Drago, Health risk assessment induced by trace toxic metals in tap drinking water: condorcet principle development, *Chemosphere*, 286 (2022) 131821, doi: 10.1016/j.chemosphere.2021.131821.
- [15] Commission Regulation (EC) No 629/2008 of 2 July 2008 Amending Regulation (EC) No 1881/2006 Setting Maximum Levels for Certain Contaminants in Food Stuffs.
- [16] B. Gómez-Nieto, M.J. Gismera, M.T. Sevilla, J.R. Procopio, Determination of essential elements in beverages, herbal infusions and dietary supplements using a new straightforward sequential approach based on flame atomic absorption spectrometry, *Food Chem.*, 219 (2017) 69–75.
- [17] U. Divrikli, A.A. Kartal, M. Soylak, L. Elci, Preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) ions in environmental samples by membrane filtration prior to their flame atomic absorption spectrometric determinations, *J. Hazard. Mater.*, 145 (2007) 459–464.
- [18] H. Karasali, G. Pavlidis, Microwave-assisted acid extraction of the major metal elements in herbal extracts followed by flame atomic absorption spectrometric (FAAS) determination, *Toxicol. Environ. Chem.*, 98 (2016) 1173–1182.
- [19] S. Popović, A. Pantelić, Z. Milovanović, J. Milinkov, M. Vidović, Analysis of tea for metals by flame and graphite furnace atomic absorption spectrometry with multivariate analysis, *Anal. Lett.*, 50 (2017) 2619–2633.
- [20] P. Pohl, A. Bielawska-Pohl, A. Dzimitrowicz, K. Greda, P. Jamroz, A. Lesniewicz, A. Szymczycha-Madeja, M. Welna, Understanding element composition of medicinal plants used in herbalism-A case study by analytical atomic spectrometry, *J. Pharm. Biomed. Anal.*, 159 (2018) 262–271.
- [21] A. Afkhami, M. Saber-Tehrani, H. Bagheri, T. Madrakian, Flame atomic absorption spectrometric determination of trace amounts of Pb(II) and Cr(III) in biological, food and environmental samples after preconcentration by modified nano-alumina, *Microchim. Acta*, 172 (2011) 125–136.
- [22] P. Konieczynski, M. Wesolowski, Determination of the water-extractable fraction of iron in selected medicinal plant raw materials: *Folium Menthae*, *Folium Urticae* and *Folium Salviae*, *Chem. Speciation Bioavailability*, 20 (2008) 261–266.
- [23] A.F. Erulas, M. Saylan, S. Topal, B.T. Zaman, E.G. Bakirdere, S. Bakirdere, A new microextraction method for trace nickel determination in green tea samples: solventless dispersion based dispersive liquid-liquid microextraction combined with slotted quartz tube-flame atomic absorption spectrophotometry, *J. Food Compos. Anal.*, 94 (2020) 103623, doi: 10.1016/j.jfca.2020.103623.
- [24] M. Tuzen, M. Soylak, Column solid-phase extraction of nickel and silver in environmental samples prior to their flame atomic absorption spectrometric determinations, *J. Hazard. Mater.*, 164 (2009) 1428–1432.
- [25] M. Ezoddina, F. Shemirani, K. Abdi, M. Khosravi Saghezchi, M.R. Jamali, Application of modified nano-alumina as a solid phase extraction sorbent for the preconcentration of Cd and Pb in water and herbal samples prior to flame atomic absorption spectrometry determination, *J. Hazard. Mater.*, 178 (2010) 900–905.
- [26] S. Ju, M. Liu, Y. Yang, Preconcentration and determination of cadmium, lead, and cobalt in *Moringa oleifera* (*Moringaceae*) using magnetic solid-phase extraction and flame atomic absorption spectrometry, *Anal. Lett.*, 49 (2016) 511–522.
- [27] V. Zarezade, M. Behbahani, F. Omid, H.S. Abandansari, G. Hesam, A new magnetic tailor made polymer for separation and trace determination of cadmium ions by flame atomic absorption spectrophotometry, *RSC Adv.*, 6 (2016) 103499–103507.
- [28] V. Zarezade, A. Aliakbari, M. Es'haghi, M.M. Amini, M. Behbahani, F. Omid, G. Hesam, Application of a new nanoporous sorbent for extraction and preconcentration of lead and copper ions, *Int. J. Environ. Anal. Chem.*, 97 (2017) 383–397.
- [29] M. Behbahani, A. Veisi, F. Omid, A. Noghrehabadi, A. Esrafil, M.H. Ebrahimi, Application of a dispersive micro-solid-phase extraction method for pre-concentration and ultra-trace determination of cadmium ions in water and biological samples, *Appl. Organomet. Chem.*, 32 (2018) e4134, doi: 10.1002/aoc.4134.
- [30] S. Parvizi, M. Behbahani, F. Zeraatpisheh, A. Esrafil, Preconcentration and ultra-trace determination of hexavalent chromium ions using tailor-made polymer nanoparticles coupled with graphite furnace atomic absorption spectrometry: ultrasonic assisted-dispersive solid-phase extraction, *New J. Chem.*, 42 (2018) 10357–10365.
- [31] M. Behbahani, V. Zarezade, A. Veisi, F. Omid, S. Bagheri, Modification of magnetized MCM-41 by pyridine groups for ultrasonic-assisted dispersive micro-solid-phase extraction of nickel ions, *Int. J. Environ. Sci. Technol.*, 16 (2019) 6431–6440.
- [32] A.H. Almertaha, M. Eftekhari, M. Chamsaz, M. Gheibi, Synthesize of silver-nanoparticles by plant extract and its application for preconcentration of cadmium followed by flame atomic absorption spectrometry, *Environ. Technol.*, 40 (2019) 1831–1839.
- [33] N.E. Sodan, A. Hol, O. Caylak, L. Elci, Use of Fe₃O₄ magnetic nanoparticles coated with polythiophene for simultaneous preconcentration of Cu(II), Co(II), Ni(II) and Zn(II) ions prior to their determination by MIS-FAAS, *Acta Chim. Slov.*, 67 (2020) 375–385.
- [34] I. Narin, M. Soylak, Enrichment and determinations of nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) ions in natural waters, table salts, tea and urine samples as pyrrolydine dithiocarbamate chelates by membrane filtration-flame atomic absorption spectrometry combination, *Anal. Chim. Acta*, 493 (2003) 205–212.
- [35] F. Shemirani, M.R. Jamali, R.R. Kozani, M. Salavati Niasari, Cloud point extraction and preconcentration for the determination of Cu and Ni in natural water by flame atomic absorption spectrometry, *Sep. Sci. Technol.*, 41 (2006) 3065–3077.
- [36] H. Xu, W. Zhang, X. Zhang, J. Wang, J. Wang, Simultaneous preconcentration of cobalt, nickel and copper in water samples by cloud point extraction method and their determination by flame atomic absorption spectrometry, *Procedia Environ. Sci.*, 18 (2013) 258–263.
- [37] R. Galbeiro, S. Garcia, I. Gaubeur, A green and efficient procedure for the preconcentration and determination of cadmium, nickel and zinc from freshwater, hemodialysis solutions and tuna fish samples by cloud point extraction and flame atomic absorption spectrometry, *J. Trace Elem. Med. Biol.*, 28 (2014) 160–165.

- [38] A.A. Gouda, R. El Sheikh, A.S. Amin, Application of cloud point extraction for separation of iron in water, food and environmental samples prior to determination by spectrophotometry, *Anal. Chem. Lett.*, 6 (2016) 296–312.
- [39] S. Saracoglu, M. Soylak, D.S.K. Peker, L. Elci, W.N.L. dos Santos, V.A. Lemos, S.L.C. Ferreira, A preconcentration procedure using coprecipitation for determination of lead and iron in several samples using flame atomic absorption spectrometry, *Anal. Chim. Acta*, 575 (2006) 133–137.
- [40] D. Fang, X. Liu, R. Zhang, W. Deng, L. Zhou, Removal of contaminating metals from soil by sulfur-based bioleaching and biogenic sulfide-based precipitation, *Geomicrobiol. J.*, 30 (2013) 473–478.
- [41] M. Roushani, Y.M. Baghelani, S. Abbasi, S.Z. Mohammadi, M. Zahedifar, M. Mavaei, Separation of Ag(I) ions from *Lepidium draba* L. plant and water and standard samples by carrier element-free coprecipitation method prior to their flame atomic absorption spectrometric determination, *Commun. Soil Sci. Plant Anal.*, 47 (2016) 1207–1215.
- [42] A.H. Sulaymon, A.A.H. Faisal, O.M. Khaliefa, Simultaneous adsorption-precipitation characterization as mechanisms for metals removal from aqueous solutions by cement kiln dust (CKD), *Desal. Water Treat.*, 57 (2016) 819–826.
- [43] E. Begu, B. Snell, Z. Arslan, Simultaneous separation of arsenic and cadmium from interfering salt matrix of multivitamin/mineral supplements by sequential coprecipitation and determination by inductively coupled plasma mass spectrometry, *Microchem. J.*, 145 (2019) 412–418.
- [44] W. Yoshimura, A. Uzawa, X.D. Liu, Determination of trace amounts of bismuth in natural water by means of coprecipitation with zirconium hydroxide and differential pulse anodic stripping voltametry, *Bunseki Kagaku*, 44 (1995) 1071–1076.
- [45] U. Joichi, M. Minami Tomoharu, Coprecipitation of trace metal ions with scandium hydroxide for graphite furnace atomic absorption spectrometry, *Chem. Lett.*, 17 (1997) 681–682.
- [46] S. Saracoglu, M. Soylak, L. Elci, Enrichment and separation of traces of cadmium, chromium, lead, manganese ions in urine by using magnesium hydroxide coprecipitation method, *Trace Elem. Electrolytes*, 18 (2001) 129–133.
- [47] S. Saracoglu, M. Soylak, L. Elci, Separation/preconcentration of trace heavy metals in urine, sediment and dialysis concentrates by coprecipitation with samarium hydroxide for atomic absorption spectrometry, *Talanta*, 59 (2003) 287–293.
- [48] M. Soylak, S. Saracoglu, U. Divrikli, L. Elci, Coprecipitation of heavy metals with erbium hydroxide for their flame atomic absorption spectrometric determinations in environmental samples, *Talanta*, 66 (2005) 1098–1102.
- [49] M. Soylak, G. Onal, Determination of trace metals by atomic absorption spectrometry after coprecipitation with europium hydroxide, *J. Hazard. Mater.*, 137 (2006) 1130–1134.
- [50] M. Tuzen, K.O. Kaygi, M. Soylak, Separation and speciation of selenium in food and water samples by the combination of magnesium hydroxide coprecipitation-graphite furnace atomic absorption spectrometric determination, *Talanta*, 71 (2007) 424–429.
- [51] D.S.K. Peker, O. Turkoglu, M. Soylak, Dysprosium(III) hydroxide coprecipitation system for the separation and preconcentration of heavy metal contents of table salts and natural waters, *J. Hazard. Mater.*, 143 (2007) 555–560.
- [52] U. Divrikli, M. Soylak, L. Elci, Determination of total chromium by flame atomic absorption spectrometry after coprecipitation by cerium(IV) hydroxide, *Environ. Monit. Assess.*, 138 (2008) 167–172.
- [53] M. Tuzen, D. Citak, D. Mendil, M. Soylak, Arsenic speciation in natural water samples by coprecipitation-hydride generation atomic absorption spectrometry combination, *Talanta*, 78 (2009) 52–56.
- [54] S. Saracoglu, M. Soylak, D. Cabuk, Z. Topalak, Y. Karagozlu, Determination of some trace elements in food and soil samples by atomic absorption spectrometry after coprecipitation with holmium hydroxide, *J. AOAC Int.*, 95 (2012) 892–896.
- [55] M. Soylak, A. Aydin, Speciation of Cr(III) and Cr(VI) in environmental samples by using coprecipitation with praseodymium(III) hydroxide and determination by flame atomic absorption spectrometry, *J. Iran. Chem. Soc.*, 9 (2012) 263–267.
- [56] M. Soylak, I. Murat, A new coprecipitation methodology with lutetium hydroxide for preconcentration of heavy metal ions in herbal plant samples, *J. AOAC Int.*, 97 (2014) 1189–1194.
- [57] E. Soriano, A. Pastor, M. de la Guardia, Multielemental determination of trace mineral elements in seawater by dynamic reaction cell inductively coupled plasma-mass spectrometry after Al(OH)₃ coprecipitation, *Microchem. J.*, 157 (2020) 104864, doi: 10.1016/j.microc.2020.104864.
- [58] H. Yoshikawa, K. Isobe, H. Iwata, N. Benitani, K. Saito, H. Seno, Determination of trace metals in vanadium metal and vanadium-aluminium alloy by ICP-AES after bismuth hydroxide coprecipitation separation, *Bunseki Kagaku*, 38 (1989) 535–537.
- [59] A. Mizuike, M. Hiraide, T. Kanematsu, Coprecipitation and flotation of traces of lead and iron(III) ions with bismuth hydroxide, *Bunseki Kagaku*, 26 (1977) 137–138.
- [60] F. Ishino, M. Munemori, Coprecipitation of mercury(II) with bismuth(III) hydroxide, *Nippon Kagaku Kaishi*, 9 (1985) 1710–1714.
- [61] S. Denmark, E. Begu, Z. Arslan, F.X. Han, J.M. Seiter-Moser, E.M. Pierce, Removal of inorganic mercury by selective extraction and coprecipitation for determination of methylmercury in mercury contaminated soils by chemical vapor generation inductively coupled plasma mass spectrometry (CVG-ICP-MS), *Anal. Chim. Acta*, 1041 (2018) 68–77.
- [62] J.A. Baig, A. Hol, A. Akdogan, A.A. Kartal, U. Divrikli, T.G. Kazi, L. Elci, A novel strategy for chromium speciation at ultra-trace level by microsample injection flame atomic absorption spectrophotometry, *J. Anal. At. Spectrom.*, 27 (2012) 1509–1517.