



Preconcentration procedure using in situ solvent formation microextraction in the presence of ionic liquid for cadmium determination in saline samples by flame atomic absorption spectrometry

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ABSTRACT

A simple in situ solvent formation microextraction methodology based on the application of ionic liquid (IL) as an extractant solvent and sodium hexafluorophosphate (NaPF_6) as an ion-pairing agent was proposed for the preconcentration of trace levels of cadmium. In this method cadmium was complexed with *O,O*-diethyldithiophosphate (DDTP) and extracted into an ionic liquid phase. After phase separation, the enriched analyte in the final solution is determined by flame atomic absorption spectrometry (FAAS). ISFME is a simple and rapid method for extraction and preconcentration of metal ions from sample solutions containing a high concentration of salt. Some effective factors that influence the microextraction efficiency were investigated and optimized. Under the optimum experimental conditions, the limit of detection (3 s) and the enhancement factor were $0.07 \mu\text{g L}^{-1}$ and 78, respectively. The relative standard deviation (R.S.D.) was obtained 2.42%. The accuracy of the method was confirmed by analyzing certified reference materials for trace elements in seawater (GBW (E) 080040 seawater). The proposed method was successfully applied for the determination of cadmium in water samples and food grade salts.

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1. Introduction

Environmental pollution nature of heavy metals has recently received considerable attention. The toxic effect of cadmium on human health has been known since 1969 [1]. The International Agency for Research on Cancer classified cadmium as a human carcinogen [2]. Cadmium is highly toxic even at low concentrations, causing damages to organs such as the kidneys, liver, and lungs [3]. The FAO/WHO Joint Expert Committee on Food Additives recommended provisional maximum tolerable daily intake of cadmium from all sources (water, food and air) of $1.0\text{--}1.2 \mu\text{g kg}^{-1}$ body mass [4]. Also, the United States Environmental Protection Agency (EPA) has set a limit of $5 \mu\text{g L}^{-1}$ for cadmium in drinking water [5]. For humans, the main sources of cadmium are from water and food. Therefore, sensitive, reproducible and accurate analytical methods are required for the determination of trace amount of cadmium in such samples.

Different analytical techniques have been reported to determine cadmium ions in various samples including flame atomic absorption spectrometry (FAAS) [6–8], graphite furnace atomic absorption spectrometry (GFAAS) [9,10], inductively coupled plasma optical emission spectrometry (ICP OES) [11,12], inductively coupled

plasma mass spectrometry (ICP-MS) [13], neutron activation analysis (NAA) [14], anodic stripping voltammetry [15,16], differential pulse stripping voltammetry [17], ion chromatography [18], electrochemiluminescence [19] and molecular absorption spectrophotometry [20,21]. From the analytical tools above listed, flame atomic absorption spectrometry is widely used because of low costs, operational facility and high sample throughput [22]. However, conventional FAAS has a detection limit that is not low enough to determine cadmium at trace levels in several types of matrix. Thus, preconcentration and separation steps are needed prior to analyte determination by flame atomic absorption spectrometry.

Several procedures such as coprecipitation [23,24], liquid–liquid extraction (LLE) [25–27], cloud-point extraction [28,29], solid-phase extraction (SPE) [30–36] and dispersive liquid–liquid microextraction [37] have been developed for the separation and preconcentration of cadmium from different matrices.

However, these methods often require large amounts of organic solvents, some of which are harmful and contaminate the environment due to their high vapor pressure. Recently, room temperature ionic liquids (RTILs) with unique properties such as negligible vapor pressure, water stability, favorable viscosity and density characteristics, good thermal stability, non-volatility and good selective solubility have been used as alternative solvents in separation [38]. Several extraction methods have been reported based on ionic liquids, such as cold induced aggregation microextraction (CIAME) [39], ionic liquid-based headspace liquid phase microextraction

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[40], ionic liquid-based single-drop microextraction [41,42] and dispersive liquid–liquid microextraction based on ionic liquid [43].

In situ solvent formation microextraction (ISFME) was proposed by authors in 2009, which is based on ionic liquids for the extraction of metal ions [44]. The main advantage of ISFME is its compatibility with high content of salt (40%, w/v). Thus, this method can be used for the extraction of cadmium in saline samples. The method is simple and fast so that the overall time of extraction and determination for each sample is about 6 min.

2. Experimental

2.1. Instrumentation

A Varian model AA-400 atomic absorption spectrometer, equipped with a deuterium lamp background and with cadmium hollow cathode lamp was used for the determination of cadmium. The lamp was operated at 4 mA, using the wavelength at 228.8 nm, slit of 0.5 nm, burner height of 8 mm and acetylene gas flow rate of 1.5 L min⁻¹. All measurements were carried out in peak area mode (measurement time of 5 s). A Universal 320R centrifuge equipped with a swing out rotor (12-place, 5000 rpm, Cat. No. 1628A) was obtained from Hettich (Kirchlengern, Germany). A Metrohm digital pH-meter (model 692, Herisau, Switzerland), equipped with a glass-combination electrode was used for pH adjustment.

2.2. Reagents

All chemicals used in this work were of analytical grade of Merck (Darmstadt, Germany) except sodium hexafluorophosphate (NaPF₆) that was purchased from ACROS (Geel, Belgium). All aqueous solutions were prepared in double-distilled deionized water. Working standard solutions were obtained by appropriate step-wise dilution of the stock standard solution (1000 mg L⁻¹ solution of cadmium in 0.5 mol L⁻¹ nitric acid). The viscosity of ILs is high and their handling is difficult, so working solutions 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF₄], 0.6 mg μL⁻¹, prepared in ethanol. A solution of 120 mg mL⁻¹ NaPF₆ was prepared by dissolving an appropriate amount of NaPF₆ in doubly distilled water. A solution of DDTP (0.1 mol L⁻¹) was prepared by dissolving an appropriate amount of this reagent in ethanol and diluting to 50 mL with distilled water and was kept in a refrigerator (≤0 °C).

2.3. Preparation of table salt

Twenty-five grams of table salt was dissolved in doubly distilled water and diluted to 100 mL. The obtained solution was filtered using a 0.45 μm pore-size membrane filter to remove suspended particulate matter. Aliquots of 5 mL sample solution were used for the analysis.

2.4. Preparation of sodium nitrate and sodium acetate

Sodium nitrate and sodium acetate solutions were prepared by dissolving 40 g of each salt in 100 mL of double-distilled deionized water individually. Afterwards, the samples were filtered through a Millipore 0.45 μm pore-size membrane to remove suspended particular matter. The amount of cadmium in 5.0 mL of sample solutions was determined by following procedure described in Section 2.5.

2.5. ISFME procedure

For this procedure, aliquots of 5 mL solution containing Cd(II), O,O-diethyldithiophosphate (0.05 mol L⁻¹), [Hmim][BF₄] (30 mg), were transferred to a 5 mL conical-bottom glass centrifuge tube.

Table 1
Operating conditions for cadmium determination.

Parameters	
FAAS conditions	
Wavelength (nm)	228.8
Lamp current (mA)	4
Spectral band width (nm)	0.5
Acetylene flow rate (L min ⁻¹)	1.5
Air flow rate (L min ⁻¹)	3.5
Measurement mode	Peak area
Measurement time (s)	5
Microextraction conditions	
Working pH	2
Cd ²⁺ concentration (μg L ⁻¹)	20
Concentration of DDTP (mol L ⁻¹)	0.03
Amount of [Hmim][BF ₄] (μL)	60
Amount of NaPF ₆ (mL)	0.5
Centrifugation time (min)	5

After shaking, 1.0 mL NaPF₆ (120 mg mL⁻¹) was added to the solution and a cloudy solution was formed immediately. Then, the mixture was centrifuged for 5 min at 5000 rpm. As a result, the fine droplets of IL settled at the bottom of the centrifuge tube (about 8 μL). The bulk aqueous phase was removed by a pipette. Afterwards, the IL-phase was dissolved in 50 μL of ethanol solution and it was aspirated to flame atomic absorption spectrometer by a microsyringe. Peak area was measured as the absorbance signal during measurement time of 5 s. The optimized conditions are listed in Table 1.

3. Results and discussion

To attain higher sensitivity, selectivity and precision for metal determination with the ISFME method, the effect of main parameters, such as pH, amounts of IL and NaPF₆, concentration of DDTP, salt concentration, centrifugation conditions and interfering ions were studied and optimized thoroughly.

3.1. Selection of diluting agents

Diluting agent must dissolve the IL and complex, completely. Acetone, methanol and ethanol were examined in this work. In the presence of acetone and methanol, maximum absorbance was obtained. But, the IL-phase could not be dissolved in 50 μL methanol and acetone, completely. In the presence of ethanol, sample was clear and good absorbance was acquired. Therefore, ethanol was chosen as the diluting agent.

3.2. Effect of pH

The formation of metal complex and its chemical stability are the two important influence factors for the extraction of metal ions, and the pH plays a unique role on metal-chelate formation and subsequent extraction. The O,O-diethyldithiophosphate (DDTP) forms stable complexes with several transition metals and semi-metals in acidic media [45–47], but does not react with alkaline and alkaline earth elements.

The effect of pH on the extraction of Cd ions from the solution was studied in the range of 1.0–9.0. According to the obtained results, the absorbance was relatively constant in the pH range of 1.5–4.0. Thus, a pH value of 2.0 was chosen for further experiments. This optimum pH value enables the use of the method directly in many aqueous samples after common acid preservation.

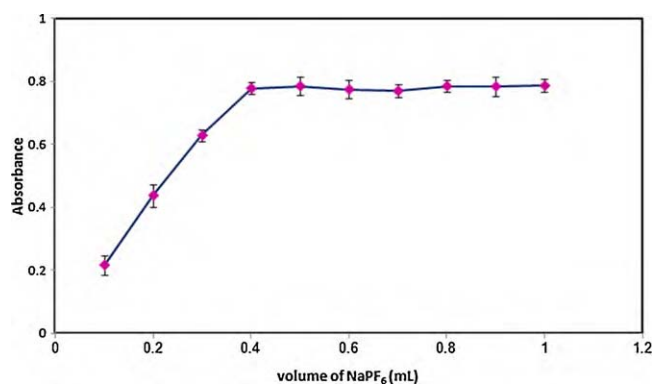


Fig. 1. Effect of NaPF₆ value on the absorbance of the complex. Conditions: cadmium 20 μg L⁻¹, DDTP 3.0 × 10⁻² mol L⁻¹, pH 2, [Hmim][BF₄] 50 μL of 0.6 mg μL⁻¹, diluting agent 50 μL.

3.3. Effect of DDTP concentration

The effect of DDTP on the absorbance of complex was studied in the range of 0–0.05 mol L⁻¹. The absorbance increased by increasing the DDTP concentration up to 0.01 mol L⁻¹ of DDTP and then remained constant. Therefore, a concentration of 0.03 mol L⁻¹ was chosen as the optimum concentration.

3.4. Effect of NaPF₆ and [Hmim][BF₄]

In order to decrease the solubility of IL-phase in brines, NaPF₆ was added to the sample solutions as an ion-pairing agent. As a consequence of reaction between the water-miscible IL and the ion-pairing agent, a water-immiscible IL with very low solubility must be formed. Ion-pairing agent must have no interference in extraction system. The solubility of IL decreases according to common ion effect, so phase separation can occur successfully. Effect of NaPF₆ was investigated in the range of 0.1–1.0 mL (120 mg mL⁻¹) in the presence of 30 mg [Hmim][BF₄] and the results are shown in Fig. 1. By adding NaPF₆, [Hmim][PF₆] was formed and according to common ion effect by increasing the amount of NaPF₆, the solubility of [Hmim][PF₆] decreased, so the absorbance increased. Thus, 0.5 mL NaPF₆ was chosen for the subsequent experiments.

The amount of [Hmim][BF₄] that is used in this preconcentration procedure is a critical factor to obtain high recovery. Therefore, the extraction system was carefully studied in order to define the lowest IL-phase volume necessary for achieving the highest recovery. Effect of [Hmim][BF₄] was studied in the range of 10–100 μL in the presence of 0.5 mL NaPF₆. As can be seen in Fig. 2, by increasing the amount of [Hmim][BF₄], the absorbance increased and then

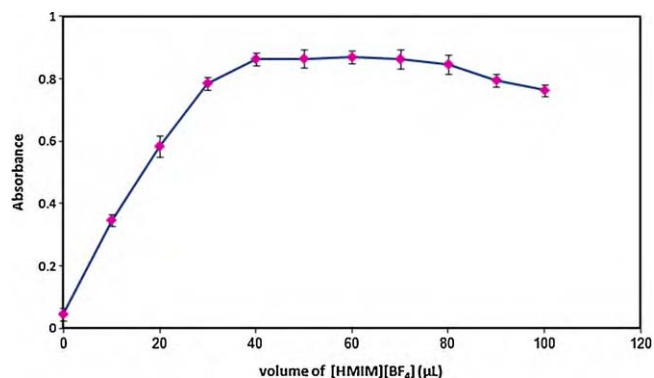


Fig. 2. Effect of [Hmim][BF₄] value on the absorbance of the complex. Conditions: cadmium 20 μg L⁻¹, DDTP 3.0 × 10⁻² mol L⁻¹, pH 2, NaPF₆ 0.5 mL of 120 mg mL⁻¹, diluting agent 50 μL.

decreased due to increase in the volume of the settled phase. Thus, 60 μL [Hmim][BF₄] was chosen for the subsequent experiments.

3.5. Effect of salt concentration

To investigate the influence of salt concentration on microextraction performance, various experiments were performed by adding different amounts of NaNO₃ (0.0–50.0%, w/v). As it is shown in Fig. 3, the addition of NaNO₃ up to 40% (w/v) has no considerable effect on the absorbance. At the higher salt content, the density of solution became higher than that of IL, so the extractant phase did not settle. Therefore, ISFME is a powerful sample preparation technique for saline solutions (up to 40%, w/v).

3.6. Effect of centrifuge conditions

The effect of centrifugation rate on the absorbance was studied in the range of 1000–5000 rpm. It was found that over 3500 rpm, IL-phase completely settled, so the rate of 5000 rpm was selected as the optimum point. At the optimum rate, absorbance was investigated as a function of centrifugation time. Over 4 min, the absorbance was constant indicating complete transfer of IL-phase to the bottom of centrifugation tube. Therefore, the optimum centrifugation time was chosen as 5 min. If the temperature of sample increases during centrifuging, some of the IL-phase may be dissolved and therefore the absorbance will decrease. So, it is necessary to investigate the effect of centrifugation temperature. Centrifugation temperature was studied at the range of 0–30 °C. It was found that centrifugation temperature in this range has no effect on the extraction process.

3.7. Effect of extraction time and temperature

Optimal equilibration temperature and equilibration time are necessary to complete reactions, and to achieve phase separation and preconcentration efficiently. Therefore, the effect of the equilibration temperature was investigated from 0 to 60 °C. It was found that the increase of temperature has no considerable effect upon the absorbance and analytical signal but, in the high temperatures a cloudy solution cannot be form immediately and it is necessary to cool the solution. Thus, room temperature was used as an equilibration temperature in the extraction process. At the room temperature, the influence of equilibration time on the absorbance was studied within a range of 0–20 min. It was observed that the equilibration time before centrifugation has no significant effect upon the absorbance. So, in order to keep analysis time as short as possible, the cloudy solu-

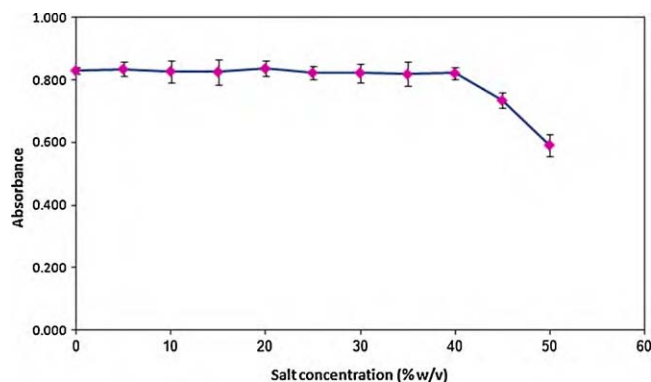


Fig. 3. Effect of salt concentration on the absorbance of the complex. Conditions: cadmium 20 μg L⁻¹, DDTP 3.0 × 10⁻² mol L⁻¹, pH 2, [Hmim][BF₄] 60 μL of 0.6 mg μL⁻¹, NaPF₆ 0.5 mL of 120 mg mL⁻¹, diluting agent 50 μL.

Table 2
Tolerance limits of interfering ions in the determination of 20 $\mu\text{g L}^{-1}$ Cd.

Ions	Foreign ion to cadmium ratio
Na ⁺	1,000,000
K ⁺	1,000,000
Mg ²⁺	100,000
Ba ²⁺	100,000
NO ₃ ⁻	100,000
Ca ²⁺	10,000
Mn ²⁺	1000
Al ³⁺	1000
Co ²⁺	1000
Pb ²⁺	1000
Hg ²⁺	1000
Zn ²⁺	1000
Cr ³⁺	1000
Ni ²⁺	1000
Fe ³⁺	1000
As ³⁺	1000
SO ₄ ²⁻	1000
Cl ⁻	1000
I ⁻	1000
V ³⁺	500
Pd ²⁺	500
Mo ⁶⁺	500
Cu ²⁺	100

tion was centrifuged immediately after the preparation at room temperature.

3.8. Effect of other ions

In order to demonstrate the selectivity of the developed microextraction system for the determination of cadmium, the effect of other ions was evaluated. The interferences were studied by analyzing 5 mL solution containing 20 $\mu\text{g L}^{-1}$ Cd²⁺ and other ions at different concentrations, according to the recommended extraction procedure. Table 2 shows the tolerance limits of the interfering ions. An ion was considered to interfere when its presence produced a variation of more than 5% in the absorbance of the analyte. Commonly encountered ions such as alkali and some alkaline earth elements do not form stable complexes with DDTP. However, Cu²⁺ interfered with the determination of Cd²⁺ in a maximum ratio of 100. This interference was eliminated using an excess of DDTP reagent in sample solutions or by masking it with a suitable reagent, such as thiourea.

Table 4
Determination of cadmium in real samples.

Sample	Cd ²⁺ added ^a ($\mu\text{g L}^{-1}$)	Cd ²⁺ found ^a ($\mu\text{g L}^{-1}$)	Recovery (%)
River water	–	0.78 ± 0.02	–
	5	5.95 ± 0.21	103.4
Seawater	–	2.53 ± 0.09	–
	5	7.46 ± 0.25	98.6
Mineral water	–	N.D ^b	–
	5	5.11 ± 0.23	102.2
	Cd ²⁺ added ^a (ng g ⁻¹)	Cd ²⁺ found ^a (ng g ⁻¹)	Recovery (%)
Sodium nitrate ^c	–	2.62 ± 0.07	–
	5	7.43 ± 0.18	97.5
Sodium acetate ^c	–	1.05 ± 0.03	–
	5	6.26 ± 0.20	104.2
Table salt ^c	–	0.60 ± 0.03	–
	5	5.79 ± 0.24	103.8

^a Mean and standard deviation of six determinations.

^b N.D: not detected.

^c From food grade.

Table 3
Analytical characteristics of the method.

Analytical parameters	
Slope	3.82 × 10 ⁻²
Intercept	0.031
Linear range ($\mu\text{g L}^{-1}$)	0.2–40.0
Correlation coefficient	0.9997
R.S.D. (%) ($n = 6$) ^a	2.42 (20)
LOD ($\mu\text{g L}^{-1}$) ^b	0.07
Enhancement factor ^c	78

^a Values in parentheses are the Cd²⁺ concentration (ng mL⁻¹) for which the R.S.D. was obtained.

^b Determined as $3S_B/m$ (where S_B and m are the standard deviation of the blank signal and the slope of the calibration graph, respectively).

^c Calculated as the slope ratio of the calibration graph for Cd²⁺ with and without preconcentration.

3.9. Figures of merit and analysis of samples

Under the optimum conditions, a calibration graph was obtained for cadmium by preconcentrating several solutions according to the procedure. Table 3 summarizes the analytical characteristics of the optimized method. The limit of detection, calculated as three times the standard deviation of the blank signal, was 0.07 $\mu\text{g L}^{-1}$ for the preconcentration of a 5 mL of sample solution. The limit of quantification (LOQ) is accepted that is usually equals about three times the LOD value. Therefore, LOQ value of Cd(II) was 0.21 $\mu\text{g L}^{-1}$. The calibration graph was linear over a dynamic range from 0.2 to 40 $\mu\text{g L}^{-1}$, with a correlation coefficient of 0.9997. The regression equation of the calibration graph was $A = 3.82 \times 10^{-2} C + 0.031$, where A is the absorbance and C is the concentration of Cd in $\mu\text{g L}^{-1}$. The relative standard deviation (R.S.D.) resulting from the analysis of solution containing 20 $\mu\text{g L}^{-1}$ Cd²⁺ was 2.42% ($n = 6$). Enhancement factor (EF = 78) was obtained from the slope ratio of calibration curve with and without preconcentration. Whereas, the accuracy of the proposed methodology was evaluated by analyzing a certified reference material (CRM), GBW (E) 080040 seawater, with a Cd²⁺ content of $1.00 \pm 0.06 \mu\text{g L}^{-1}$. Using the proposed method in this work, the Cd²⁺ content found in the CRM was $1.04 \pm 0.05 \mu\text{g L}^{-1}$ (means ± S.D., $n = 6$). The results were compared with the certified value using a t -test at 95% confidence limits. A good agreement was obtained between the estimated content by the proposed method and the certified value.

Table 5

Characteristic performance data using ISFME and other preconcentration techniques for the determination of cadmium in water samples by FAAS.

Preconcentration method	Salt concentration % (w/v)	LOD ^a ($\mu\text{g L}^{-1}$)	EF	Sample volume (mL)	R.S.D. ^b (%)	Reference
SPE ^c	1	0.25	50	10	5.1	[50]
SPE ^c	8.5	0.093	200	100	3.7	[51]
CPE ^c	1	0.9	–	8	4	[28]
CPE ^c	–	1.0	14.7	10	0.8–3	[52]
SFODME ^c	–	0.0079	635	160	5.4	[53]
USAEME ^c	5	0.91	13.4	8	2.56, 1.62	[54]
HFRLM ^c	Saturated $(\text{NH}_4)_2\text{SO}_4$	1.3	120	20	5.5	[55]
ISFME	40	0.07	78	5	2.4	This work

^a Limit of detection.^b Relative standard deviation.^c SPE: solid-phase extraction; CPE: cloud-point extraction; SFODME: solidification of floating organic drop microextraction, USAEME: ultrasound-assisted emulsification–microextraction, HFRLM: hollow fiber renewal liquid membrane.

The method was applied for the determination of cadmium in saline samples including water samples (seawater, spring water and river water) and food additives (table salt, sodium nitrate and sodium acetate [48,49]) and the results are shown in Table 4. As it can be seen, the cadmium concentration ranges are from below the limit of detection to $2.53 \mu\text{g L}^{-1}$ for the water samples and $0.60\text{--}2.62 \text{ ng g}^{-1}$ for the food additives. The relative cadmium recoveries from these samples at the spiked values were in the range of 97.5–104.2%. The results indicate that the proposed method can be reliably used for the determination of cadmium in saline matrices.

The presented method was compared with the other preconcentration methods used for the determination of cadmium by FAAS [28,50–55] and the results are shown in Table 5. As it can be seen, ISFME shows a comparatively low detection limit. Furthermore, this method is robust against a very high content of salt in comparison with other methods. In addition, the ISFME is free of volatile organic solvent using the ionic liquid as the green extraction solvent. These characteristics are of key interest for laboratories doing routine trace metal ion analysis.

4. Conclusions

The in situ solvent formation microextraction (ISFME) technique was successfully used for the preconcentration of trace amount of cadmium in saline samples. $[\text{HMIM}][\text{BF}_4]$ was chosen as a green medium and an alternative to traditional volatile organic solvents for this extraction system. Determination was carried out by flame atomic absorption spectrometry. DDTP, used as complexing agent, is stable in acidic medium, which is of advantage because samples are prepared and preserved at low pH values, thus facilitating the preconcentration steps. The relative standard deviation, detection limit and the duration time of this procedure are also satisfactory. This method is simple, rapid, safe and robust against very high content of salt (up to 40%). Therefore, ISFME is a powerful sample preparation technique for saline solutions and salt products used in food and pharmacological industries. The preconcentration method was successfully applied to the cadmium determination in water samples and food grade salts, with good accuracy and reproducibility. Furthermore, the accuracy of the method was confirmed by analyzing certified reference materials for trace elements in water (GBW (E) 080040 seawater).

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