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Preconcentration via ion associated complexes combined with inductively coupled plasma optical emission spectrometry for determination of heavy metals

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ABSTRACT

A method of separation and preconcentration of cadmium, cobalt, copper, nickel, lead and zinc at trace level from plant matrix using 2,2′-bipyridyl and rose Bengal is proposed. The above heavy metals were determined after preconcentration by inductively coupled plasma optical emission spectrometry (ICP-OES). The results were compared with those obtained using flame atomic absorption spectrometry (F-AAS). The influence of several parameters such as pH, molar ratio of 2,2′-bipyridyl to rose Bengal, duration of co-precipitation was examined. Moreover, effects of inorganic matrix on recovery of the determined elements were studied. The detection limits (DL) for ICP-OES were 0.36, 0.66, 3.3, 1.4, 3.5 and 3.2 μg L^{-1} for Cd, Co, Cu, Ni, Pb and Zn, respectively, whereas for F-AAS DL were 0.77, 5.8, 1.1, 3.2, 3.0 and 0.71 μg L^{-1}. The recovery of the method for the determined elements was better than 94% with relative standard deviation between 0.68% and 1.7%. The preconcentration factor was 40. The proposed method was applied for determination of Cd, Co, Cu, Ni, Pb, and Zn in plant materials. Accuracy of the proposed method was verified using certified reference material (NCS ZC85006 Tomato).

1. Introduction

Preconcentration–separation methods including chemical methods such as solid phase extraction [1–3], cloud point extraction [4–6], membrane filtration [7], liquid–liquid extraction [8], and physical method such as evaporation [9] have been widely used for preconcentration and separation of heavy metal ions from various matrices.

Co-precipitation has also an important place among preconcentration and separation methods, because it is a simple and non-time consuming procedure. Various carriers including copper [10], aluminum [11], erbium [12], europium [13], gadolinium [14], indium [15], samarium [16], cerium [17], lanthanum [18–20] have been used for preconcentration and separation of heavy metal ions at trace levels. Inorganic ligands, such as hydroxide ion [21], and organic ligands [22–25] like rubeanic acid, dithiocarbamates, mercaptobenzothiazole etc. have been used for this purpose.

Ionic associations are also used as organic carriers. Ionic associations can be formed in the following system: a cationic chelate metal complex – an anion of a non-chelating organic dye. They form sparingly soluble precipitations. These precipitates are insoluble in acids and well soluble in hydroxide solutions and in organic solvents. Till now, formation of ionic associates of metal–heterocyclic base–xanthene acidic dye type was used mainly for development of sensitive extraction-spectrophotometric methods for single element determination [26] and spectrofluorimetric methods [27]. In this work, the insoluble precipitates of ionic associations were applied to group separation and preconcentration of Cd, Co, Cu, Ni, Pb, and Zn. Analytes were co-precipitated with ionic associate La–2,2-bipyridyl–rose Bengal as a carrier. The developed method was applied in determination of heavy metals in plant material by inductively coupled plasma optical emission spectrometry (ICP-OES) and flame atomic absorption spectrometry (F-AAS). White and red cabbage, and potatoes were selected for the analysis. Accuracy of the developed method was tested using certified reference material NCS ZC85006 Tomato.

2. Experimental

2.1. Apparatus

An optical emission spectrometer, ICP Model M (Spectro Analytical Instruments, Germany) was used for determination of Cd, Co, Cu, Ni, Pb, and Zn. The sequential spectrometer was used with the following parameters: frequency, 27.12 MHz; power, 1.1 kW; demountable quartz torch, Ar/Ar/Ar; coolant gas Ar, 14.0 L min^{-1}; auxiliary gas Ar, 0.5 L min^{-1}; nebulizer gas Ar, 1.0 L min^{-1}; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott, sample flow rate, 1.0 mL min^{-1}; observation height 11 mm; holographic grating, 2400 grooves mm^{-1}; dispersion of grating in

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the first reciprocal order, 0.55 nm mm^{-1}; wavelength range of monochromator 165–460 nm. The wavelengths (integration time) were 228.80 nm (3 s), 228.62 nm (4 s), 324.75 nm (3 s), 221.65 nm (5 s), 220.35 nm (5 s), 213.87 (4 s) for Cd, Co, Cu, Ni, Pb, and Zn, respectively.

A flame atomic absorption spectrometer (Solaar M6 TJA Solutions) with deuterium arc background correction, equipped with a hollow cathode lamp was used for determination of Cd, Co, Cu, Ni, Pb, and Zn. An air–acetylene burner was used. The wavelengths (spectral band pass) were 228.8 nm (0.5 nm), 240.6 nm (0.2 nm), 324.8 nm (0.5 nm), 232.0 nm (0.1 nm), 217.0 nm (0.5 nm), 213.9 nm (0.5 nm) for Cd, Co, Cu, Ni, Pb, and Zn, respectively. The nebulizer flow rate was 5.0 mL min^{-1}.

2.2. Reagents and solutions

All chemicals were of analytical reagent grade. All reagents were dissolved and diluted with high purity water obtained from Milli-Q system. The following reagents were used in the experiment: 2,2′-bipyridyl (POCh, Gliwice, Poland), rose Bengal–disodium salt of tetrachlorotetraiodofluoresceine (Serva, Heidelberg, Germany), lanthanum(III) nitrate(V) (Loba Feinchemie, Fischamend, Austria), nitric acid, hydrochloric acid, sodium hydroxide, ammonia, nitrates(V) of sodium, potassium, magnesium, calcium, strontium, barium, aluminum, iron(III), manganese (all from POCh, Gliwice, Poland), stock standard solutions of cadmium, cobalt, copper, nickel, lead, and zinc at a concentration of 1000 mg L^{-1} (Merck, Darmstadt, Germany). Sodium acetate buffer solution was prepared by adding an appropriate amount of acetic acid to sodium acetate solution until pH 4 was obtained. The accuracy of the method was assessed by analyzing the certified reference material (CRM): NCS ZC85006 Tomato (China National Analysis Center for Iron & Steel 2000).

2.3. Procedures

2.3.1. General procedure of co-precipitation

0.2 mg of lanthanum(III), 5 mL of 0.01 mol L^{-1} solutions of 2,2′-bipyridyl and 5 mL of 0.01 mol L^{-1} solutions of rose Bengal were added to 100 mL of a solution containing 2 μg of Cd and Co, 10 μg of Pb and Ni, and 20 μg of Cu and Zn. The pH value of the obtained solution was adjusted to 4 using the acetate buffer. Then, the solution was heated in a water bath for 20 min in the temperature of 60 °C. Precipitate formed under these conditions was then centrifuged and the solution was decanted. Precipitate was digested in 1 mL of 0.2 mol L^{-1} solution of sodium hydroxide for ICP-OES measurement or in 1 mL of ammonia solution (1 + 1) for F-AAS measurement. The solution was diluted to 5 mL with water (final volume) and analyzed.

The calibration samples were prepared using 100 mL of standard solution containing analytes in the ranges: 0.2–4 μg of Cd and Co, 1–20 μg of Ni and Pb, 2–40 μg of Cu and Zn. The standard solutions were prepared using co-precipitation procedure described above.

2.3.2. Preparation of the plant material

Potatoes and white and red cabbage were selected for the analysis. The analyzed material was cleaned, broken up and dried in a laboratory drier at the temperature of 45 °C. Dried cabbage leaves and potato bulbs were ground in a high-speed rotor mill (Fritsch, Germany), in order to obtain a homogeneous sample with grain diameter of 1 mm. The plant material was stored in labeled, tightly sealed polyethylene containers.

The plant material was mineralized in the following way: 1 g of the sample was digested in 10 mL of concentrated nitric acid using a microwave pressure mineralizer. The following program was applied: step 1 (time: 3 min, power: 60%), step 2 (time: 5 min, power: 80%) and step 3 (time: 7 min, power: 100%). Then, the obtained solution was diluted to a volume of about 50 mL. Next, the sample was prepared using the co-precipitation procedure. The same procedure was used for the blank solutions.

In the case of certified reference material (NCS ZC85006 Tomato), 0.5 g of the sample was digested in 6 mL of concentrated nitric acid using a microwave pressure mineralizer and the program described above.

3. Results and discussion

The method developed for preconcentration of cadmium, cobalt, copper, nickel, lead, and zinc is based on reactions of ionic associates formation. The mechanism of traces concentration is as follows:

- The metal cation reacts with a heterocyclic base, forming a chelate complex with positive charge:

$$M^{2+} + n\text{bip} \rightarrow [M(\text{bip})_n]^{2+}$$

- The complex formed is coupled with an anion of xanthene dye, which results in formation of a new ionic associate:

$$[M(\text{bip})_n]^{2+} + \text{RB}^{2-} \rightarrow [M(\text{bip})_n]\text{RB}$$

- In the presence of lanthanum(III), an excess of the heterocyclic base and an excess of the acidic dye form a precipitate of an ionic associate performing as a carrier:

$$2\text{La}^{3+} + 2n\text{bip}_{\text{excess}} + 3\text{RB}^{2-}_{\text{excess}} \rightarrow [\text{La}(\text{bip})_n]_2\text{RB}_3\downarrow$$

- Ionic associates containing traces of heavy metals co-precipitated with the precipitate formed according to surface adsorption mechanism:

$$[M(\text{bip})_n]\text{RB} + [\text{La}(\text{bip})_n]_2\text{RB}_3\downarrow \rightarrow$$

$$\{[M(\text{bip})_n]\text{RB} + [\text{La}(\text{bip})_n]_2\text{RB}_3\}\downarrow$$

where M^{2+} – Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}; bip – 2,2′-bipyridyl; RB – rose Bengal.

3.1. Optimization of operating conditions

3.1.1. Precipitation

The La–2,2′-bipyridyl–rose Bengal ionic associate precipitates in acidified solution. Influence of pH in the range from 2 to 7 on the recovery of the determined elements was examined. Fig. 1

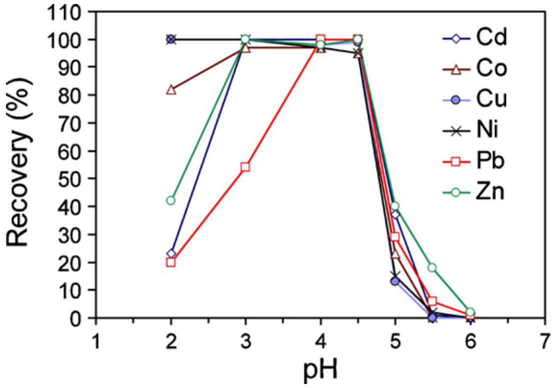

Fig. 1. Effect of pH on the quantitative co-precipitation of the elements studied.

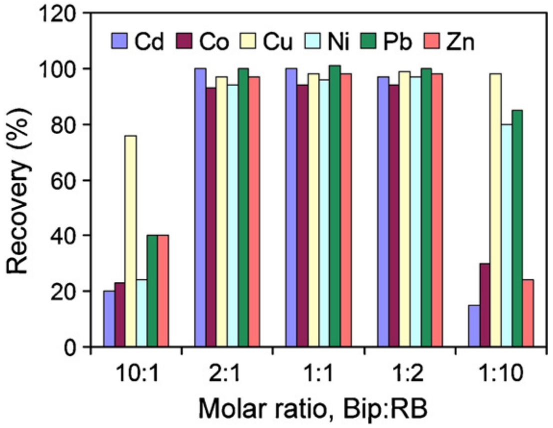

Fig. 2. Effect of 2,2′-bipyridyl to rose Bengal molar ratios on the quantitative co-precipitation of the elements studied.

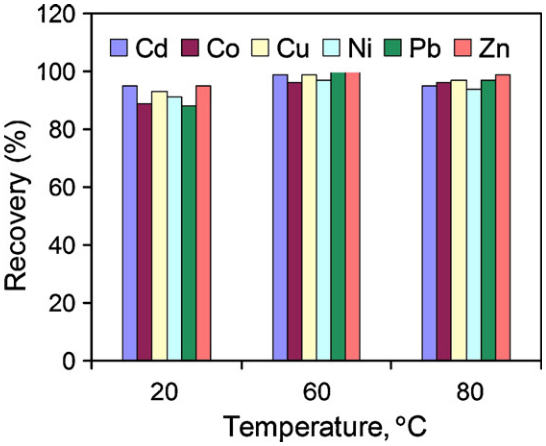

Fig. 3. Effect of temperature on the quantitative co-precipitation of the elements studied.

shows the effect of pH on co-precipitation of cadmium, cobalt, copper, nickel, lead, and zinc. For pH higher than 4.5, the recoveries decrease rapidly. The best recovery was observed at pH 3–4.5 for all studied elements, except for lead. The best recovery for lead was observed at pH 4–4.5. Hence, pH at 4 was chosen for these analytes.

An optimum molar ratio of 2,2′-bipyridyl to rose Bengal was determined. The following molar ratios of 2,2′-bipyridyl to rose Bengal were examined: 10:1; 2:1; 1:1; 1:2; 1:10. The results are shown in Fig. 2. The best recoveries for all determined elements were observed at the following molar ratios: 2:1; 1:1; 1:2. In next experiments, molar ratio of 1:1 was selected.

The influence of duration of the co-precipitate's ageing on the recoveries of the analytes was studied in the range from 10 to 120 min. Quantitative recoveries for all analytes were obtained in the whole examined time range. Therefore, the studies were performed at duration of 20 min.

The effect of temperature of co-precipitation on the recoveries of the analytes was studies in the range of 20–80 °C. The results are shown in Fig. 3. The highest recoveries, exceeding 90%, were obtained for temperatures of 60 and 80 °C. In the next experiments, temperature of 60 °C was selected.

The influence of amount of lanthanum(III) as a carrier element on the recoveries of the analyte ions was examined in the range of 0.1–0.5 mg. Quantitative recoveries of metal ions were obtained for the lanthanum(III) amounts ranging from 0.2 to 1.0 mg. All further works were carried out using 0.2 mg of lanthanum(III) as the carrier element.

The influence of the sample volume on the recoveries of the analytes was investigated in the range from 25 to 500 mL. The analytes were quantitatively (95%) recovered for the sample volume ranging from 25 to 200 mL. Therefore, a preconcentration factor value of 40 can be achieved using the proposed methodology if the precipitate is dissolved and diluted to 5 mL.

3.1.2. Effect of matrix components on co-precipitation

The developed preconcentration method was applied for determination of selected metals in plant material. Therefore, it was advisable to investigate the influence of inorganic matrix on the efficiency of preconcentration of the determined metals. Taking into consideration the literature data and the certified reference materials, an average content of matrix elements in plant material was examined. The following elements were chosen: Na, K, Mg, Ca, Sr, Ba, Al, Mn, Fe, and Cr. Both influence of single elements and of the whole matrix on the recovery was studied. Table 1 shows that Fe has the largest influence on preconcentration and determination of all analytes, besides Cu. In the case of Cd, Co, Ni, Pb, and Zn, a decrease in the recovery of the analytes is observed (ca. 20%), whereas in the case of Cu, the recovery is 97%. The inorganic matrix has the largest effect on the concentration and determination of Co and Pb. The obtained results are ca. 10% lower than those obtained for samples without the inorganic matrix. For other analytes, the differences between results for samples with and without matrix do not exceed 5%.

3.1.3. Analytical precision and detection limit

Table 2 presents recoveries of spiked samples, repeatabilities, linear calibration ranges, detection limits and sensitivities for ICP-OES and F-AAS. The recoveries ranging from 94% to 102% for ICP-OES and from 97% to 100% for F-AAS, are satisfactory and confirm the accuracy of the proposed procedure. The relative standard

Table 1
Effect of foreign ions on the pre-concentration and determination of Cd, Co, Cu, Ni, Pb and Zn.

Ions	Concentration (μg)	Recovery (%)					
		Cd	Co	Cu	Ni	Pb	Zn
Na^+	5000	96	92	94	99	87	91
K^+	20,000	98	91	95	101	88	94
Mg^{2+}	2000	100	89	96	99	98	101
Ca^{2+}	10,000	103	92	97	101	102	100
Sr^{2+}	100	93	93	93	93	90	94
Ba^{2+}	100	99	96	91	92	92	97
Al^{3+}	500	95	98	96	99	100	100
Cr^{3+}	5	90	89	95	95	85	93
Mn^{2+}	100	94	83	95	101	92	93
Fe^{3+}	500	73	78	97	76	62	75
All matrix elements		96	86	90	96	84	101
Without matrix elements		100	100	98	98	97	97

Table 2
Specification of presented method at optimum conditions for each element ($n = 8$) and results of multi-elemental analysis ICP-OES and F-AAS methods after preconcentration. Samples spiked with 2 μg Cd and Co, 10 μg Pb and Ni, 20 μg Cu and Zn ($p = 0.95$).

Parameters	Cd	Co	Cu	Ni	Pb	Zn
ICP-OES						
Determined (μg)	1.89 ± 0.01	1.87 ± 0.01	19 ± 0.2	9.7 ± 0.1	10.3 ± 0.1	20.1 ± 0.2
Recovery (%)	94	94	97	97	102	100
RSD (%)	0.79	0.68	1.7	1.5	1.3	1.1
Calibration range (mg L^{-1})	0.02–0.4	0.02–0.4	0.2–4.0	0.1–2	0.1–2	0.2–4
DL (μg L^{-1})	0.36	0.66	3.3	1.4	3.5	3.2
Sensitivity (mg L^{-1})	0.030	0.058	0.048	0.071	0.30	0.038
F-AAS						
Determined (μg)	1.99 ± 0.03	2.01 ± 0.04	19.6 ± 0.2	9.8 ± 0.1	9.7 ± 0.1	19.5 ± 0.2
Recovery (%)	100	100	98	98	97	97
RSD (%)	1.5	2.1	1.2	1.1	1.6	1.0
Calibration range (mg L^{-1})	0.05–0.4	0.1–0.4	0.5–4	0.25–2	0.5–2	0.5–4
DL (μg L^{-1})	0.77	5.8	1.1	3.2	3.0	0.74
Sensitivity (mg L^{-1})	0.072	0.019	0.027	0.022	0.012	0.083

Table 3
Analysis of certified reference material NCS ZC85006 Tomato by ICP-OES and F-AAS. Results in mg kg^{-1} ($n = 4$, $p = 0.95$).

Metal	Certified value	ICP-OES	Relative differences (%)	F-AAS	Relative differences (%)
Cd	0.82 ± 0.09	0.79 ± 0.01	3.6	0.80 ± 0.02	2.4
Co	0.67 ± 0.04	0.63 ± 0.09	6.0	0.65 ± 0.06	3.0
Cu	21.1 ± 2.5	20.5 ± 0.7	2.8	20.4 ± 0.5	3.3
Ni	2.23	2.2 ± 0.1	1.3	2.20 ± 0.05	1.3
Pb	4.97 ± 0.54	4.8 ± 0.6	3.4	4.9 ± 0.5	1.4
Zn	36.2 ± 3.1	36 ± 1	0.5	36 ± 1	0.5

deviation (RSD) usually does not exceed 2% what indicates that Cd, Co, Cu, Ni, Pb, and Zn can be determined in solution samples with high precision.

In the case of such elements as Co, Cu, Ni, and Pb, the sensitivity is higher for analytes determination using ICP-OES technique. In the case of F-AAS technique, Cd and Zn may be assayed with higher sensitivity. The detection limits are at μg L^{-1} level both using ICP-OES and F-AAS.

In calculation of detection limits, BEC (background equivalent concentration) was considered

$$\mathrm{BEC} = \frac{c}{I_{L+T} - I_T} \cdot I_T$$

Detection limits for ICP-OES technique were determined using the following formula:

$$\mathrm{DL} = \frac{(c/(I_{L+T} - I_T)) \cdot I_T \cdot S_r \cdot 3}{100}$$

where c – concentration of the element being determined in the standard, I_{L+T} – intensity of signal generated by the standard, I_T – intensity of signal generated by the blank test, and S_r is relative standard deviation of the blank test.

Sensitivity of the method was determined for ICP-OES technique using measured signal intensities, generated by the elements

Table 4
Analysis of vegetables and samples spiked with 1.0 mg kg^{-1} of Cd, Co, Pb and 3.0 mg kg^{-1} of Cu, Ni ($n = 6$, $p = 0.95$).

Element	ICP-OES			F-AAS		
	Found (mg kg^{-1})	Spiked vegetables (mg kg^{-1})	Recovery (%)	Found (mg kg^{-1})	Spiked vegetables (mg kg^{-1})	Recovery (%)
White cabbage						
Cd	0.71 ± 0.01	1.7 ± 0.4	99	0.77 ± 0.01	1.79 ± 0.07	102
Co	0.072 ± 0.007	1.07 ± 0.08	100	nd	0.95 ± 0.08	95
Cu	2.36 ± 0.05	5.4 ± 0.8	101	2.82 ± 0.08	5.8 ± 0.1	99
Ni	2.30 ± 0.08	5.3 ± 0.3	100	2.7 ± 0.1	5.6 ± 0.2	97
Pb	0.69 ± 0.06	1.7 ± 0.1	101	nd	1.00 ± 0.03	100
Zn	59 ± 1	–	–	58.4 ± 0.2	–	–
Red cabbage						
Cd	0.87 ± 0.03	1.88 ± 0.06	101	0.91 ± 0.02	1.91 ± 0.03	100
Co	0.06 ± 0.01	1.06 ± 0.07	100	nd	0.97 ± 0.08	97
Cu	3.6 ± 0.1	6.7 ± 0.8	103	3.89 ± 0.04	6.8 ± 0.5	97
Ni	3.2 ± 0.1	6.2 ± 0.5	100	3.03 ± 0.07	6.04 ± 0.05	98
Pb	1.1 ± 0.1	2.0 ± 0.2	90	nd	1.02 ± 0.07	102
Zn	95 ± 4	–	–	99.8 ± 0.7	–	–
Potatoes						
Cd	0.33 ± 0.01	1.3 ± 0.1	97	0.36 ± 0.02	1.36 ± 0.08	100
Co	0.06 ± 0.01	1.05 ± 0.05	100	nd	0.93 ± 0.05	93
Cu	4.9 ± 0.1	7.9 ± 0.4	99	5.5 ± 0.1	8.6 ± 0.3	103
Ni	1.95 ± 0.03	5.0 ± 0.6	102	1.69 ± 0.09	4.64 ± 0.03	98
Pb	1.2 ± 0.1	2.1 ± 0.3	90	nd	0.95 ± 0.08	95
Zn	34.8 ± 0.4	–	–	32.9 ± 0.5	–	–

nd: not detected.

studied in the standard solutions, based on the following formula:

$$m = \frac{c}{I_{L+T} - I_T}$$

where c – concentration of the element in the standard, I_{L+T} – intensity of signal measured for the standard, I_T – intensity of signal measured for the blank test.

In the case of Co, the detection limit is higher for ICP-OES than for F-AAS, whereas inverse situation is observed for Zn. The other analytes have comparable limits of detection. Detection limits presented in Table 2 were obtained for 100 mL of the sample.

3.2. Analysis of the certified reference material

Accuracy of the developed method was verified by analysis of the certified reference material (NCS ZC 85006 Tomato). The obtained results for ICP-OES and F-AAS measurements are shown in Table 3. Considering that there is no significant difference between the certified values and the results obtained using ICP-OES and F-AAS techniques, the developed method of preconcentration of Cd, Co, Cu, Ni, Pb, and Zn can be successfully used for determination of selected metals in unknown plant materials.

3.3. Applications

White and red cabbage, and potatoes were analyzed. The obtained results for ICP-OES and F-AAS are shown in Table 4. In addition, recovery experiments for various amounts of Cd, Co, Cu, Ni, and Pb were carried out. Good agreement between the analyte amounts added and recovered using the proposed procedure was obtained. The recovery values calculated for the samples spiked with analyte ions were always higher than 95%. The obtained results confirm the accuracy of the procedure and the absence of matrix effects.

4. Conclusions

The study shows that ionic associations can be used as organic carriers. Until now, such associations have been used mainly for development of extraction-spectrophotometric and spectrofluorimetric [27] methods in single element determination. In this paper, formation of ionic associates was applied in group preconcentration and simultaneous determination of several metals. Elimination of harmful organic solvents used for extraction is an advantage of the developed method.

The developed method of simultaneous preconcentration of selected heavy metals can be applied to multi-element analysis of plant materials using ICP-OES and F-AAS techniques. The method is characterized by good precision and accuracy. Recoveries of the analytes are higher than 90%. It is advisable to prepare standard solutions for calibration in both ICP-OES and F-AAS in the same way as the unknown samples. Such strategy allows to eliminate the matrix effects. This method is simple, rapid, safe and robust.

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