

Determination of heavy metals by ICP-OES and F-AAS after preconcentration with 2,2'-bipyridyl and erythrosine

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Abstract

The applicability of 2,2'-bipyridyl and erythrosine co-precipitation method for the separation and preconcentration of some heavy metals, such as Cd, Co, Cu, Ni, Pb and Zn in actual samples for their determination by ICP-OES and F-AAS was studied. Experimental conditions influencing the recovery of the investigated metals, such as pH, molar ratio of 2,2'-bipyridyl to erythrosine, the effect of time on co-precipitation were optimized. The analytical characteristics of the method (e.g. limit of detection, sensitivity, linear range and preconcentration factor) were obtained. The limits of detection LOD (ng mL^{-1}) of the ICP-OES (F-AAS) method were: Cd: 4.0 (7.75), Co: 3.1 (57.2), Cu: 18 (10.3), Ni 21.3 (32.8), Pb: 35.9 (29.2) and Zn: 10.2 (6.90). The recovery of all the elements tested was more than 93%. The influence of inorganic matrix was examined. The proposed method was applied to determination of Cd, Co, Cu, Ni, Pb and Zn in vegetables and certified reference material (NCS ZC85006 Tomato). © 2007 Elsevier B.V. All rights reserved.

Keywords: Co-precipitation; 2,2'-Bipyridyl; Erythrosine; ICP-OES; F-AAS; Plant materials; Heavy metals

1. Introduction

Contemporary instrumental techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES) or atomic absorption spectrometry (AAS) allow for simultaneous or sequential determination of a large number of elements, if only they exceed a threshold concentration, defined by corresponding limit of detection and by adequate spectral resolution of the instrument. The requirement for the analyzed element concentration to exceed its limit of detection is rarely met in trace analysis. Hence the necessity of concentrating the sample components occurring at trace level.

Separation techniques such as co-precipitation, liquid–liquid extraction, solid phase extraction, cloud point extraction and on-line co-precipitation using a knotted reactor have been successfully employed to determine trace levels of metals.

Co-precipitation is one of the most efficient separation and enrichment techniques for trace heavy metal ions. The main requirement for this technique is that the collector should separate easily from the matrix solution. This can be done by filtering,

centrifuging and washing off the precipitate. The advantages of this technique are its simplicity and the fact that various analyte ions can be preconcentrated and separated simultaneously from the matrix. Inorganic or organic co-precipitants have been used as efficient collectors of trace elements. Table 1 lists several methods for determining metals in many samples, using co-precipitation as the separation and preconcentration technique.

Formation of ionic associations may also be used as organic carriers, e.g. ionic associations forming in systems: a cationic chelate metal complex—an anion of a non-chelating organic dye. They form sparingly soluble precipitations. These precipitations are insoluble in acids, but they dissolve well in hydroxides solutions and in organic solvents.

Solubility in organic solvents has been used for development of many spectrophotometric methods of assay of metals after their separation by extraction [17].

In this work, a possibility of formation of sparingly soluble precipitations of ionic associations has been applied to group separation and concentration of Cd, Co, Cu, Ni, Pb, and Zn, using co-precipitation with a carrier.

This paper concerns a selection of conditions for group separation and concentration of Cd, Co, Cu, Ni, Pb, and Zn, from aqueous solutions, using an ionic associate La–2,2'-bipyridyl–erythrosine as a carrier. The developed concentration

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Table 1
Preconcentration procedures using co-precipitation for the determination of metals

Analytes	Collector	Recovery (%)	LOD ($\mu\text{g L}^{-1}$)* (ng L^{-1})	R.S.D. (%)	PF	Technique	Sample	Reference
Se, Cu, Pb, Zn, Cd, Fe, Co, Ni, Mn, Cr	Sodium diethyldithiocarbamate	>98	0.7 (Zn, Cd), 10 (Pb), 1 (Cu, Co), 7 (Ni)	–	40	ICP-OES	River water	[1]
Sb, As, Cd, Cr, Cu, Fe, Pb, Mo, Ni, Ag, V, Zn	Sodium diethyldithiocarbamate	–	0.1–3.0	–	–	ICP-OES	Natural water	[2]
Cd, Pb, Ni	Copper diethyldithiocarbamate	>95	0.23 (Cd), 3.2 (Pb), 2.2 (Ni)	1.4–2.2	–	F-AAS	Natural water	[3]
Fe, Pb	Lanthanum phosphate	>97	–	1.6 (Pb)	–	ICP-OES	Water	[4]
Al., Cd, Mo, V, W, Ti, Zn, Au, Bi, Co, Cu, Fe, Ni, Pb, Pd	Manganese dioxide	96–105	1 (Cd, Zn), 5 (Co, Cu, Ni, Pb)	8	80	F-AAS ICP-OES	Ground water	[5]
Pb	Manganese dioxide	>95	3.2	5	–	ICP-OES	River water	[6]
Cd, Cu, Pb	Aluminum hydroxide	>95	6 (Cd), 3 (Cu), 16 (Pb)	2–3	–	F-AAS	Seawater, mineral water	[7]
Cu, Co, Pb, Cd, Ni	Cerium(IV) hydroxide	>95	0.18 (Cu), 0.4 (Cd), 7 (Pb), 0.57 (Co), 1.56 (Pb)	6.5–8.9	–	F-AAS	Seawater, drinking water, sediment	[8]
Cu, Mn, Co, Cr, Fe, Pb	Erbium hydroxide	>95	0.11 (Cu), 0.25 (Co), 0.24 (Pb)	1–9	25	F-AAS	Tap water, sediment, urine	[9]
Al., Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Pb	Gallium hydroxide	–	0.5 (Pb), 0.01 (Cu, Zn)	10	–	ICP-OES	Seawater	[10]
Cd, Co, Cr, Cu, Mn, Ni, Pb	Magnesium hydroxide	89–100	0.08 (Cd), 0.14 (Co), 0.33 (Cu), 0.74 (Ni)	4.7–7.7	–	ET-AAS	Dialysis concentrate	[11]
Cd, Fe, Co, Cr, Cu, Mn, Ni, Pb	Samarium hydroxide	95–100	1.1 (Cu), 3.1 (Ni), 4.5 (Co), 24.0 (Pb), 0.4 (Cd)	0.2–10.2	–	ET-AAS	Urnies, sediment and dialysis concentrates	[12]
Be, Cr, Fe, Co, Ni, Cu, Cd, Pb	Zirconium hydroxide	–	0.85* (Co), 0.88* (Ni), 1.5* (Cu), 0.38* (Cd), 0.42* (Pb)	<10	–	ET-AAS	Natural water	[13]
Cd, Co, Cr, Cu, Pb	Indium hydroxide	94–103.5	0.6–8.6	0.75–4.2	–	F-AAS	Seawater, wastewater, springwater	[14]
Co, Ni, Cu, Cd, Pb	Magnesium oxinate	–	0.025 (Co), 0.019 (Ni), 0.006 (Cu), 0.001 (Cd), 0.017 (Pb)	10	–	ET-AAS	River water, seawater	[15]
Cu, Cd, Pb	Palladium	95–103	–	3.8	50	ET-AAS	Seawater	[16]
Cd, Co, Cu, Ni, Pb, Zn	La–2,2'-bipyridyl–erythrosine	94–98	4.0 (Cd), 3.1 (Co), 18 (Cu), 21.3 (Ni), 35.9 (Pb), 10.2 (Zn)	0.76–1.70	50	ICP-OES	Cabbage, potatoes	This work

PF, preconcentration factor.

method was applied in multi-elemental analysis with ICP-OES and F-AAS techniques, for assay of heavy metals in plant material destined for food preparation. White and red cabbage, and potatoes from GOP (Upper Silesia Industrial District) were selected for the tests. Accuracy of the developed method of concentration and determination of Cd, Co, Cu, Ni, Pb, and Zn was tested analyzing Certified Reference Material NCS ZC85006 Tomato.

It is noteworthy that the proposed analytical procedure of concentration does not require specialist apparatus for sample preparation. It is simple and fast, and in the course of the analysis, relatively small amounts of available reagents are used.

Till now, formation of ionic associates of type: metal–heterocyclic base–xantene acidic dye was used mainly for development of sensitive extraction–spectrophotometric methods of single elements' determination. In this paper, formation of ionic associates was applied to group separation and simultaneous determination of several metals. Elimination of harmful organic solvents used for extraction is another advantage of the developed method. Basing on the investigations carried out, it was ascertained that analyzed heavy metals may be concentrated and assayed in plant material using the developed methods, without prior separation of the inorganic matrix.

2. Experimental

2.1. Apparatus

An M-9 mineralizer (WSL, Bytom, Poland) and a mineralizer UniClever microwaves (Plazmatronika BM-1z, Poland) were used for dissolution of the actual samples. An LW-8 water bath (SWL Bytom, Poland) and MPW-350 (Warsaw, Poland) centrifuge were used to achieve and accelerate the phase separation process, respectively. Separation of two phases was achieved heating and accelerated by centrifugation for 5 min at 400 rpm. An N-1570 pH-meter (Mera-Elwro, Wrocław, Poland) with a glass ESAgP-309 electrode was employed for measuring pH values in the aqueous phase. A Pulverisette 14 variable speed rotor mill (Fritsch, Germany) was used to obtain a homogeneous sample.

A spectroflame atomic emission spectrometer, ICP Model M (Spectro Analytical Instruments, Germany) was used for the determination of Cd, Co, Cu, Ni, Pb and Zn. The sequential spectrometer was used with 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 the first reciprocal order, 0.55 nm mm⁻¹; wavelength range of monochromator 165–460 nm. The wavelengths (integration time) for Cd: 228.80 nm (3 s), Co: 228.62 nm (4 s), Cu: 324.75 nm (3 s), Ni: 221.65 nm (5 s), Pb: 220.35 nm (5 s), and Zn: 213.87 (4 s).

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

2.2. Reagents and solutions

Stock standard solutions of cadmium, cobalt, copper, nickel, lead and zinc at a concentration of 1000 mg L⁻¹ were obtained from Merck. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. The solution of 2,2'-bipyridyl at a concentration 0.01 mol L⁻¹ was prepared by dissolving 0.7810 g of the reagent (from POCh, Poland) in 500 mL of water. The solution of erythrosine (disodium salt tetraiodofluoresceine) at a concentration 0.01 mol L⁻¹ was prepared by dissolving 7.24 g of the reagent (from Chemapol-Praha) in 1000 mL of water. The solution of lanthanum at a concentration 1 mg La mL⁻¹ was prepared by dissolving 1.5584 g La(NO₃)₃·6H₂O (from Loba Feinchemie) in 500 mL of water. Buffer solution of pH 4.5 was prepared by mixing of a 55 mL acetic acid at a concentration of 0.2 mol L⁻¹ and 45 mL sodium acetate solution at a concentration of 0.2 mol L⁻¹. Other chemicals used: NaOH, NH₃·H₂O, HNO₃, H₂O₂, HF, NaNO₃, KNO₃, Mg(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Sr(NO₃)₂, Ba(NO₃)₂, Al(NO₃)₃·9H₂O, Mn(NO₃)₂·4H₂O, Fe(NO₃)₃·9H₂O (all from POCh, Poland). All the chemicals were of analytical grade quality. Water was purified with an Elix 3 system (Millipore, USA). The accuracy of the method was assessed by analyzing the following certified reference material (CRM): NCS ZC85006 Tomato (China National Analysis Center for Iron & Steel 2000).

2.3. Procedures

2.3.1. Co-precipitation of the elements studied in a model solution

Lanthanum (0.2 mg) and 1 mL of 10⁻² mol L⁻¹ solutions of 2,2'-bipyridyl and erythrosine were added to the mixture of assayed metals which contained 2 µg of Cd and Co, 10 µg of Pb and Ni and also 20 µg of Cu and Zn in 100 mL. Then, pH of the precipitate (4.5) was fixed using an acetate buffer. The obtained samples were heated on the water bath for 20 min in the temperature of 60 °C. Deposits formed in these conditions were centrifuged and the solution was decanted. Precipitate were digested in 1 mL of sodium hydroxide with concentration of 0.2 mol L⁻¹ for ICP-OES method or in 1 mL of ammonia solution (1 + 1) for F-AAS method. The solutions were diluted to 10 mL with water (final volume). The metals content of the final solution was determined by ICP-OES and F-AAS. Calibration was carried using different standard solutions of Cd, Co, Cu, Ni, Pb and Zn submitted to the same preconcentration and determination procedures.

2.3.2. Preparation of the plant material for the investigations

White and red cabbage, and potatoes from GOP were selected for the tests. The plant material delivered to the laboratory was preliminarily broken up and cleaned. Outer leaves were removed from the cabbage. Then the plant material was 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 prepared in such a way was stored in labeled, tightly sealed polyethylene containers.

In order to transfer the sample to the solution, wet decomposition in an open system using a mixture of concentrated nitric acid and 30% hydrogen peroxide was carried out. Sample mineralization was carried out in an M-9 mineralizer as follows:

- 1 g of the examined material sample was mineralized in an open system at the temperature of 175–178 °C, using 10 mL of concentrated nitric acid and 5 mL of hydrogen peroxide. The obtained straw-colored mineralizate was transferred quantitatively to volumetric flasks with 25 mL volume and diluted with demineralized water.
- It was processed co-precipitation further as described above. The 2,2'-bipyridyl and erythrosine solutions was added 5 mL each.

2.3.3. Mineralization of the certified reference material

Certified reference material (NCS ZC85006 Tomato) was mineralized in a microwave pressure mineralizer (Plazmatronika BM-1z, Poland) using 6 mL of concentrated nitric acid and 0.25 mL of concentrated hydrofluoric acid. Mineralization time was 10 min under pressure of 45 atm.

3. Results and discussion

The methods developed for the upconcentration of cadmium, cobalt, copper, nickel, lead and zinc are based on reactions of ionic associates formation.

The mechanism of traces concentration is as follows:

- $M^{2+} + nL \rightarrow [M(L)_n]^{2+}$
Metal cation reacts with a heterocyclic base, forming a chelate complex with positive charge.
- $[M(L)_n]^{2+} + Q^{2-} \rightarrow [M(L)_n]Q$
The complex formed is coupled with an anion of a xantene dye, resulting in formation of a new ionic associate.
- $La^{3+} + nL_{\text{excess}} + Q^{2-}_{\text{excess}} \rightarrow [La(L)_n]Q \downarrow$
In the presence of lanthanum, excess of the heterocyclic base and excess of the acidic dye form a precipitate of an ionic associate performing as a carrier.
- $[M(L)_n]Q + [La(L)_n]Q \downarrow \rightarrow \{[M(L)_n]Q + [La(L)_n]Q\} \downarrow$
Ionic associates containing traces of heavy metals co-precipitate with the precipitate formed according to a surface adsorption mechanism, where $M = \text{Cd, Co, Cu, Ni, Pb, and Zn}$; $L = 2,2'$ -bipyridyl; and $Q = \text{erythrosine}$.

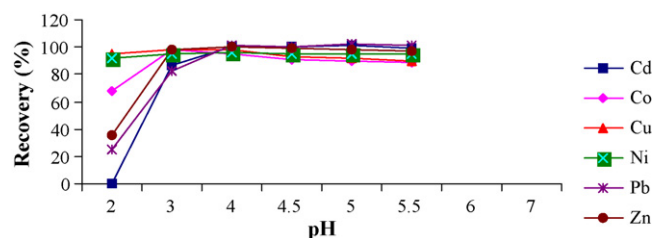


Fig. 1. Effect of pH on the quantitative co-precipitation of the elements studied.

3.1. Optimization of operating conditions

3.1.1. Precipitation

Optimum conditions for group concentration of Cd, Co, Cu, Ni, Pb, and Zn were selected.

The La–2,2'-bipyridyl–erythrosine ionic associate precipitates in acidified media. Influence of pH in the range of 2–7 was examined. Fig. 1 shows the effect of pH on the quantitative co-precipitation of cadmium, cobalt, copper, nickel, lead and zinc. At pH higher than 5.5 the precipitate does not form. The best recovery of the results was observed at pH 4–5 for all the elements studied. Hence, a middle range of pH at 4.5 was chosen for these analytes. The effect of pH on the precipitation and determination using ICP-OES analysis was studied according to the procedure described in Section 2.3.1.

An optimum molar ratio of 2,2'-bipyridyl to erythrosine was settled. The following molar ratios of 2,2'-bipyridyl to erythrosine were examined: 10:1; 2:1; 1:1; 1:2; 1:10. The results obtained are shown in Fig. 2. The best recovery of the results was observed at molar ratios of 2,2'-bipyridyl to erythrosine equal to: 2:1; 1:1; 1:2. The value of 1:1 was assumed as an optimum molar ratio of the base to the dye.

Cu, Pb and Ni are well recovered and for Cd, Zn and Co the decrease in recovery is observed. The observed dependency results from the values of stability constants for 2,2'-bipyridyl–metal complexes. Logarithms of stability constants for complexes of 2,2'-bipyridyl with individual metals have the following values [18]: Cu, 8.2; Ni, 7.0; Co, 5.7; Zn, 5.2; Cd, 4.3; and Pb, 3.0. Cu and Ni complexes are more stable than Co and Cd complexes, what results also from the Irving–Williams stability series.

The effect of time on co-precipitation was studied. The precipitate was allowed to stand for from 10 min up to 2 h in the temperature of 60 °C. Basing on the obtained results, it was ascertained that heating did not influence the efficiency of the

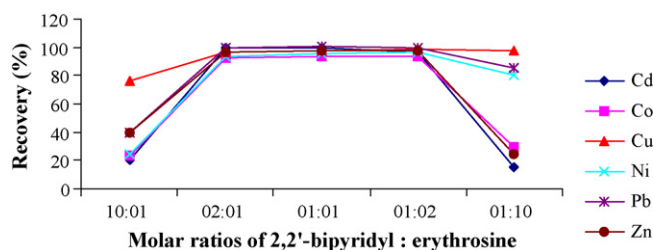


Fig. 2. Effect of molar ratios 2,2'-bipyridyl to erythrosine on the quantitative co-precipitation of the elements studied.

Table 2
Results of multi-elemental analysis ICP-OES and F-AAS methods after preconcentration using carrier

	Cd	Co	Cu	Ni	Pb	Zn
ICP-OES						
Determined (μg)	1.97 \pm 0.02	1.89 \pm 0.01	19.24 \pm 0.26	9.70 \pm 0.06	9.53 \pm 0.14	18.54 \pm 0.14
Recovery (%)	98	94	96	97	95	93
R.S.D. (%)	1.22	0.79	1.63	0.76	1.70	0.89
Preconcentration factor (PF)	50					
F-AAS						
Determined (μg)	2.00 \pm 0.03	2.04 \pm 0.05	19.95 \pm 0.31	9.85 \pm 0.16	9.84 \pm 0.19	20.43 \pm 0.17
Recovery (%)	100	102	100	98	98	102
R.S.D. (%)	1.77	2.78	1.85	1.96	2.26	0.85
PF	50					

Sample volume: 200 mL, final volume: 10 mL. Added: 2 μg Cd and Co, 10 μg Pb and Ni, 20 μg Cu, and Zn; $n = 10$, $P = 0.95$.

Table 3
Analytical characteristics of the ICP-OES method

Element	Dynamic range ($\mu\text{g mL}^{-1}$)	Regression equation	R	LOD ($\mu\text{g mL}^{-1}$)	Sensitive ($\mu\text{g mL}^{-1}$)
Cd	0.02–0.40	$I = 12379C + 654.23$	0.9997	4.0×10^{-3}	0.030
Co	0.02–0.40	$I = 6327.6C + 273.35$	0.9994	3.1×10^{-3}	0.058
Cu	0.20–4.00	$I = 18619C + 381.47$	1.0000	1.8×10^{-2}	0.048
Ni	0.10–2.00	$I = 5164.1C + 374.18$	1.0000	2.13×10^{-2}	0.071
Pb	0.10–2.00	$I = 1052.3C + 574.47$	0.9969	3.59×10^{-2}	0.303
Zn	0.20–4.00	$I = 7926C + 1948.2$	0.9979	1.02×10^{-2}	0.038

I , intensity. C , concentration ($\mu\text{g mL}^{-1}$). LOD, limit of detection, calculated as three times the standard deviation (3σ).

metals' concentration, however it promoted the decantation. It was established that 20 min was sufficient to ensure results of good precision.

The influence of lanthanum quantity (in the range of 0.1–0.3 mg) on the recovery was also examined. Using 0.2 mg of La when concentrating from the volume of 100 mL, the recoveries of the metals analyzed were higher than 90%. Lanthanum (0.2 mg) was used as an optimal quantity.

Statistic evaluation of the developed concentration method was carried out for 10 model samples prepared according to Section 2.3.1. R.S.D., being a measure of precision of the developed method, was calculated. Confidence intervals at significance level 95 were also determined. Accuracy, that is the consistence with the actual result, was displayed by recovery expressed in percent. Concentration process was carried out from volume of 100 mL. Final volume of a sample was 10 mL. The results of determination of metals in the samples using ICP-OES and F-AAS techniques were shown in Table 2.

3.1.2. Calibration, precision and detection limits

Calibration graphs were obtained by preconcentrating according to the procedure described in Section 2.3.1. In this case, linear relationships between the intensity ratio (for ICP-OES) or absorbance (for F-AAS) measured and the concentration of metal prepared for the calibration solution were obtained. Table 3 (for ICP-OES) and Table 4 (for F-AAS) gives the calibration parameters, the detection limits and the sensitivities.

The calibration curves obtained for determination of analytes studied using ICP-OES and F-AAS techniques are rectilinear.

In order to determine LOD of the analytes after their concentration and the following determination using F-AAS technique, 10 independent measurements were carried out for 10 independently prepared blank tests. Basing on the results obtained in this way, mean value and standard deviation were calculated. Mean value raised by threefold value of standard deviation was assumed as the LOD value.

Table 4
Analytical characteristics of the F-AAS method

Element	Dynamic range ($\mu\text{g mL}^{-1}$)	Regression equation	R	LOD ($\mu\text{g mL}^{-1}$)	Sensitive ($\mu\text{g mL}^{-1}$)
Cd	0.05–0.40	$A = 0.0708C + 0.0016$	0.9999	7.75×10^{-3}	0.071
Co	0.10–0.40	$A = 0.0187C + 0.0002$	0.9992	5.72×10^{-2}	0.019
Cu	0.50–4.00	$A = 0.0280C + 0.0002$	1.0000	1.03×10^{-2}	0.028
Ni	0.25–2.00	$A = 0.0187C + 0.0004$	0.9996	3.28×10^{-2}	0.019
Pb	0.50–2.00	$A = 0.0089C + 0.0006$	0.9973	2.92×10^{-2}	0.009
Zn	0.50–4.00	$A = 0.0751C + 0.0155$	0.9999	6.90×10^{-3}	0.075

A , absorbance. C , concentration ($\mu\text{g mL}^{-1}$). LOD, limit of detection, calculated as three times the standard deviation (3σ).

For F-AAS technique, value of slope of the calibration curve was assumed as the sensitivity.

In order to determine LOD of the analytes after their concentration and following assay using ICP-OES technique, six series of standard solutions were prepared by precipitation according to Section 2.3.1. Signal intensity at the peak maximum was measured for the prepared solutions.

Limit of detection for ICP-OES technique was determined using the following formula [19,20]:

$$\text{LOD} = \frac{c/(I_{L+T} - I_T)S_r I_T 3}{100}$$

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

Sensitivity of method was determined for ICP-OES technique using measured signal intensities, generated by the elements studied in the standard solutions, basing on the following formula:

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

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

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 a higher sensitivity. In the case of cobalt, LOD is higher when using ICP-OES method, whereas in the case of zinc—for F-AAS method. Rest of the analytes has comparable limits of detection.

3.1.3. Effect of matrix components on co-precipitation and subsequent F-AAS determination

The developed concentration method was applied to determination of selected metals in plant material. Therefore it was advisable to investigate the inorganic matrix effect on efficiency of concentration of the determined metals. Using literature data and attestations of the certified reference materials, an average contents of matrix elements in plant material was determined. The influence of the following elements was examined: Na, K, Mg, Ca, Sr, Ba, Al, Mn, Fe, and Cr.

The effect of every element contained in the inorganic matrix on the results of selected metals' determination after their concentration using developed methods was examined. The effect

Table 5

Effect of foreign ions on the preconcentration and determination of cadmium (2 µg), cobalt (2 µg), copper (20 µg), nickel (10 µg), lead (10 µg) and zinc (20 µg)

Ions	Concentration (µg)	Recovery (%)					
		Cd	Co	Cu	Ni	Pb	Zn
Na ⁺	5000	100	92	95	95	100	100
K ⁺	20000	100	90	97	100	100	100
Mg ²⁺	2000	98	88	94	91	100	98
Ca ²⁺	10000	96	92	92	95	100	96
Sr ²⁺	100	95	90	96	97	100	95
Ba ²⁺	100	100	96	97	97	100	100
Al ³⁺	500	86	98	95	96	100	98
Cr ³⁺	5	99	89	96	97	100	99
Mn ²⁺	100	82	83	82	84	94	82
Fe ³⁺	500	98	88	94	93	100	97
All matrix		91	82	92	89	94	98
Not matrix		98	94	96	97	95	93

of the whole matrix on efficiency of analytes' concentration was investigated too. Other experimental conditions were as described in Section 2.3.1. The results are shown in Table 5.

Manganese has the largest influence on concentration and determination of Cd, Co, Cu, Ni, and Zn. It causes an average 10% decrease in the results of analytes' determination. Aluminum influences concentration and determination of Cd. No effect of the inorganic matrix on Pb determination was observed.

The inorganic matrix has the largest effect on concentration and determination of Co. The results of the determination are underrated by 10% on the average, comparing with the determination results for samples not containing the inorganic matrix. The effect of matrix addition is slightly lower while determining Ni. These results are underrated by ca. 6–7%. For other analytes, the differences between determination results for samples with and without matrix do not exceed 5%, and they remain within margin of error for the analysis.

3.2. Analysis of the certified reference material

Accuracy of the developed methods of concentration and determination of Cd, Co, Cu, Ni, Pb, and Zn was verified by analysis of the certified reference material. NCS ZC85006 Tomato was analyzed. The results are shown in Table 6.

Mean determined contents of the metals studied, obtained for the reference material using the developed method and ICP-OES and F-AAS techniques remain, together with their confidence intervals, within confidence intervals of the certified reference

Table 6

Determination of Cd, Co, Cu, Ni, Pb and Zn (µg g⁻¹) dry mass in Certified Reference Material NCS ZC85006 Tomato by ICP-OES and F-AAS, $n = 4$, $P = 0.95$

Metal	Certified value	Our value by ICP-OES	R.S.D. (%)	Our value by F-AAS	R.S.D. (%)
Cd	0.82 ± 0.09	0.79 ± 0.02	1.62	0.79 ± 0.03	1.62
Co	0.67 ± 0.04	0.58 ± 0.09	10.76	nd ^a	–
Cu	21.1 ± 2.5	20.25 ± 0.87	2.72	20.25 ± 0.42	1.45
Ni	2.23	2.10 ± 0.11	3.25	2.07 ± 0.12	1.70
Pb	4.97 ± 0.54	4.58 ± 0.35	4.76	4.41 ± 0.53	7.49
Zn	36.2 ± 3.1	35.10 ± 0.74	1.33	35.34 ± 0.49	2.53

^a nd: not detected.

Table 7

Determination of Cd, Co, Cu, Ni, Pb and Zn ($\mu\text{g g}^{-1}$) dry mass in vegetables by ICP-OES, $n=6$, $P=0.95$

Metal	White cabbage	R.S.D. (%)	Red cabbage	R.S.D. (%)	Potatoes	R.S.D. (%)
Cd	0.66 ± 0.029	4.18	0.83 ± 0.039	4.43	0.34 ± 0.005	1.50
Co	nd ^a	–	0.05 ± 0.009	18.32	0.06 ± 0.005	8.76
Cu	2.24 ± 0.082	3.47	3.76 ± 0.114	2.89	5.40 ± 0.093	1.64
Ni	2.26 ± 0.069	2.91	3.40 ± 0.047	1.34	1.91 ± 0.057	2.48
Pb	0.57 ± 0.064	10.18	0.99 ± 0.094	9.03	1.12 ± 0.172	14.57
Zn	57.44 ± 1.08	1.08	88.74 ± 2.40	2.58	33.86 ± 0.41	1.15

^a nd: not detected.

Table 8

Determination of Cd, Co, Cu, Ni, Pb and Zn ($\mu\text{g g}^{-1}$) dry mass in vegetables by F-AAS, $n=6$, $P=0.95$

Metal	White cabbage	R.S.D. (%)	Red cabbage	R.S.D. (%)	Potatoes	R.S.D. (%)
Cd	0.79 ± 0.024	3.66	0.92 ± 0.035	3.62	0.32 ± 0.006	1.80
Co	nd ^a	–	nd	–	nd	–
Cu	2.65 ± 0.054	2.43	3.97 ± 0.034	0.82	5.83 ± 0.052	0.85
Ni	2.50 ± 0.086	4.09	2.97 ± 0.039	1.25	1.49 ± 0.041	2.59
Pb	nd	–	nd	–	nd	–
Zn	65.80 ± 1.20	2.18	94.24 ± 0.78	0.79	32.91 ± 0.63	1.83

^a nd: not detected.

Table 9

Cd, Co, Cu, Ni and Pb recovery ($n=6$) by ICP-OES

Samples	Added ($\mu\text{g g}^{-1}$) dry mass					Measured ($\mu\text{g g}^{-1}$) dry mass					Recovery (%)				
	Cd	Co	Cu	Ni	Pb	Cd	Co	Cu	Ni	Pb	Cd	Co	Cu	Ni	Pb
White cabbage	–	–	–	–	–	0.66	nd	2.24	2.26	0.57	–	–	–	–	–
	1	1	3	3	1	1.67	0.99	5.19	5.23	1.54	101	99	98	99	97
Red cabbage	–	–	–	–	–	0.83	0.05	3.76	3.40	0.99	–	–	–	–	–
	1	1	3	3	1	1.89	1.05	6.67	6.39	1.97	106	100	97	100	98
Potatoes	–	–	–	–	–	0.34	0.06	5.40	1.91	1.12	–	–	–	–	–
	1	1	3	3	1	1.32	1.08	8.38	4.95	2.09	98	102	99	101	97

material. Consistence of the NCS ZC85006 Tomato analysis results with the certified contents proves correctness of the used analytical procedure, and the obtained determination results are credible.

Considering the fact that there is no significant difference between the certified values and the results obtained using ICP-OES and F-AAS techniques, these methods may be used interchangeably for determination of selected metals in actual material after prior concentration of the metals using the developed method.

3.3. Applications

In order to test the reliability of the proposed methodology suitable for the assay of the six targeted metal ions, it was applied to determine their concentration in white and red cabbage and potatoes.

The results are shown in Table 7 (for ICP-OES) and Table 8 (for F-AAS). For calibration purposes, the working standard solutions were subjected to the same preconcentration procedure as used for the analyte solutions.

Table 10

Cd, Co, Cu, Ni and Pb recovery ($n=6$) by F-AAS

Samples	Added ($\mu\text{g g}^{-1}$) dry mass					Measured ($\mu\text{g g}^{-1}$) dry mass					Recovery (%)				
	Cd	Co	Cu	Ni	Pb	Cd	Co	Cu	Ni	Pb	Cd	Co	Cu	Ni	Pb
White cabbage	–	–	–	–	–	0.79	nd	2.65	2.50	nd	–	–	–	–	–
	1	1	3	3	1	1.74	0.99	5.70	5.42	1.52 0.54 ^a	95	99	102	97	98
Red cabbage	–	–	–	–	–	0.92	nd	3.97	2.97	nd	–	–	–	–	–
	1	1	3	3	1	1.95	0.98	6.91	6.02	1.66 0.68 ^a	103	98	98	102	98
Potatoes	–	–	–	–	–	0.32	nd	5.83	1.49	nd	–	–	–	–	–
	1	1	3	3	1	1.36	0.94	8.74	4.45	2.10 1.11 ^a	104	94	97	99	99

^a Amount of Pb determined by the method of the standard addition.

In addition, recovery experiments for different amounts of Cd, Co, Cu, Ni and Pb were carried out. The results shown in Table 9 (for ICP-OES) and Table 10 (for F-AAS) confirm the validity of the proposed method.

When the method of the standard addition was carried out Pb was determined by F-AAS technique.

4. Conclusions

The developed method of simultaneous concentration of selected heavy metals may be applied to multi-element analysis of actual materials using ICP-OES and F-AAS techniques. Introductory group concentration of the analytes allow for one-order reduction of limit of detection of these metals using both techniques. Developed methods are characterized by good precision and accuracy. Recovery percentages of the analytes amount to more than 90%. The results of determination of the analytes studied, after their prior concentration, obtained by ICP-OES technique, are comparable with the ones obtained using F-AAS technique. It is advisable to prepare standard solutions for calibration curve in both techniques in the same way as the samples. It allows to eliminate the effect of reagent matrix.

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