Determination of toxic and other trace elements in calcium-rich materials using cloud point extraction and inductively coupled plasma emission spectrometry

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A B S T R A C T

A cloud point extraction (CPE) procedure for the simultaneous separation and preconcentration of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn from materials rich in calcium prior to trace element analysis by inductively coupled plasma optical emission spectrometry (ICP OES) was developed. The method is based on the formation of hydrophobic complexes of the metal ions with PAN or 5-Br-PADAP, followed by their extraction into a surfactant-rich phase using Triton X-114 as the surfactant. The main variables affecting the extraction process, such as pH, concentration of surfactant and chelating agent were optimised. Under the optimum conditions the obtained limits of detection for Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were of 4.0, 4.3, 2.1, 1.9, 0.3, 5.6, 40 and 2.0 $\mu g\,L^{-1}$, respectively. The RSD values for 10 replicates were from 1.5% for Mn to 11% for Pb. The accuracy of the procedure was verified by analysis of certified reference material NIST 1400 (Bone Ash) and by recovery tests. The optimised method was successfully applied for the simultaneous determination of trace elements in dolomites used by different fertiliser factories.

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1. Introduction

In addition to typical hazardous materials such as waste, sludge, many other materials can be a danger to people and the environment due to contamination with trace toxic chemicals, especially heavy metals. Trace elements incorporated in the structure of the materials can change their physical and chemical characteristics, and may limit their usefulness for many purposes. Bone meal, oyster shells, products formed from dolomite and other calcium minerals processed with inorganic compounds are commonly used as solid and liquid fertilisers [1–3] and can be potential sources of heavy metals in agricultural soils, increasing the risk of crop and food chain contamination. Hence, a control of heavy metal concentrations in fertilisers or their main components is very important considering the hazard of the accumulation of toxic metals in soil or their leaching into surface waters. On the other hand, materials such as shells, corals and other biogenic marine carbonates can serve as indicators of pollution and climate variation [4], and the trace element content of bone is used as an indicator of disease and/or long-term poisoning [5].

The determination of heavy metals in calcium-rich materials is not an easy task due to the low levels of concentration and strong matrix interferences. In atomic absorption spectrometry, the depression of analyte absorbance by up to 50% due to a cal-

cium matrix has been observed [6,7]. A hydroxyapatite matrix was shown to cause significant signal suppression (from 17 to 54%) for most of the trace elements during ICP MS measurements [8]. In ICP OES, interferences caused by calcium and other alkali earth metals were observed to be considerable, and often led to over- or under-estimation of analyte concentrations [9–11]. To overcome or reduce matrix effects, different calibration methods such as external calibration, matrix matching calibration, standard addition or internal standards have been proposed. Matrix matching calibration is often not possible due to unknown or changing sample composition, as in the case of some minerals. The use of an internal standard should be specific for many analytes due to the dependence of matrix effect magnitude on spectral line properties, as in ICP OES [9,11].

Matrix separation methods based on derivatisation, extraction, co-precipitation, chromatographic and flotation processes are used in both on-line and off-line modes [12–16].

Cloud point extraction (CPE), successfully applied for the separation and preconcentration of species like metal ions, biomaterials or organic compounds [17–20] seems to be a promising and suitable procedure for the separation of analytes from calcium matrices. There are only a few works dealing with the application of CPE to the multielemental trace analysis of samples with complex matrices, and they concern water samples of high salinity or hardness [21–28].

Matrix effects and the separation of analytes from interfering elements have been previously investigated; however, to the best our knowledge, the separation of trace elements from calcium matrices by the CPE method has not been reported. It concerns both

model solutions with high Ca concentrations, and natural samples such as dolomites and bones.

The main object of the present study was the development of an analytical method based on cloud point extraction separation that could be applied with the use of ICP OES and other spectroscopic methods to simultaneously determine trace elements (including hard toxic as Cd and Pb) in calcium-rich samples. Optimisation of the CPE procedure using Triton X-114 as a non-ionic surfactant and two pyridylazo chelating agents was performed to determine eight elements (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) in dolomites and bone tissues by means of ICP OES detection.

2. Experimental

2.1. Instrumentation

The concentrations of elements (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) were measured with the use of a Jobin Yvon sequential inductively coupled plasma emission spectrometer (JY 38S). The operating parameters and analytical line wavelengths used are shown in Table 1. The pH values were measured with a CP-401 pH meter (Elmetron) equipped with a combined glass electrode. A thermostatic bath maintained at the desired temperature was used for the cloud point experiments. A MPW-350 centrifuge (Med. Instruments) was used to accelerate the phase separation. Ultrasonic extraction of the samples was performed using an ultrasonic bath (UltrasonsH Selecta).

2.2. Reagents and standard solutions

All reagents used in this study were of analytical grade. The non-ionic surfactant Triton X-114 (10%) (Fluka GmBh, Switzerland) was used for the extraction experiments. The 1% solution of 5-Br-PADAP [2-(5-bromo-2-pyridylazo)-5-diethylaminophenol] and 1% solution of PAN [1-(2-pyridylazo)-2-naphthol] (Sigma–Aldrich, Germany) were prepared by dissolving appropriate amounts of these reagents in ethanol (POCh S.A., Poland). A multielemental stock standard solution of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn ($100\,mg\,L^{-1}$) was prepared from the single element ICP OES standard solutions ($1000\,mg\,L^{-1}$). Working standard solutions were prepared daily by suitable dilutions. Solutions of Ca and Mg were prepared from their nitrate salts (POCh). An ammonia buffer solution of pH 10 and 1% NaOH served for adjustment of the pH of samples.

For ultrasonic extraction, 1.0 M HCl (Merck KGaA, Germany) was applied as a leaching agent. With each set of extractions, a blank sample was simultaneously prepared through the complete procedure, analysed and then used for a correction of the analytical signals. All dissolutions and dilutions were performed

Table 1
Instrumental and operating conditions for ICP-OES.

Generator	40.68 MHz
Rf power	1200 W
Injector i.d.	2.5 mm
Spray chamber	Cyclonic
Nebuliser	Burgener (MiraMist)
Monochromator	1 m with 4320/2400 grooves/mm grating
Plasma observation zone	12 mm above load coil
Ar flow rates	Plasma gas: $14\,L\,min^{-1}$
	Sheath gas: $0.2\,L\,min^{-1}$
	Carrier gas: $0.3\,L\,min^{-1}$
Sample uptake	$0.9\,mL\,min^{-1}$
Lines (wavelengths in nm)	Cd II (228.80), Co II (238.89), Cr II (267.72), Cu I (324.75), Mn II (259.37), Ni II (221.65), Pb II (220.35), Zn I (213.86)
	I: atomic; II: ionic lines.

with deionised water ($18.3\,M\Omega\,cm^{-1}$) obtained from EASYpure™ (Baernstaed, Thermolyne Corporation, USA). All glassware was cleaned with 10% nitric acid in an ultrasonic bath and rinsed several times with deionised water.

2.3. Samples and sample preparation

In our experiments, model solutions and two kinds of natural samples, dolomites and bone ash (NIST 1400 Bone Ash), were used. Dolomites were taken from different fertiliser factories.

About 0.5 g of bone ash or 2 g of dolomite were accurately weighted into a polyethylene tube, treated with 50 mL of 1 M HCl and placed into the ultrasonic bath for 40 min at 60 °C. After the extraction, the sample solutions were quantitatively transferred into 100 mL volumetric flasks and made up to volume with deionised water. Before CPE, all of the solutions were filtered through a hard filter paper.

2.4. Cloud point extraction procedure

An aliquot of 20.00 mL of the standard or sample solution was placed in a tube then 1 mL of buffer solution, 0.26–0.6 mL of Triton X-114 and appropriate amounts of 5-Br-PADAP or PAN solutions, were added. The sample solutions before buffer addition were neutralised by NaOH. The tubes were kept in a thermostatic bath at 50 °C for 40 min. The separation of the two phases was accelerated by centrifugation of the solution for 12 min at 3500 rpm. The tube was then placed in an ice bath for 30 min to increase the viscosity of the surfactant-rich phase. The aqueous phase was decanted by inverting the tube. In order to decrease the viscosity of the organic phase, 1 mL of HNO_3 was added and the solution was transferred to the flask and made up to 10.0 mL with deionised water. Blanks were submitted to the same procedure in parallel with the samples.

3. Results and discussion

3.1. Optimising the CPE procedure

The cloud point extraction procedure was optimised here using the synthetic solutions (aqueous standards) of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, simultaneously for the metal ions. The effects of pH, surfactant and chelating agent concentrations were examined and the
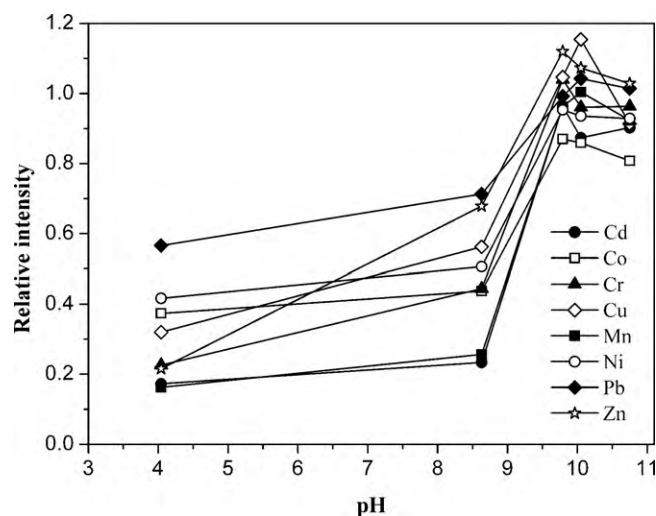

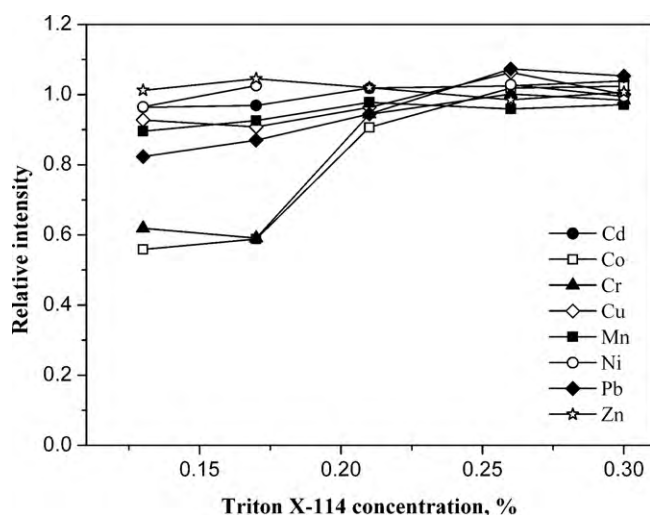**Fig. 1.** Effect of pH on CPE efficiency using 5-Br-PADAP as chelating agent ($c_{Triton\,X-114} = 0.20\%$).

Fig. 2. Effect of Triton X-114 concentration on the efficiency of CPE with 5-Br-PADAP (pH = 10).

Fig. 3. Effects caused by the Ca–Mg matrix before and after the CPE procedure ($c_{Ca} = 2300$ mg L^{-1}, $c_{Mg} = 1500$ mg L^{-1}, pH = 10.0, $c_{Triton X-114} = 0.25\%$, $c_{5-Br-PADAP} = 1.3 \times 10^{-2}\%$, $c_{PAN} = 2.0 \times 10^{-3}\%$). Error bars represent the standard deviations ($n = 3$).

other parameters, i.e. equilibration time, incubation temperature and centrifugation conditions were taken from our earlier study [29] and the literature [17–20].

The pH is a critical parameter in the formation of hydrophobic complexes of metal ions with chelating agents and their subsequent extraction. Optimal pH values for complexation of the metal ions with PAN and CPE were established earlier [29], with the optimal value being 9. At the use of 5-Br-PADAP as a chelating agent, the effect of pH was studied within the pH range from 4.0 to 10.8 and was presented in Fig. 1. The relative intensity (ratio of the line intensity measured for the solution after CPE to the intensity measured for the standard solution at the same element concentrations) was the highest for the all metal ions in the pH range of 9.8–10.1. For
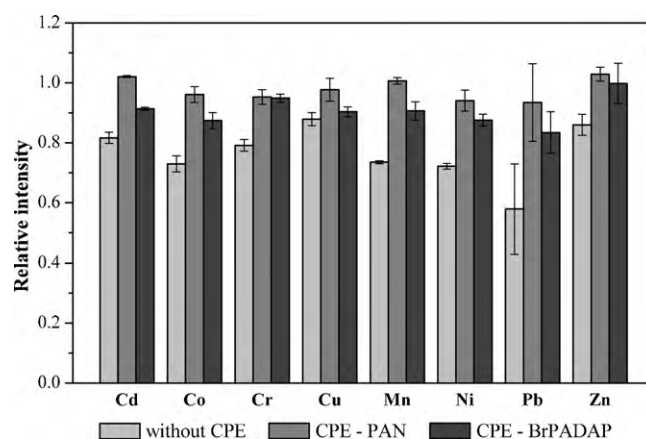
further simultaneous extraction of the metal ions with the use of 5-Br-PADAP, pH 10 was chosen.

The effect of Triton X-114 concentration was studied in the range of 0.13–0.30% (v/v). Similar to the results obtained during experiments with PAN [29], the extraction efficiency using 5-Br-PADAP increased with the Triton X-114 concentration up to 0.25% (v/v). Above this value, the efficiency remained approximately constant as shown in Fig. 2. A surfactant concentration of 0.25% (v/v) was chosen for both chelating agents as the optimum concentration for performing CPE of all metal ions.

The success of the CPE procedure depends mainly on the hydrophobicity of the formed complexes and also on their efficient kinetic transfer into the surfactant-rich phase [18]. The complexation of the analytes with 5-Br-PADAP was found to be suitable

Table 2
Analytical characteristics of the CPE procedure.

Element	Chelating agent	Slope	Concentration range (μg L^{-1})	Correlation coefficient	RSD (%)	LOD (μg L^{-1})
Cd	PAN	164,303	20–500	0.9996	1.6	4.0
	5-Br-PADAP	149,586	15–500	0.9999	3.3	5.3
Co	PAN	89,637	15–300	0.9897	3.4	4.6
	5-Br-PADAP	77,463	15–300	0.9939	4.8	4.3
Cr	PAN	174,862	15–1000	0.9994	1.5	2.1
	5-Br-PADAP	171,548	10–1000	0.9999	3.1	2.5
Cu	PAN	172,504	10–500	0.9998	3.0	1.9
	5-Br-PADAP	167,396	15–500	0.9997	2.4	2.6
Mn	PAN	1,090,253	2–1000	0.9995	1.5	0.3
	5-Br-PADAP	1,002,282	2–1000	0.9999	4.1	0.7
Ni	PAN	73,545	40–400	0.9964	4.8	5.6
	5-Br-PADAP	75,503	20–400	0.9911	3.4	14
Pb	PAN	7750	100–5000	0.9996	10.5	69
	5-Br-PADAP	7199	100–5000	0.9952	7.0	40
Zn	PAN	89,286	20–5000	0.9994	2.2	2.0
	5-Br-PADAP	89,802	40–5000	0.9989	5.8	4.7

Table 3
Concentrations of the major components in samples, in mg g^{-1} (average $\pm$ SD, $n = 3$).

	Bone ash		Dolomite 1		Dolomite 2		Dolomite 3	
	ICP OES[a]	Certified	ICP OES[a]	Titration	ICP OES[a]	Titration	ICP OES[a]	Titration
Ca	383.6 ± 3.0	381.8 ± 1.3	206.6 ± 6.2	220.9 ± 2.5	196.6 ± 4.2	216.7 ± 1.6	265.6 ± 3.8	279.7 ± 2.0
Mg	6.83 ± 0.16	6.84 ± 0.13	87.4 ± 7.0	87.62 ± 0.78	82.3 ± 9.6	85.3 ± 2.0	36.0 ± 4.2	39.74 ± 0.54

[a] Calibration based on aqueous standards.

Table 4
Analytical recoveries of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in different natural samples ($n = 3$).[a]

Element	Added (µg mL^{-1})	Bone ash		Dolomite 1				Dolomite 2		Dolomite 3	
		5-Br-PADAP		5-Br-PADAP		PAN		PAN		5-Br-PADAP	
		Found (mean ± SD)	Recovery (%)	Found (mean ± SD)	Recovery (%)	Found (mean ± SD)	Recovery (%)	Found (mean ± SD)	Recovery (%)	Found (mean ± SD)	Recovery (%)
Cd				0.015 ± 0.001		0.020 ± 0.001		0.007 ± 0.002		0.015 ± 0.003	
	0.2	0.190 ± 0.005	95.0	0.202 ± 0.004	94.0	0.208 ± 0.009	94.5	0.198 ± 0.004	95.7	0.189 ± 0.001	87.9
Co								0.033 ± 0.001		0.028 ± 0.003	
	0.2	0.171 ± 0.004	85.5	0.184 ± 0.040	92.0	0.216 ± 0.030	108	0.221 ± 0.003	94.8	0.226 ± 0.006	99.1
Cr		0.022 ± 0.001		0.019 ± 0.001		0.017 ± 0.002				0.008 ± 0.002	
	0.2	0.206 ± 0.005	92.8	0.210 ± 0.004	95.9	0.206 ± 0.007	94.9	0.182 ± 0.007	91.0	0.193 ± 0.006	92.8
Cu				0.036 ± 0.006		0.030 ± 0.003		0.021 ± 0.003		0.027 ± 0.001	
	0.2	0.174 ± 0.02	87.0	0.228 ± 0.001	96.6	0.221 ± 0.008	96.1	0.211 ± 0.001	95.5	0.210 ± 0.005	92.5
Mn		0.044 ± 0.007		5.18 ± 0.11	108.1[b]	5.29 ± 0.01	108.2[b]	13.1 ± 0.4	95.6[b]	16.8 ± 0.05	102.1[b]
	0.2	0.220 ± 0.014	90.2	5.658 ± 0.028	105.2	5.467 ± 0.100	99.6	13.5 ± 0.3	101.5	17.5 ± 0.3	102.9
Ni		0.024 ± 0.008		0.068 ± 0.015		0.064 ± 0.002		0.032 ± 0.005		0.041 ± 0.007	
	0.2	0.230 ± 0.010	103	0.287 ± 0.014	107	0.282 ± 0.013	107	0.262 ± 0.008	112.9	0.274 ± 0.005	113.7
Pb				0.642 ± 0.054		0.672 ± 0.004		0.418 ± 0.062		0.567 ± 0.074	
	0.2	0.222 ± 0.004	111	0.919 ± 0.033	109.1	0.859 ± 0.062	98.5	0.590 ± 0.018	95.5	0.816 ± 0.035	106.4
Zn		0.438 ± 0.03		0.971 ± 0.065	92.5[b]	1.085 ± 0.064	103.3[b]	2.09 ± 0.03	96.8[b]	8.88 ± 0.70	99.2[b]
	0.2	0.634 ± 0.05	99.4	1.202 ± 0.076	102.6	1.242 ± 0.020	96.6	2.30 ± 0.07	100.4	9.02 ± 0.04	99.3

[a] Calibration based on aqueous standards submitted to the optimised CPE procedure.

[b] Recoveries calculated in relation to 25-fold diluted sample solutions.

Table 5
Analytical results obtained for reference material (NIST 1400 Bone Ash) after ultrasound-assisted extraction without and with the CPE procedure.

Element	Concentration[a]		
	With CPE[b]	Without CPE[c]	Certified value
Cr	6.49 ± 0.20	6.6 ± 1.4	
Cu	3.9 ± 0.2	3.9 ± 0.8	2.3[d]
Mn	16.9 ± 1.4	10.4 ± 0.4	17[d]
Ni	8.5 ± 1.0	5.04 ± 0.35	
Pb	9.18 ± 0.65	9.42 ± 1.1	9.07 ± 0.12
Zn	182 ± 4.5	177.4 ± 3.9	181 ± 3

[a] Mean values $\pm$ SD ($\mu g\, g^{-1}$), $n = 3$.
[b] Calibration based on aqueous standards submitted to the optimised CPE procedure.
[c] Standard addition calibration.
[d] Information value.

when the molar concentration ratio of chelating agent to metal ion was higher than 10. For simultaneous extraction of the ions with PAN as a chelating agent, according to an earlier study [29], at least a 5-fold molar excess of PAN over the sum of the ions was used.

3.2. Matrix effects

The matrix effect was expressed here as a relative intensity, i.e. the ratio of intensity obtained for the solution with the matrix to the intensity for the solution without the matrix at the same element concentration. Calcium is regarded as one of the elements that produces the most serious interferences in ICP OES [10,30]. A lowering of the analytical signals reaches 40% depending on the element and the line used for measurements [10,31]. The feasibility the CPE procedure for the determination of metal ions in calcium-rich matrices was investigated in the range of Ca concentration from 500 to $5000\, mg\, L^{-1}$. Extraction efficiencies for Cd, Ni, Cu, Pb, Mn and Zn were quantitatively independent of the Ca concentration, up to a 0.5% Ca content. Only for Cr and Co at calcium concentration above 0.2%, the efficiencies were about 90%.

In some materials (dolomites, supplements), in addition to the high calcium content, a smaller but considerable amount of magnesium was present. Therefore, samples with Ca–Mg matrices were also investigated.

Two synthetic solutions (matrix A: Ca-$2300\, mg\, L^{-1}$, Mg-$1500\, mg\, L^{-1}$ and matrix B: Ca-$3000\, mg\, L^{-1}$ and Mg-$700\, mg\, L^{-1}$) were used to compare the effects caused by Ca and Mg on the determination of trace elements without and with the CPE procedure. The differences between the effects observed for samples "A" and "B" were negligible, in practice. The results for the matrix A are presented in Fig. 3. Although the concentrations of Ca and Mg were not high and the plasma was operated under robust conditions (Mg II-to-Mg I intensity ratio was about 11), presence of Ca and Mg in the samples caused considerable lowering of the analytical signals, from 10% for Cu to above 40% for Pb. After conducting the CPE procedure, the relative intensities were in the range of 0.95–1.03 for PAN. Slightly worse results (up to 10%) were obtained using 5-Br-PADAP as chelating agent. It concerned such elements as Cd, Co, Mn and Ni. For the other elements the differences were in limits of standard deviation uncertainties. It leads to the conclusion that PAN is more universal agent assuring better reduction of the Ca and Mg induced interferences.

3.3. Analytical figures of merit

Calibration curves were obtained by preconcentration of 20 mL of the solutions containing known amounts of the analyte (in the range of 0–$0.40\, mg\, L^{-1}$) under the experimental conditions specified in the optimised procedure. Good linear regression with

high correlation coefficients was established between the plasma emission response and the ion concentration both for PAN and 5-Br-PADAP. In the case of cobalt the linear range was as high as $0.3\, mg\, L^{-1}$. Above this value, the extraction efficiency for cobalt gradually decreased. In other investigations on cobalt determination using the CPE procedure, the linear dynamic range for Co was also very limited [32,33].

The precision of the procedure was determined as the relative standard deviation (RSD) obtained for $n = 10$ independent samples containing $100\, \mu g\, L^{-1}$ of metal ions subjected to the complete procedure. The RSD values were from 1.5% for Mn to 11% for Pb. The limit of detection (LOD) was calculated in the standard way (criterion 3σ) from the expression LOD = $3\sigma/a$, where a is a slope coefficient connected to a sensitivity and σ means the standard deviation of the blank samples for 12 independent measurements. The analytical characteristics for both 5-Br-PADAP and PAN method was provided in Table 2. The limits of detection were lower, from two to five times, compared to those obtained without the CPE method.

As the amount of the target ions is measured after CPE in final volume of 1.5 mL (0.5 mL surfactant-rich phase and 1.0 mL of nitric acid) the solution is concentrated by a factor of 13. Higher preconcentration can be obtained using more volume of the sample solution. However for simultaneous multielemental analysis and repeatability of intensity measurements by ICP OES such a preconcentrated solution was diluted a few times to have sufficient sample volume for the all measurements.

3.4. Analysis of natural samples

The developed method was applied to dolomites and bone ash in order to evaluate its feasibility for assaying trace metals in natural samples. In addition to the trace element analysis, the matrix elements i.e. Ca and Mg were also determined to complete and extend our knowledge of the examined materials. The Ca and Mg concentrations in the HCl extracts of the samples were measured by ICP OES in 25- and 200-fold diluted solutions. The results were compared with the certified values for bone ash and with the results of a conventional complexometric titration method for the dolomites, and are presented in Table 3. In the complexometric determination, titration with EDTA using eriochrome black T at pH 10 for the sum of Ca and Mg and using murexide at pH 12 for the Ca determination was applied [34,35]. The agreement between measured and certified contents for Ca and Mg has seemed to be worthy to note it.

Ultrasound-assisted (US) extraction as a sample preparation method was used in accordance with papers devoted to comparisons of the US extraction of various materials with acidic media and other digestion methods [36,37]. US leaching usually allows for high recoveries of many elements, with the exception of some metals such as Al, Fe or Ti. For bone ash and the dolomites, the leaching yields of Ca and Mg were almost quantitative, above 90%.

In the bone extract solutions subjected to CPE, the calcium concentration was about $2500\, mg\, L^{-1}$. Concentrations of Ca and Mg in the extract solutions of the dolomites were about 2500 and $1100\, mg\, L^{-1}$ for dolomites 1 and 2, and 3300 and $500\, mg\, L^{-1}$ for dolomite 3. The iron concentration in the dolomite extracts was $40–50\, mg\, L^{-1}$.

The recovery experiments were carried out by spiking the samples with known amounts of Cd, Cu, Co, Cr, Mn, Ni, Pb and Zn before CPE. The results for bone ash and dolomites are shown in Table 4. In addition, the concentrations of Zn and Mn measured after 25-fold dilution of the dolomite extracts, when the matrix effects were negligible, served to calculate the Zn and Mn recoveries for the non-spiked sample solutions (see Table 4).

Table 6
Analyte separation methods recently applied for multielemental trace analysis of calcium-rich samples.

Sample	Separation method	Analyte (LOD[a])	RSD (%)	Ratio (m/v)[b]	Detection technique	Reference
Gypsum, Calcite, Dolomite	Flotation with Pb(HMDTC)$_2$ collector	Cd(60), Cr(100), Co(130), Cu(160), Ni(300), Tl(7710), Zn(200)	Not given	0.5 g/1 L	ICP OES	[39]
Dolomite, Calcite, Gypsum	Flotation with Co(HMDTC)$_3$ collector	Ag(105), Cd(80), Cr(195), Cu(142), Ni(212), Pb(450), Zn(235)	0.9–3.8	0.4–0.5 g/1 L	ICP OES	[40]
Aragonite	Flotation with Fe(HMDTC)$_3$ collector, extraction of carbamate complexes into MIBK	Co(8), Cu(17), Ni(9), Pb(7.2)	2.6–5.3 (flotation)	1 g/1 L	ET AAS	[7]
			1.6–4.3 (extraction)	0.2–0.5 g/15 mL		
Dolomite, Gypsum	Flotation with Fe(HMDTC)$_3$ collector	Ag(21), Cd(19), Cr(14), Mn(1500), Tl(110), Zn(800)	2.0–6.3	1 g/1 L	ET AAS, FAAS	[6]
Fish otoliths	FI separation on iminodiacetate resin	Cu(0.3), Ni(1.1), Zn(1.2), Co(0.01), Pb(0.1), Cd(0.55), Fe(1.1)	0.1–3.3	0.2–0.5 g/50 mL	ICP MS	[13]
Bone ash, Dolomite	CPE	Cd(100), Co(108), Cr(52), Cu(48), Mn(8), Ni(149), Pb(1000), Zn(50)	1.5–10.5	0.5–2 g/100 mL	ICP OES	This study

[a] LOD values given in $\mu g\,g^{-1}$.
[b] Mass of sample (m); volume of sample (v).

The recoveries obtained after the CPE procedure were very high (above 90%) for most of the investigated elements. For the samples with higher calcium contents (extracts of bone ash), the extraction yields were slightly lower for Cu and Co.

Comparison of the calcium and magnesium concentrations in solutions before and after CPE showed that only up to 10% Ca and 20% Mg was retained with analytes in the surfactant-rich phase. The matrix effects at such low Ca (and Mg) concentrations are negligible. The surfactant presence in the sample did not change the plasma parameters or plasma responses [29,38]; therefore, the use of aqueous standard solutions without matrix matching is sufficient for calibration and avoids additional risk of contamination. In Table 5, the results obtained for some trace elements in bone ash after ultrasound-assisted extraction with and without the CPE procedure are compared with the certified values.

The information about calibration procedure adopted in each case was provided as footnotes in Tables 3–5.

A comparison between the characteristics of the proposed CPE method and other methods used for analyte separation from calcium-rich samples is summarised in Table 6. As can be seen our quick and simple method allows the analysis of highly concentrated sample solutions with the limits of detection comparable to those obtained using the other techniques.

4. Conclusion

We developed a cloud point extraction (CPE) procedure that can be successfully applied as a separation step prior to multielemental determination of trace elements (including toxic metals) by ICP OES in samples with calcium-rich matrices. The proposed method allows the separation of the analyte from the matrix with almost 90% efficiency and eliminates or significantly reduces interferences caused by Ca. The analytical figures of merit, such as accuracy and precision, were good and the limits of detection were lower by several fold. The analysis of spiked samples and certified reference material showed that the method represents a promising approach to determining Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn in calcium-rich samples of environmental, toxicological and industrial interest.

Additionally, the method is characterized by simplicity, high efficiency, a low cost, and is in accordance with the green chemistry concept. It is a good alternative to solvent extraction and other methods of separation, and seems to be applicable not only to ICP OES, but also to other techniques used for multielemental analysis. Furthermore, ultrasound-assisted leaching with diluted HCl, applied here, can replace the total digestion of some calcium-rich samples, as demonstrated by analysis of the certified reference material.

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