APPLICATION OF FLEXIBLE MULTI-ELEMENTAL ICP-OES DETECTION IN FRACTIONATION OF POTENTIALLY TOXIC ELEMENT CONTENT OF SOLID ENVIRONMENTAL SAMPLES BY A SEQUENTIAL EXTRACTION PROCEDURE

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ABSTRACT
Remediation of areas contaminated by potentially toxic elements (PTE) requires the appropriate assessment of the environmental mobility of contaminants. The fractionation techniques developed for agrochemical and environmental purposes model the pathways of environmental mobilization mainly by sequential extraction procedures. In Europe mostly the simplified extraction scheme proposed by Community Bureau of Reference (BCR) in 1993 is widely used, why only to this certified sediment sample (BCR 701) is available, certified for fractionation of six elements (Cu, Cd, Cr, Ni, Pb, Zn). In the BCR extracts the reagent-solvents applied in leaching steps cause strong matrix interferences when for determination the PTE-contents of these solutions the multielemental capacity of inductively coupled plasma optical emission spectrometry (ICP-OES) should be utilized. Due to the different source of contamination the flexible multi-elemental ICP-OES method should be applied for analysis of the different BCR-extractant-solvent media which makes possible the reliable detection of all occurring PTE in the area. For this purpose as the most adequate solution the application of ICP-OES spectrometer with *charge-coupled device* (CCD)-detection was selected which is able to record the entire spectral range between 120-800 nm. On the basis of detailed study of BCR-solvent-matrix- and expected-analite-line interferences it was established that the sensitivities of the prominent lines of pollutant elements strongly depend on the type of extractants. For improving the accuracy of analytical results obtained for soils and environmental sediments, matrix matched calibration, internal standardization and robust plasma conditions were recommended and optimized. The successful application of this methodology is presented for a PTE-contamited lake sediment sample and for selected typical Hungarian soil samples stored in sample bank of Hungarian Soil Protection Information and Monitoring System.

Keywords: potentially toxic element; sequential extraction; fractionation; ICP-OES; multielemental determination; sediments and soils.

1. INTRODUCTION
Mobility and biological impact of potentially toxic elements (PTE) is determined by the chemical speciation of these elements in the environmental systems. According to recommendation of IUPAC Committees [1] speciation means the quantitative distribution of a given element among its chemical species identifiable in the system. Total biological risk assessment in PTE-contaminated areas should be based on complete speciation of detectable

contaminant elements, however complete speciation is an impracticable analytical task, As a compromise, fractionation techniques were developed in which the solvents (reagents) modeling the pathways of environmental mobilization are applied sequentially for the extraction of PTE content of solid environmental samples as proposed by Tessier [2]. In Europe it is the simplified extraction scheme issued by Community Bureau of Reference (BCR) in 1993 and modified in 2001 that is most widely used [3, 4]. Up to now this has been only a fractionation procedure, to which certified sediment samples (BCR 601 and 701) were issued [4, 5, 6, 7, 8, 9, 10], therefore was it selected for present quality assessment studies.

In the 1st, 2nd and 3rd steps of the BCR procedure batch leaching technique is applied, the solid sediment or soil sample is shaken by the reagent-solvents for 16 hours and the extracts are separated by centrifugation respectively. By this way the chemical structures of the sediment or soil samples are gradually decomposed and the following mobility fractions of PTE can be distinguished:

1st step: Water-soluble and carbonate-bound fraction, dissoluble in diluted acetic acid;

2nd step: Associated with reducible Fe- and Mn-oxides, dissoluble in hydroxilamine hydrochloride;

3rd step: Organic complexed and sulphides, dissoluble after oxidation by H_2O_2 in ammonium-acetate;

(+1) step: Residual fraction, soluble by digestion in oxidative acids (HNO_3/H_2O_2, or aqua regia).

The certification is given only for the 1st, 2nd and 3rd fractions, for determination of the (+1) residual fraction and for direct analysis of PTE content of original BCR 701 CRM sample only indicative values are given for aqua regia extraction according to ISO Norm 11466 [11].

Standardization of the BCR procedure, however, has up to now been hindered by methodological problems:

- The solvents applied in the BCR system do not model natural mobilization processes and do not preserve intact species forms for further speciation analysis.
- The time demands of the batch leaching extraction steps is too long (4-5 days).
- Certified reference material (CRM) sample which is certified for the fractionation of six elements (Cu, Cd, Cr, Ni, Pb, Zn) is available only for freshwater sediments, therefore the extension of validation for other environmental matrices (soils, rocks, ores, solid wastes) and for further PTE is limited.
- The results of completion the BCR sequential extraction procedure is four solutions with the excess concentration of reagents applied in leaching steps. When for determination the PTE-contents of these solutions the multi-elemental capacity of spectrochemical analytical techniques like inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) should be utilized, we have to calculate with significant solvent-matrix interferences, which may strongly influence the reliability of analytical results.

Up to now methodological developments to improve the BCR system have been mainly focused on extraction procedures: continuous flow systems were developed [12, 13, 14, 15, 16,17], alternative reagents were applied [18, 19, 20, 21,22] and acceleration of batch leaching by sonication [23] or microwave treatment [24] was applied. A review of the methodological development of the BCR sequential extraction procedure was given in our previous papers [25a,b].

When the elaboration and the modification of BCR procedure was performed in 1993 and in 2001 the matrix interferences caused by the reagent content of BCR extractant-solvents during spectrochemical element detection were not systematically assessed. In those interlaboratory analytical campaigns all participating laboratories have applied their own

methodology and quality assurance individually for element analysis, and the results of different methods as applied in different laboratories were compared statistically to detect sources of methodological errors of analytical procedures [3, 4, 5, 6, 7, 8, 9, 10]. For the determination of Cu, Cd, Cr, Ni, Pb, Zn concentrations in BCR extracts flame atomic absorption spectrometry (FAAS), electrothermal atomization atomic absorption spectrometry (ETA-AAS), ICP-OES and ICP-MS methods were applied in the different laboratories and the solvent matrix interferences were mainly reduced by solvent-matrix-matched calibration and in several cases by standard addition. The calibrations were optimized for the above six elements individually and only in a few cases ICP-OES or ICP-MS multi-elemental calibration was applied.

In spite of the above methodological problems the application of BCR procedure in risk assesment of PTE-contaminations is exponentially growing. Most of the applications were elaborated for PTE contaminated sediments. Soils and other environmental matrices were less often considered, because CRM is available only for sediments to the BCR procedure. Demand for the extension of application and validation to more PTE in other matrices (soils, rocks, sewage sluids, red mud, gravitation dust, compost, biofilm, etc.), however, is continuously growing, and for this purpose the application of robust simultaneous multi-elemental spectrochemical methods with flexible selection of analite elements seems to be the optimal choice [26-49]. Considering this trend the main goal of our recent study was to support the extension of BCR-fractionation to different solid matrices and to more PTE by means of elaboration a robust and flexible multielemental ICP-OES methodology. For this purpose the HORIBA Jobin Yvon ACTIVA-M ICP-OES spectrometer was selected which is equipped with rapid scanning charge-coupled device (CCD)-detection system and is able to record and acquisite the entire spectral range between 120-800 nm and supplied with a data base of single-element spectra with spectroscopic data under standard ICP operating conditions for 75 elements [50,51]. This data base, the instrument arrengement and operation mode provides appropriate information for multi-line selection adopted to the analytical task [52]. The program suggests more lines for each analyte that are adequate for the defined concentration range and that are not interfered by the concomitant elements when they are present at their highest expected concentration. The number of lines to be suggested, as well as sensitivity and interference filtering criteria, are user-defined. The analyte spectrum can be displayed along with those of concomitant elements and the blank spectrum. This helps in the acceptance or rejection of a line, and to determine the correct background correction positions [52]. In the users manual there are several proposal for optimal conditions for multi-elemental analysis of different type of samples (aequeos, oil, organic, salt), however such a complex task as the sequential extraction when four different aqeous solvent-matrix is applied requires additional study of matrix effects caused by BCR-extractants during multi-elemental ICP-OES determination, and a careful survey of spectral line coincidences of proposed analite lines [53, 54].

In a preliminary study BCR-solvent matrix matched multi-elemental ICP-OES calibration was applied for ten elements (Cd, Cr, Cu, Ni, Pb, Zn, Co, Fe, Mn, V) and the ICP-OES operating conditions were applied according to producer's manual proposal to aeqeous matrices [54] and accuracy of BCR procedure was controlled by fractionation of element content of BCR-701 sediment CRM sample. It was established that the sensitivity of ICP-OES determinations is strongly influenced by calibration solvent matrix, and the summarized recoveries of certified concentrations of the three certificated extraction steps are acceptable for all certified elements. However in the individual extraction steps for several elements are significantly outlying from the acceptable limits [25b]. For reliable application therefore this simple matrix matched calibration was not proved satisfactory and further improvement was necessary

based on study of the extractant-solvent matrix interferences [55] and controlling the interelement analite interferences. Utilizing the possibility of whole analytical spectral range acquisition the BCR solvent blank spectra, single elemental analite element spectra in each BCR solvent and finally the multi-elemental analite spectra in each BCR solvent were recorded with expected highest concentrations. All these spectra were stored in an electronic library and then the best interference-free spectral lines were selected on the basis of a detailed comparison of these spectra for all extractant media and for all analytical lines proposed by the instrument producer. After this the multi-elemental matrix matched calibration was repeated at elevated RF-power for reduction the solvent matrix effects [49, 55] with more robust plasma conditions, and internal standardization was applied to improve the reliability. Main goal of this methodological studies was the elaboration of such multielemental ICP-OES method which is flexibly and reliably applicable for evaluation of PTE-mobility in soils and in sediments by BCR-fractionation. The successful application of this optimalized method is presented on real lake-sediment and soil samples.

2. EXPERIMENTAL
2.1. BCR Sequential Extraction Procedure and its Quality Assesment

Quality assessment of BCR procedure with the CRM 701 sediment, reference sample was performed. The fractionation of its element content was performed according to the modified BCR protocol in triplicates, as described in Table 1 [10]. The 1st, 2nd and 3rd batch leaching steps were performed for 16 hours using a mechanical end-over-end shaker, at a speed of 240 ± 10 rpm, followed by centrifugation at 3000 g for 20 minutes.

Table 1. The BCR sequential extraction scheme

Extraction step	Extractant solvent	Element fraction
1st	0.11 M acetic acid (HOAc)	Exchangeable, water soluble, carbonate bound fraction
2nd	0.5 M NH_2–OH·HCl (adjusted to pH = 1.5 by adding 25 mL 2 M HNO_3)	Reducible fraction (joint to Fe/Mn oxides, oxyhydroxides)
3rd	(preliminary oxydization by 8.8 M H_2O_2) then 1 M NH_4OAc (pH = 2)	Oxidizable element fraction (bound to organic matter or sulphides)
(+1)	cc. HNO_3/H_2O_2 microwave supported digestion	Residual fraction (soluble in oxydative acids)

For the extraction of residual fraction in the (+1) step microwave supported cc. HNO_3/H_2O_2 digestion was applied according to the former Hungarian Standard [56].
Total soluble element content of the CRM 701 sample was determined also by microwave supported cc. HNO_3/H_2O_2 digestion of the original sample.
The results of microwave supported cc. HNO_3/H_2O_2 digestion-extraction were compared with aqua regia digestion-extraction according to ISO Norm 11466 [11] and with microwave supported aqua regia digestion-extraction.

2.2. Element Analytical Instrument [54]
HORIBA Jobin Yvon ACTIVA-M ICP-OES spectrometer was employed, which is able to record the entire UV-VIS spectrum range by rapid scanning CCD detection.
Generator: radio frequency, solid-state, 40.68 MHz, water cooled, 800-1550 W.

Plasma: fully demountable torch (3 mm i.d., alumina injector) with software controlled gas flow system. The gas-flows can be set by switching between valves of fix nominal cross-flow capacity:

Plasma gas flow:	P1: 12 L/min,	P2: 16 L/min.	
Sheath gas flow:	G1: 0.3 L/min,	G2: 0.5 L/min,	G3: 0.7 L/min.
Auxiliary gas flow:	OFF: 0 L/min,	ON: 0.6 L/min.	
Nebulizer gas pressure:		2.86 bar.	

Sample introduction: concentric glass nebulizer, cyclonic glass spray chamber, 3 channels peristaltic pump. Aerosol transport by the sheath device (patented HORIBA Jobin Yvon system).

Optical system: thermo-regulated, 0.64 meter focal length, dual back-to-back gratings, 4343 g/mm and 2400 g/mm used in the 1st order with optical resolution <10 pm for 120-430 nm and <18 pm for 430-800 nm.

Wavelength range: 120-800 nm, reference line set by the user (C 193.026 nm, or the Ar 404.442 nm).

Detection: back thinned illuminated CCD, 2048x512 pixels (13.5x13.5 μm), Peltier cooled.

2.3. ICP-OES Operational Parameters, Optimalization of Calibration

In the first stage of this study BCR-solvent matrix matched multi-elemental calibration was applied for ten elements (Cd, Cr, Cu, Ni, Pb, Zn, Co, Fe, Mn, V) applying operational analytical parameters and lines according to producer's manual proposed for multi-elemental analysis of environmental water samples (1st settings) [25b, 54]. Study of solvent matrix effects and spectral interferences was performed applying this 1st settings. Study of spectral interferences in the different calibration solutions is described in APPENDIX 1.

After that the matrix matched calibration was repeated at elevated RF-power and for all elements at least two analytical lines were selected (2nd settings) with gas flows proposed by producer to the applied RF-power. In 3rd settings the same RF-power was applied as in the 2nd settings but sheet gas flow was reduced and the Yttrium internal standard was applied, and interference-free analytical lines were selected for all elements (Table 2 and Table S2).

Table 2. ICP-OES operational parameters during optimalization of calibration

OPERATION PARAMETERS	1st settings	2nd settings	3rd settings
Incident RF-power	1000 W	1200 W	1200 W
Outer gas flow (Argon)	13.14 L/min	15.94 L/min	15.94 L/min
Sheet gas flow (Argon)	0.32 L/min	0.62 L/min	0.32 L/min
Auxiliary gas flow (Argon)	OFF	0.604 L/min	0.604 L/min
Nebulizer gas pressure (Argon)	2.86 bar	2.86 bar	2.86 bar
Nebulizer solution uptake (Meinhardt-cyclonic spray chamber)	0.85 mL/min	0.85 mL/min	0.85 mL/min
Internal standard	-	-	1 mg/L Yttrium

2.4. Preparation of Matrix Matched Calibration Solutions

For preparing the calibration solutions MERCK CertiPUR ICP multi-element 1.11355.0100 standard solution was used, containing elements Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn in 1000 mg/L concentraion. Volumes corresponding to 0, 5 and 20 mg/L concentrations were pipetted into a 50 ml volumetric flask and then diluted by solvents applied in the steps of BCR sequential extraction procedure:

1st step: 0.11 M acetic acid
2nd step: 0.5 M hydroxylamine-hydrochloride
3rd step: 1 M ammonium-acetate
(+1) step: 13 (m/m)% nitric acid

3. RESULTS

3.1. Fractionation Results Obtained with BCR-solvent Matrix Matched Multi-elemental Calibration for the Three Different Operational Settings

At producer proposed analytical line wavelengths several spectral overlapping was occurred as described in APPENDIX 1. On Figure S1, S2, S3, S4 characteristic interelemental line coincidences are presented for Cd, Co, Pb and Zn lines proposed to application. As a result of interelemental line coincidence study it was establiahed that primary producer proposed analytical lines can be used for Cr, Cu, Fe, Mn, Pb, and Zn, but low level spectral interferences occur for Zn and Pb. For Cd, Co, Ni the primary proposed lines could not be used. As an example for result of rejection of primary proposed analytical line the analytical calibration lines obtained for Cd at three different operational settings in case of different solvents are presented on Figure S5(a). For comparison on Figure S5(b) the analytical calibration lines obtained for Zn using the primary proposed lines at three different operational settings in case of different solvents are presented.

For detailed comparison the parameters of analytical calibration lines, the background equivalent concentrations (BEC) and the instrumental detection limits [LOD(3σ)] obtained for different extraction matrices at three different ICP-OES operational settings are summarized in Tables S3, S4, S5 of APPENDIX 2. Data in Table S3 of APPENDIX 2 were published earlier [25b], but as a reference for comparison is given there too.

It can be observed that the calibration solvent media strongly influences the slope of the analytical calibration lines (i.e. the B sensitivity values) at the three different operational settings. The residual standard deviation values show, that the best fitting of analytical lines was achieved at 3rd operational settings. The solvent matrix influence can be easier compared if the B sensitivity values are normalized to the (+1) step solvent [13 (m/m) % nitric acid] while in general nitric acid medium is used in ICP-OES calibration (Table 3).

Table 3. The ratio of B sensitivity values in different extractant media related to the corresponding sensitivity values obtained in 13 (m/m) % nitric acid medium at the three operational setting.

Element	1st setting			2nd setting			3rd setting		
	HOAc	NH₂OH	NH₄OAc	HOAc	NH₂OH	NH₄OAc	HOAc	NH₂OH	NH₄OAc
Cd 214.441	0.586	0.639	0.937	1.158	1.254	0.512			
Cd 228.802				0.976	1.078	0.825	0.973	0.972	0.817
Co 230.785	0.835	0.881	1.094	1.109	1.149	0.548			
Co 228.615				1.062	1.098	0.506	0.949	0.967	0.929
Cr 205.571	0.820	0.819	1.108	1.210	1.164	0.545	0.944	0.912	0.961
Cr 283.563				1.272	1.252	0.690			
Cu 324.754	1.532	1.570	1.447	0.905	1.007	0.873	1.032	1.014	0.887
Cu 327.395				0.937	1.001	0.916			
Fe 240.489				1.156	1.210	0.556			
Fe 259.940	0.948	0.944	1.190	1.375	1.394	0.854	0.965	1.000	0.915
Mn 257.610	0.854	0.863	1.222	1.112	1.225	0.634	0.963	0.981	0.966
Mn 279.482				0.799	0.847	0.636			
Ni 221.650				0.987	1.067	0.405			
Ni 222.296	0.771	0.809	1.067	0.983	1.061	0.421			
Ni 231.604							0.964	0.977	0.907
Pb 217.000				0.906	0.992	0.532			
Pb 220.353	0.630	0675	0.911	0.797	0.905	0.273	0.763	0.945	0.855
V 309.311	1.013	1.014	1.217	1.228	1.313	0.681			

V 311.071				1.224	1.285	0.700			
Zn 213.857	0.691	0.729	0.910	1.391	1.426	0.755	0.812	0.937	0.832
Zn 280.087				0.789	0.838	0.645			
AVERAGE	**0.871**	**0.891**	**1.092**	**1.067**	**1.128**	**0.626**	**0.929**	**0.967**	**0.897**

It can be established that at the **1st operational settings** using the acetic acid and hydroxilamin-hydrocloride containing calibrant solvents significant decrease of sensitivity was obtained which mainly can be attributed to the nebulization matrix-effects [55]. On contrary the 1 M ammonium-acetate containing calibration solvent resulted in significant, but uneven increase of sensitivities for different elements. In this case probably chemical matrix interferences have overcompensated the nebulization-matrix effects.

When the incident RF-power was increased to get more robust plasma at **2nd settings** the reverse situation was experienced: in the acetic acid and hydroxilamin-hydrocloride containing calibrant solvents significant, but uneven increase of sensitivities was obtained while the ammonium-acetate containing calibration solvent resulted in dramatic decrease of sensitivities for different elements. These effects probably can be attributed to change of plasma shape due to the elevated sheet gas flow, while the position of observation height is fixedly set to optimal compromise conditions by the producer.

When **3rd settings** was used the sheet gas flow was reduced at elevated RF-power and Yttrium internal standard was applied. In this case the sensitivities in all three calibrant media shows more uniform picture the ratios in all cases are less than 1.000, in the case of acetic acid and hydroxilamin-hydrocloride containing calibrant solvents these differences are not significant. At this 3rd settings the background equivalent concentrations (BEC) are minimal and change in a narrow range supporting the right selection of Yttrium internal standard. If solutions of such diverse composition should be analyzed reliably application of an internal standard is necessary.

The robustness of the three plasma operational settings was controlled by the determination of intensity ratio of magnesium ionic and atomic lines [MgII(280.271 nm)/MgI(285.213 nm)] as proposed by J.M. Mermet [57]. The results summarized in Table 4 clearly show that the robustness of plasma drastically decreased at 2nd operational settings and by the 3rd operational settings was improved related to the 1st operational settings which is proposed by the manufacturer to multi-elemental analysis of environmental water samples.

Table 4. Results of robustness control of three operational settings by determination of the MgII(280.271 nm)/MgI(285.213 nm) ionic/atomic line intensity ratio measured in different BCR extracts. (In brackets MgI 285.213 nm line/background intensity ratios are given.)

BCR extractant	Intensity ratio of MgII(280.271 nm)/MgI(285.213 nm) lines					
	1st settings		2nd settings		3rd settings	
0.11 M HOAc	8	(64.7)	3	(119.3)	9	(70.9)
0.5 M NH$_2$OH·HCl	8	(61.3)	3	(137.3)	10	(66.7)
1 M NH$_4$ OAc	9	(64.6)	3	(55.0)	11	(66.5)
13 (m/m) % HNO$_3$	8	(61.7)	3	(142.8)	9	(70.4)

Summarizing the above it may be concluded that improving the robustness of the plasma and elimination of matrix effects caused by the calibrant solvents is not possible by increasing the incident RF-power only while in this case the MgI 285.213 nm line/background intensity ratios were changed drastically and to achieve more robust conditions the sheet gas flow must be adopted properly.

3.2. Accuracy of fractionation applying the BCR-solvent Matrix Matched Multi-elemental Calibration

Accuracy of the above described improvement of calibration can be justified when we compare the fractionation results of the BCR-701 CRM sample applying the 1st and 3rd settings in Table 5. The measured concentrations of three repeated fractionations were compared by Student test with certified values. With the 1st operational settings at $p = 1\%$ level in 11 case, while at $p = 0.1\%$ level in 4 case the measured values significantly differ from the certified values. With the 3rd operational settings were no significant differences at $p = 1\%$ level and at $p = 5\%$ level was in 1 case significant difference (Cr 1st step).

Table 5. Average results and standard deviations of three repeated fractionation of PTE content of BCR-701 CRM sample using the 1st and 3rd ICP-OES operational settings. Symbol * means the significant difference at $p = 1\%$ level and symbol ** means the significant difference at $p = 0.1\%$ level.

		First setting [mg/kg]	Recovery		Third setting [mg/kg]	Recovery		Certified [mg/kg]
1st	Cd	6.45± 0.07	88%	*	7.02± 0.45	96%		7.34 ± 0.35
	Cr	1.88± 0.08	83%		3.07± 0.14	136%		2.26 ± 0.16
	Cu	44.93± 0.25	91%	*	50.4± 2.5	102%		49.3 ± 1.7
	Ni	12.52± 0.34	81%		14.2± 1.0	92%		15.4 ± 0.9
	Pb	1.92± 0.19	60%		1.97± 0.20	62%		3.18 ± 0.21
	Zn	160± 4	78%	*	210± 8	103%		205 ± 6
2nd	Cd	3.96± 0.08	105%		3.37± 0.62	89%		3.77 ± 0.28
	Cr	26.53± 0.78	58%	*	43.5± 8.1	95%		45.7 ± 2
	Cu	87.61± 0.81	71%	**	105± 20	85%		124 ± 3
	Ni	19.55± 0.35	73%	*	26.7± 4.7	100%		26.6 ± 1.3
	Pb	92.2± 2.24	73%	*	111± 18	88%		126 ± 3
	Zn	98.8± 2.27	87%		106± 17	93%		114 ± 5
3rd	Cd	1.17± 0.01	435%	**	0.34± 0.07	126%		0.27 ± 0.06
	Cr	196.41± 8.24	137%		137± 35	96%		143 ± 7
	Cu	63.59± 2.92	115%		76.1± 14.4	138%		55.2 ± 4
	Ni	24.49± 0.35	160%	*	17.9± 3.7	117%		15.3 ± 0.9
	Pb	60.14± 0.82	647%	**	11.9± 2.5	128%		9.3 ± 2
	Zn	66.44± 0.62	145%	**	45.5± 9.1	99%		45.7 ± 4
(+1)	Cd	1.38± 0.01			0.14± 0.03			
	Cr	101± 4.79			80.1± 3.5			
	Cu	49.48± 1.92			32.1± 0.1			
	Ni	44.50± 1.36			32.3± 1.2			
	Pb	12.77± 0.30			6.17± 0.22			
	Zn	127± 1.36			73.7± 2.1			
pseudo total	Cd	9.64± 0.12			8.47± 0.53			
	Cr	291± 6.87			233± 12			
	Cu	258± 3.98			211± 17			

Ni	77.30± 1.28	72± 5
Pb	158± 3.32	108± 10
Zn	418± 8.73	343± 18

With the operational parameters of third setting the fractionation of PTE content of BCR-701 CRM sample was performed in three repeation using:
(1) aqua regia digestion-extraction according to ISO Norm 11466 [11],
(2) microwave supported aqua regia digestion-extraction,
(3) microwave supported cc. HNO_3/H_2O_2 digestion-extraction
for determination of residual (+1) fraction and pseudototal fraction. The summaries of the $\Sigma[1^{st}+2^{nd}+3^{rd}+(+1)]$ fractions were compared with the pseudototal fractions statistically, there were no significant differences in the three above cases. On Figures S6(a) and S6(b) this comparison presented graphically for Cr and Ni.

3.3. Application for real samples

PTE-contaminated lake sediment

In our previous paper [25a] was published a longterm study of transformation of potentially toxic element pollution in a lake system Gödöllő by means of BCR-fractionation procedure. In Table 6 is presented the fractionation results of one of the most polluted sediment sample (Gödöllő-Lake VII. 0-10 cm layer) and the BCR CRM 701 sample. The reliability of the optimized ICP-OES method for evaluation of environmental mobility of PTE-pollution was controlled by the simultaneously performed fractionation of the BCR CRM 701 sample [25a].

Table 6. The results of fractionation of BCR 701 CRM sample and the Gödöllő-lake sediment sample according to BCR sequential extraction scheme. (*: significant at p=1% level)

[mg/kg]		BCR protocol			
		BCR CRM 701	Certified value	Recovery of the certified value, %	Gödöllő (2013) Lake VII. 0-10 cm
1st	Cd	6.96 ± 0.09	7.3 ± 0.4	95.34	7.25 ± 0.18
	Cr	2.68 ± 0.02	2.26 ± 0.16*	118.58	4.13 ± 0.13
	Cu	46.8 ± 0.1	49.3 ± 1.7*	94.93	0.2 ± 0.0
	Ni	15.8 ± 1.6	15.4 ± 0.9	102.60	21.1 ± 0.4
	Pb	3.55 ± 0.22	3.18 ± 0.21	111.64	6.32 ± 0.25
	Zn	192 ± 2	205 ± 6	93.66	344 ± 13
2nd	Cd	3.66 ± 0.55	3.77 ± 0.28	97.08	21 ± 0.9
	Cr	46.6 ± 6	45.7 ± 2.0	101.97	294 ± 9
	Cu	112 ± 2	124 ± 3	90.32	14 ± 1
	Ni	29 ± 4.7	26.6 ± 1.3	109.02	83.9 ± 2.1
	Pb	116 ± 3	126 ± 3	92.06	257 ± 11
	Zn	117 ± 15	114 ± 5	102.63	737 ± 22
3rd	Cd	0.09 ± 0.05	0.27 ± 0.06	33.33	0.51 ± 0.04
	Cr	118 ± 9	143 ± 7	96.55	551 ± 61
	Cu	53.1 ± 1.2	55 ± 4	96.55	136 ± 2

	Ni	14.9 ± 4.2	15.3 ± 0.9	94.77	37.9 ± 0.4
	Pb	9.2 ± 0.8	9.3 ± 2.0	98.93	97.8 ± 0.6
	Zn	42.4 ± 2.5	46 ± 4	92.17	101 ± 1
(+1)	**Cd**	1.68 ± 0.03			0.97 ± 0.15
	Cr	131 ± 1			101 ± 2
	Cu	37.8 ± 1.3			52.2 ± 0.2
	Ni	59.6 ± 1.8			30.5 ± 0.1
	Pb	15.2 ± 0.58			14.4 ± 0.56
	Zn	139 ± 2			70.7 ± 2.2
Pseudototal	**Cd**	9.52 ± 0.53			25.7 ± 0.9
	Cr	235 ± 12			932 ± 32
	Cu	210 ± 17			154 ± 54
	Ni	72 ± 5			127 ± 4
	Pb	112 ± 10			291 ± 10
	Zn	347 ± 18			1139 ± 39

Soil samples from Hungarian Soil Protection Information and Monitoring System (four different type)

In this study the applicability of BCR-fractionation for agrochemical purposes was studied using different
physical wives soil samples. For this study four samples (Sandy soil, Sandy loam soil, Loam soil and Clay soil) were selected and the information content of BCR fractionation was compared with the information content with single step extractions applied in agrochemical practice. This project is still running and hereby only the results of BCR fractionation for 11 elements are presented (Table S6). For BCR-procedure no soil CRM is available, therefore only for the pseudototal element content certified ERM-CC141 soil sample was applied for quality assessment (Table 7). These data clearly show that the BCR-procedure with the optimized ICP-OES element detection reliably applicable for agricultural soil analysis and the number of analite elements can be increased, accordingly with the agrochemical interest (Al, Ca, Fe, K, Mg, Mn, Na)

Table 7. Measured pseudototal PTE concentrations and certified concentrations of a soil CRM sample.

LOAM SOIL ERM-CC141	Measured value [mg/kg]	Certified value [mg/kg]
Cd 214.441 nm	0,25 ± 0,03	0,25 ± 0,04
Cr 205.571 nm	37,7 ± 1,8	31 ± 4
Cu 324.754 nm	9,9 ± 0,6	12,4 ± 0,9
Mn 257.610 nm	324 ± 16	387 ± 17
Ni 222.296 nm	13,9 ± 1,7	21,9 ± 1,6
Pb 220.353 nm	27,0 ± 2,11	32,2 ± 1,4
Zn 213.857 nm	40,3 ± 3,6	50 ± 4

4. CONCLUSION

It can be concluded that optimalization of the flexible multielemental calibration for various solvent matrices gained by BCR-sequential extraction is necessary even when we apply it for fractionation of PTE content of freshwater-lake sediments. In this case the reliability of the fractionation results can be strictly controlled by simultaneous fractionation of BCR CRM 701 sample as it seems in Table 6. This procedure was successfully applied for controlling the remediation of PTE contaminated lakes like the Gödöllő-lake system [25a, 15, 22, 48]. For characterization of environmental mobility of PTE, and other micro- and macroelement content of soils the optimalized ICP-OES method can be applied successfully too. In these case the lack of soil CRM certified for BCR-fractionation does not make possible the strict control of accuracy of 1st, 2nd, and 3rd BCR-extraction step, only the pseudototal element content can be controlled by analysis of appropriate soil CRM samples. The reliability in this case can be evaluated on the basis of comparison of the sum of $[1^{st}+2^{nd}+3^{rd}+(+1)]$ fractions with the certificated pseudototal values. This comparison for data presented in Table S6 has shown an acceptable agreement. The application of BCR-fractionation for different type soil seems to be advantageous related to single step extraction procedures applied in agrochemical practice [56]. By this way about the biologically available PTE content can be characterized better and relationships with the soil properties can be also estimated. For example the influence of lime content, Fe-and Mn-oxides, and the humus content for mobilization/immobilization processes can be evaluated. This question is the subject of our ongoing project in this field. Recently this methodology is being applied for study of PTE- and radionuclide migration in a spoil area of the abandoned Uranium mine in Hungary too.

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APPENDIX

1. STUDY OF SPECTRAL INTERFERENCES IN THE DIFFERENT CALIBRATION SOLUTIONS

To detect the interfering line coincidences the following spectra were recorded in the 185-400 nm range applying the 1st operational settings:

- In 0.11 M acetic acid:
  -- 5 mg /L mono-elemental Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn solutions;
  -- 5 mg/L multi-elemental (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) solution.
- In 0.5 M hydroxylamine-hydrochloride:
  -- 5 mg dm^{-3} mono-elemental Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn solutions;
  -- 5 mg dm^{-3} multi-elemental (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) solution.
- In 1 M ammonium-acetate:
  -- 5 mg dm^{-3} mono-elemental Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn solutions;
  -- 5 mg dm^{-3} multi-elemental (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) solution.
- In 13 (m/m)% nitric acid:
  -- 5 mg dm^{-3} mono-elemental Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn solutions;
  -- 5 mg dm^{-3} multi-elemental (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) solution.

For preparation of monoelemental solutions mono-elemental standard solution (Précis Certified Standards for ICP Spectroscopy, HORIBA Scientific, France) were used.

All these spectra were stored in an electronic library and then the best interference-free spectral lines were selected on the basis of a detailed comparison of these spectra for all calibrant media and for all analytical lines proposed by the instrument producer. The results of the detectable interferences are summarized in Table S1. These results were considered when analytical lines were selected for 3rd settings operational conditions. It can be seen that primary proposed analytical lines could be used for Cr, Cu, Fe, Mn, Pb and Zn, but in some cases one has to calculate with some low level spectral interferences (Zn, Pb). For Cd, Co, Ni and V the primary proposed lines could not be used. Some tipical overlapping are presented on Figures S1, S2, S3, S4.

Figures S1. Ni and Cd overlapping at 361 nm
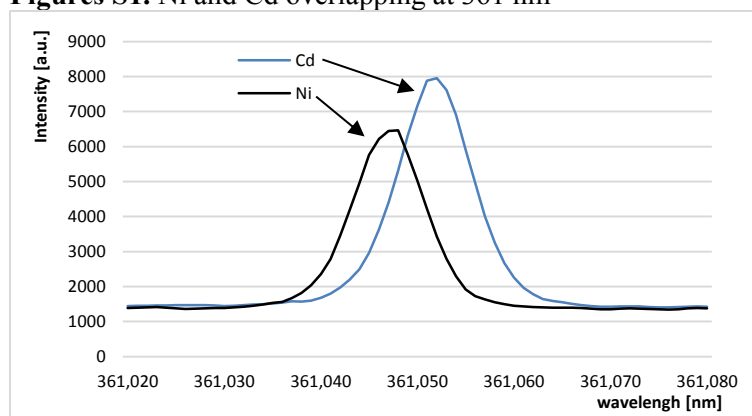
Figures S2. Pb and Cu overlapping at 224 nm
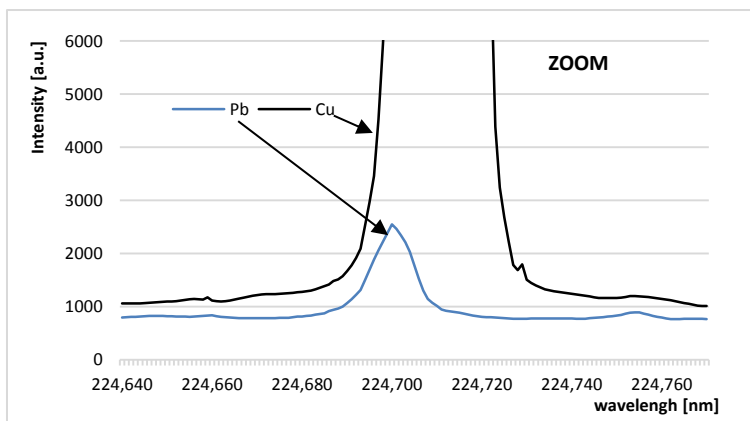
Figures S3. Pb and Co overlapping at 261 nm
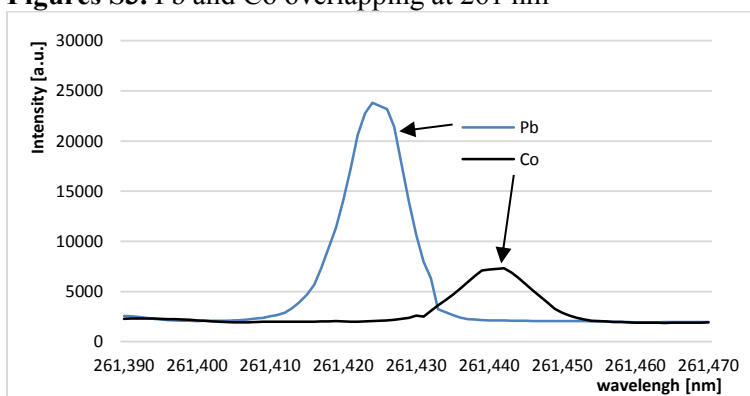
Figures S4. Zn and Cu overlapping at 213 nm
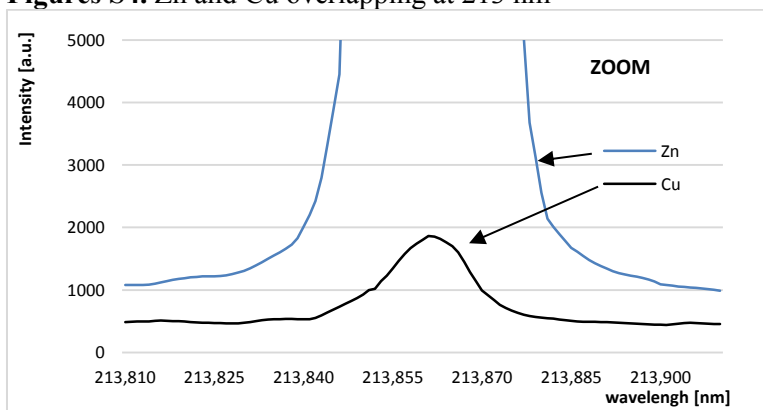
Figure S5. The analytical calibration lines obtained for Cd (a) and Zn (b) at three different operational settings in case of different solvents.

(a)

| 1st settings | 2nd settings | 3rd settings |

(b)

| 1st settings | 2nd settings | 3rd settings |
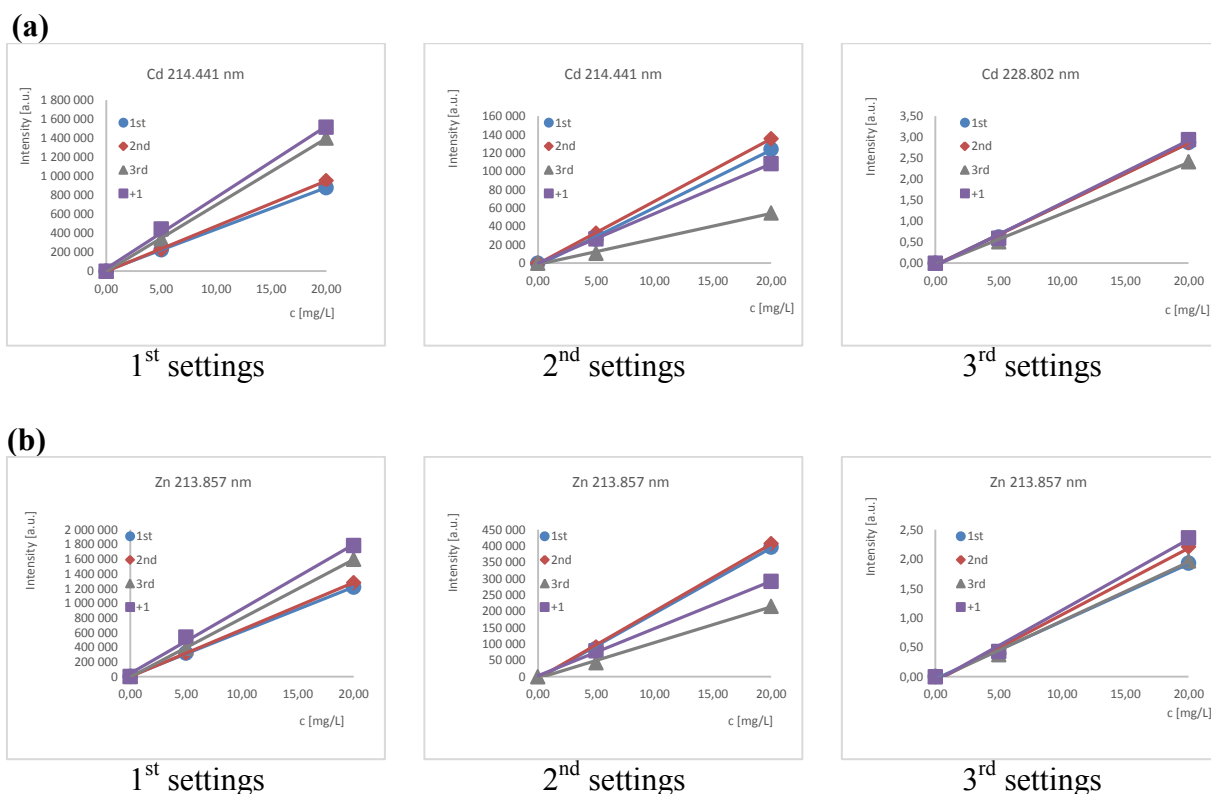
Table S1. Interfering line coincidences in the different BCR-extractant media. Meaning of symbols:
t: total overlapping, **p:** partial overlapping, **m:** minimal overlapping;
c: commeasurable intensity, **l:** lower than 1:10 intensity ratio, **h:** higher than 10:1 intensity ratio.

Analytical line	Coincident lines BCR solvent			
	1st	2nd	3rd	(+1)
Cd 361.051	Ni 361.046 **t**,**c**	Ni 361.046 **t**,**c**	Ni 361.046 **t**,**c**	Ni 361.046 **t**,**c**
Cd 361.051	-	-	-	Mn 361.030 **p**,**l**
Co 238.891	Fe 228.863 **m**,**c**	Fe 228.863 **m**,**c**	Fe 228.863 **m**,**c**	Fe 228.863 **m**,**c**
Cr 357.869	V 359.333 **p**,**l**	-	-	-
Cr 359.349	-	V 359.333 **m**,**c**	V 359.333 **m**,**c**	V 359.333 **p**,**l**
Cu 224.700	Pb 224.689 **t**,**l**	Pb 224.689 **t**,**l**	Pb 224.689 **t**,**l**	Pb 224.689 **t**,**l**
Ni 232.003	Cr 232.008 **t**,**l**	Cr 232.008 **t**,**l**	Cr 232.008 **t**,**l**	-
Pb 261.418	Fe 261.382 **m**,**c**	Fe 261.382 **m**,**c**	Fe 261.382 **m**,**c**	Fe 261.382 **m**,**h**
Pb 261.418	-	-	Co 261.436 **p**,**c**	Co 261.436 **p**,**c**
V 310.230	matrix origine **p**,**l**	matrix origine **p**,**l**	matrix origine **p**,**l**	matrix origine **p**,**l**
V 309.311	matrix origine **p**,**l**	-	-	-
Zn 213.856	Cu 213.851 **t**,**l**	Cu 213.851 **t**,**l**	-	-
Zn 202.551	Cu 202.548 **t**,**l**	Cu 202.548 **t**,**l**	-	-
Zn 206.196	-	-	Cr 206.154 **m**,**c**	Cr 206.154 **m**,**c**

Table S2. Analytical lines selected at different operational settings. In the case of 1st, 2nd, and the (+1) extracts the wavelength readout was started from the C 193.026 nm reference line. In

the case of 3rd extracts, correct wavelength readout was only possible when the readout was started from the Ar 404.442 nm reference line due to the high C-content of 1 M ammonium-acetate solution.

Element	Spectral line nm		
	1st settings	2nd settings	3rd settings
Cd	214.441 -	214.441 228.802	- 228.802
Co	230.785 - -	230.785 237.862 -	- - 228.615
Cr	205.571 -	205.571 283.563	205.571 -
Cu	324.754 -	324.754 327.395	324.754 -
Fe	- 259.940	240.489 259.940	- 259.940
Mn	257.610 -	257.610 279.482	257.610 -
Ni	- 222.296 -	221.650 222.296 -	- - 231.604
Pb	- 220.353	217.000 220.353	- 220.353
V	309.311 -	309.311 311.071	- -
Zn	213.857 -	213.857 280.087	213.857 -
Y	-	-	371.029

2. PARAMETERS OF ANALYTICAL CALIBRATION LINES, THE BACKGROUND EQUIVALENT CONCENTRATIONS (BEC) AND THE INSTRUMENTAL DETECTION LIMITS [LOD(3σ)] OBTAINED FOR DIFFERENT BCR-EXTRACTION-SOLVENT MATRICES AT THREE DIFFERENT ICP-OES OPERATIONAL SETTINGS

Table S3. The parameters of calibration lines (I = A+Bc), at wavelength λ in nm, correlation R^2 values, the relative residual standard deviations (RSD %), the background equivalent concentrations (BEC) in µg/L and the instrumental detection limits $[C_L(3\sigma)]$ in µg/L obtained for 1st setting of operational parameters in case of different solvents [24].

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
	Cd	214.441	0,3	17	2867	43778	0.9999	1.1
	Co	230.785	0,4	18	6064.7	41860	0.9997	2.5
CH₃COOH	Cr	205.571	0,5	25	3184.2	18298	0.9996	2.9
	Cu	324.754	0,3	14	19374	159951	0.9998	2.0
	Fe	259.940	0,4	18	14716	205720	0.9999	1.2
	Mn	257.610	0,2	12	94673	902188	0.9999	1.8
	Ni	222.296	0,3	13	823.38	7154	0.9998	2.0
	Pb	220.353	0,4	22	68.946	4087.4	1.0000	0.3
	V	309.311	0,6	31	8897	259817	1.0000	0.5
	Zn	213.857	0,4	21	8951	60540	0.9998	2.2

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
NH₂OH*HCl	**Cd**	214.441	0,2	11	-4145.2	47809	0.9999	1.5
	Co	230.785	0,3	15	-856.49	44538	1.0000	0.3
	Cr	205.571	0,1	7	-258.4	18911	1.0000	0.2
	Cu	324.754	0,2	12	11765	163871	1.0000	1.0
	Fe	259.940	0,2	12	236,82	204879	1.0000	0.2
	Mn	257.610	0,2	12	57160	911472	0.9999	1.1
	Ni	222.296	0,4	20	471.04	7505.8	1.0000	1.0
	Pb	220.353	0,1	5	-17.636	4375.2	1.0000	0.2
	V	309.311	0,6	32	-15164	260057	1.0000	1.0
	Zn	213.857	0,4	18	2845.5	63846	1.0000	0.5

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
CH₃COONH₄	**Cd**	214.441	0,5	24	-4008.3	70051	1.0000	1.0
	Co	230.785	0,3	16	-119.26	54840	1.0000	0.03
	Cr	205.571	0,3	17	546.52	25579	1.0000	0.3
	Cu	324.754	0,2	8	32156	151053	0.9994	3.5
	Fe	259.940	0,4	19	41379	258243	1.0000	0.6
	Mn	257.610	0,4	22	2013	1291505	1.0000	0.02
	Ni	222.296	0,3	14	-170.25	9902	1.0000	0.3
	Pb	220.353	0,7	34	-874.08	5905.2	0.9997	2.6
	V	309.311	0,4	20	26636	312207	0.9999	1.4
	Zn	213.857	1,1	55	2643.2	79775	0.9968	1.9

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
HNO₃ & H₂O₂	**Cd**	214.441	0,3	16	29293	74770	0.9980	6.6
	Co	230.785	0,2	11	16009	50151	0.9986	5.4
	Cr	205.571	0,1	5	7580.7	23088	0.9986	5.5
	Cu	324.754	0,2	12	35859	104399	0.9985	5.6
	Fe	259.940	0,6	29	47594	216961	0.9995	3.2
	Mn	257.610	0,5	23	222941	1056725	1.0000	3.6
	Ni	222.296	0,4	20	2974.7	9282.3	0.9987	5.4
	Pb	220.353	0,5	26	1717.4	6483.7	0.9991	4.4
	V	309.311	0,2	9	13775	256488	1.0000	0.9
	Zn	213.857	0,6	28	45308	87624	0.9968	8.3

Table S4. The parameters of calibration lines (I = A+Bc), at wavelength λ in nm, correlation R^2 values, the relative residual standard deviations (RSD %), the background equivalent concentrations (BEC) in µg/L and the instrumental detection limits [C_L(3σ)] in µg/L obtained for 2nd setting of operational parameters in case of different solvents.

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
	Cd	214.441	0,6	6	-2302.3	6266.8	0.9982	3.5
	Cd	228.802	0,6	4	-8738.2	24401	0.9983	3.4
	Co	230.785	0,6	32	-2598.8	9300.5	0.9990	2.6
	Co	237.862	0,5	27	-3922.1	14524	0.9990	2.6
	Cr	205.571	0,4	12	-1322.2	2856.5	0.9972	4.4
	Cr	283.563	0,6	6	-5868.8	28616	0.9997	1.3
	Cu	324.754	0,2	1	-35553	116869	0.9988	2.9
CH₃COOH	Cu	327.395	0,2	5	-19663	57149	0.9984	3.3
	Fe	240.489	0,3	3	-2481.1	10901	0.9993	2.4
	Fe	259.940	0,3	9	-6768.6	50922	0.9998	1.3
	Mn	257.611	0,2	7	-35757	182196	0.9995	1.9
	Mn	279.482	0,2	12	-13028	41790	0.9987	3.0
	Ni	221.650	0,6	31	-3764.1	6390	0.9975	4.1
	Ni	222.296	0,1	6	-677.06	1721.6	0.9979	3.7
	Pb	217.000	0,7	35	-179.9	570.82	0.9987	2.9
	Pb	220.353	0,4	21	-443.93	1295.1	0.9986	3.0
	V	309.311	0,6	17	-3654.7	64377	1.0000	0.6
	V	311.071	0,7	33	-5084.6	43546	0.9998	1.1
	Zn	213.857	0,4	18	-85.253	201.42	0.9992	2.3
	Zn	280.087	0,5	10	-6784.8	22556	0.9988	2.8

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
	Cd	214.441	0,4	10	-537.31	6788.6	0.9999	0.7
	Cd	228.802	0,4	20	42.772	26967	1.0000	0.1
	Co	230.785	0,3	5	-615.72	9640.7	0.9999	0.6
	Co	237.862	0,4	18	7.8438	15018	1.0000	0.1
	Cr	205.571	0,5	5	274.45	2749	0.9999	0.9
	Cr	283.563	0,4	22	-746.66	28173	1.0000	0.1
	Cu	324.754	0,3	2	-40004	130134	0.9987	2.9
	Cu	327.395	0,1	4	-19750	61028	0.9986	3.1
NH₂OH*HCl	Fe	240.489	0,5	10	-235.02	11413	1.0000	0.2
	Fe	259.940	0,4	3	1214.7	51631	1.0000	0.2
	Mn	257.611	0,3	3	2407.5	200778	1.0000	0.2
	Mn	279.482	0,3	7	-4501.2	44299	0.9999	0.9
	Ni	221.650	0,5	26	-983.1	6908.3	0.9997	1.4
	Ni	222.296	0,2	9	-181.54	1869.3	0.9999	1.0
	Pb	217.000	0,5	6	-69.386	625.02	0.9998	1.1
	Pb	220.353	0,5	6	-99.847	1471.1	0.9999	0.6
	V	309.311	0,6	3	105.47	68849	1.0000	0.1
	V	311.071	0,7	34	-1075.6	45733	1.0000	0.1
	Zn	213.857	0,3	15	-70.59	206.56	0.9995	1.8
	Zn	280.087	0,4	4	-2030.4	23955	0.9999	0.8

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
CH₃COONH₄	Cd	214.441	0,4	21	-1303.7	2771.5	0.9968	4.3
	Cd	228.802	0,2	12	-7503.1	20628	0.9981	4.0
	Co	230.785	0,7	37	-2340.5	4594.9	0.9970	3.8
	Co	237.862	0,3	15	-3618.9	6924.9	0.9962	4.6
	Cr	205.571	0,5	8	-539.51	1286.6	0.9985	3.4
	Cr	283.563	0,5	16	-8358	15530	0.9981	3.2
	Cu	324.754	0,2	9	-32032	112779	0.9989	2.5
	Cu	327.395	0,3	5	-18472	55844	0.9985	2.2
	Fe	240.489	0,3	4	-1233.3	5340.7	0.9993	2.1
	Fe	259.940	0,3	6	-2854.2	31611	0.9999	0.8
	Mn	257.611	0,3	6	-36247	103860	0.9984	2.8
	Mn	279.482	0,3	8	-15239	33253	0.9972	4.0
	Ni	221.650	0,4	10	-979.15	2620.8	0.9971	4.0
	Ni	222.296	0,5	7	-383.4	738.2	0.9973	4.0
	Pb	217.000	0,5	26	-253.87	334.49	0.9968	4.2
	Pb	220.353	0,3	10	-272.21	444.12	0.9966	4.1
	V	309.311	0,6	9	-8690.8	35701	0.9992	2.3
	V	311.071	0,3	9	-5532.2	24919	0.9994	2.1
	Zn	213.857	0,3	4	-4913.3	10927	0.9973	1.6
	Zn	280.087	0,2	8	-9582.7	18455	0.9964	4.1

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
HNO₃ & H₂O₂	Cd	214.441	0,3	15	-346.95	5413.9	0.9999	0.6
	Cd	228.802	0,4	20	-4700.6	25009	0.9995	2.1
	Co	230.785	0,6	2	-670.38	8389.7	0.9999	0.7
	Co	237.862	0,2	10	-385.93	13675	1.0000	0.2
	Cr	205.571	0,8	39	-61.74	2360.8	1.0000	0.2
	Cr	283.563	1,9	96	-472.46	22500	0.9999	0.7
	Cu	324.754	0,2	10	-21137	129210	0.9996	1.5
	Cu	327.395	0,6	3	-11000	60995	0.9996	1.6
	Fe	240.489	0,3	15	478.75	9431.1	1.0000	0.5
	Fe	259.940	0,3	3	11891	37029	0.9986	3.0
	Mn	257.611	0,3	3	25160	163870	0.9997	1.4
	Mn	279.482	0,3	4	-9757.3	52313	0.9995	1.6
	Ni	221.650	0,8	42	-829.98	6475.8	0.9998	1.1
	Ni	222.296	0,7	35	-130.38	1752.6	0.9999	0.7
	Pb	217.000	0,4	20	-111.39	630.17	0.9995	1.7
	Pb	220.353	0,7	34	122.18	1624.6	0.9999	0.7
	V	309.311	0,7	4	10330	52447	0.9995	1.9
	V	311.071	1,1	56	4538.5	35583	0.9998	1.2
	Zn	213.857	0,5	24	2862.5	14481	0.9995	1.8
	Zn	280.087	0,4	2	-5293.1	28598	0.9995	1.7

Table S5. The parameters of calibration lines (I = A+Bc), at wavelength λ in nm, correlation R^2 values, the relative residual standard deviations (RSD %), the background equivalent concentrations (BEC) in µg/L and the instrumental detection limits [C_L(3σ)] in µg/L obtained for 3rd setting of operational parameters in case of different solvents.

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
CH₃COOH	Cd	228.802	0,1	4	-0.051	0.1452	0.9984	0,20
	Co	228.615	0,5	4	-0.268	0.0779	0.9984	0,15
	Cr	205.571	0,1	4	-0.0144	0.0267	0.9961	0,10
	Cu	324.754	0,3	4	-0.0558	0.1369	0.9978	0,07
	Fe	259.940	0,3	5	-0.046	0.254	0.9995	0,34
	Mn	257.611	0,3	4	-0.5194	1.2908	0.9978	0,70
	Ni	231.604	0,4	4	-0.0201	0.0582	0.9984	0,16
	Pb	220.353	0,2	4	-0.0026	0.0058	0.9974	0,10
	Zn	213.857	0,2	4	-0.0394	0.0978	0.9977	0,05

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
NH2OH*HCl	Cd	228.802	0,1	5	-0.0445	0.145	0.9987	0,14
	Co	228.615	0,6	5	-0.0279	0.0794	0.9984	0,13
	Cr	205.571	0,6	5	-0.013	0.0258	0.9966	0,10
	Cu	324.754	0,3	5	-0.0598	0.1345	0.9974	0,05
	Fe	259.940	0,8	5	-0.0878	0.2633	0.9982	0,11
	Mn	257.611	0,4	5	-0.6642	1.3146	0.9966	0,07
	Ni	231.604	0,3	5	-0.024	0.0588	0.9978	0,05
	Pb	220.353	0,6	5	-0.0046	0.0072	0.9945	0,26
	Zn	213.857	0,3	5	-0.0742	0.1129	0.9939	0,30

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
CH3COONH4	Cd	228.802	0,3	5	-0.0422	0.1219	0.9984	0,15
	Co	228.615	0,5	5	-0.0238	0.0763	0.9987	0,19
	Cr	205.571	0,5	5	-0.0145	0.0272	0.9962	0,11
	Cu	324.754	0,2	5	-0.0359	0.1177	0.9986	0,17
	Fe	259.940	0,6	5	-0.0371	0.2407	0.9996	0,37
	Mn	257.611	0,3	5	-0.4897	1.2953	0.9981	0,10
	Ni	231.604	0,4	5	-0.0185	0.0546	0.9985	0,16
	Pb	220.353	0,4	5	-0.0039	0.0065	0.9951	0,18
	Zn	213.857	0,3	5	-0.0541	0.1003	0.9958	0,15

		λ	C_L (3 σ)	BEC	I = A + Bc		R^2	RSD
		nm	µg/L	µg/L	A	B		%
HNO3 & H2O2	Cd	228.802	0,3	5	-0.0646	0.1492	0.9975	0,03
	Co	228.615	0,6	5	-0.0342	0.0821	0.9977	0,05
	Cr	205.571	0,5	5	-0.016	0.0283	0.9957	0,15
	Cu	324.754	0,2	5	-0.0508	0.1327	0.9981	0,10
	Fe	259.940	0,3	5	-0.0989	0.2632	0.9980	0,08
	Mn	257.611	0,3	5	-0.6393	1.3408	0.9970	0,03
	Ni	231.604	0,4	5	-0.0219	0.0602	0.9982	0,11
	Pb	220.353	0,3	5	-0.0046	0.0076	0.9952	0,21
	Zn	213.857	0,3	5	-0.0752	0.1205	0.9948	0,23

Figure S6. Comparison of the summaries of the $\Sigma[1^{st}+2^{nd}+3^{rd}+(+1)]$ fractions with the pseudototal fractions for Cr (a) and Ni (b) applying (1) aqua regia digestion-extraction according to ISO Norm 11466 [11], (2) microwave supported aqua regia digestion-extraction, (3) microwave supported cc. HNO_3/H_2O_2 digestion-extraction for determination of residual (+1) fraction and pseudototal fraction.

(a)
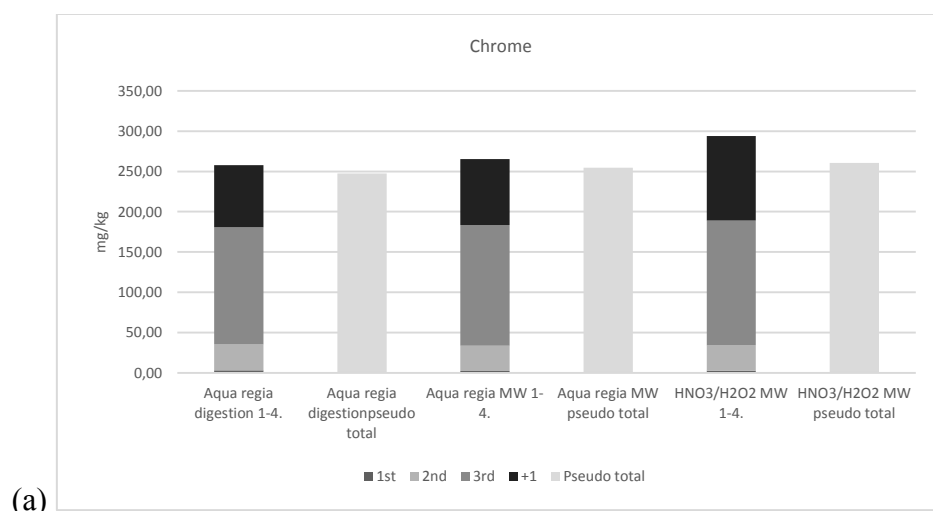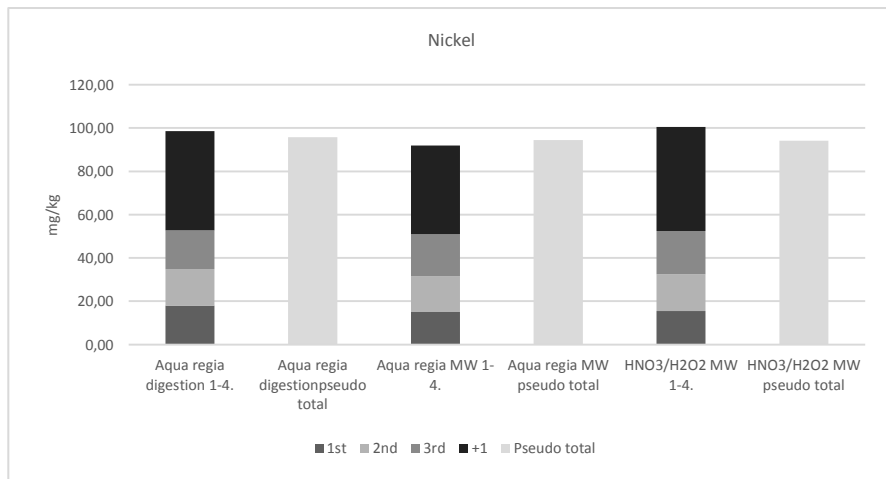
(b)

3. APPLICATION of BCR FRACTIONATION for DIFFERENT TEXTURE TYPE SOILS

Table S6. Application of BCR fractionation for different texture type of soils

Steps	Elements	Sandy soil (I 1904)			Sandy loam soil (I 0509)			Loam soil (I 1104)			Clay soil (I 4615)		
1st	Al	12,7	±	0,2	38,6	±	0,2	17,0	±	0,2	56,5	±	1,3
	Ca	13109	±	549	2529	±	65	10175	±	168	133	±	26
	Cd	0,05	±	0,03	0,02	±	0,00	0,01	±	0,00	0,01	±	0,00
	Cr	0,09	±	0,03	0,07	±	0,01	0,05	±	0,00	0,02	±	0,01
	Cu	0,05	±	0,03	0,04	±	0,03		n.d.		0,07	±	0,03
	Fe	0,24	±	0,02	0,80	±	0,07	0,22	±	0,06	1,45	±	0,21
	K	133	±	19	84,8	±	3,0	274	±	245	77,7	±	1,5
	Mg	1057	±	54	213	±	28	707	±	11	13,6	±	3,8
	Mn	71,7	±	0,8	78,4	±	1,5	85,6	±	1,3	106	±	1
	Na		n.d.			n.d.			n.d.			n.d.	
	Ni	0,82	±	0,05	2,00	±	0,04	0,88	±	0,05	0,91	±	0,07
	Pb		n.d.			n.d.			n.d.		0,01	±	0,02
	Zn		n.d.			n.d.			n.d.			n.d.	
2nd	Al	1764	±	64	1213	±	55	1086	±	43	261	±	19
	Ca	3864	±	158	1319	±	6	2742	±	70	23,2	±	3,7
	Cd	0,31	±	0,01	0,27	±	0,01	0,21	±	0,02	0,01	±	0,01
	Cr	1,17	±	0,01	1,33	±	0,03	0,88	±	0,04	0,23	±	0,01
	Cu	1,80	±	0,11	2,03	±	0,12	0,73	±	0,08	0,21	±	0,07
	Fe	1157	±	33	1970	±	100	830	±	26	577	±	33
	K	184	±	7	110	±	2	122	±	4	43,0	±	2,9
	Mg	296	±	6	205	±	11	205	±	9	17,4	±	0,2
	Mn	581	±	15	532	±	26	443	±	12	318	±	18
	Na		n.d.			n.d.			n.d.			n.d.	
	Ni	14,0	±	0,5	10,7	±	0,4	9,47	±	0,23	0,87	±	0,08
	Pb	15,4	±	0,6	15,2	±	0,2	13,8	±	0,5	11,7	±	0,6
	Zn	17,8	±	1,1	12,4	±	0,5	10,5	±	0,4	1,15	±	0,32
3rd	Al	1310	±	12	864	±	13	996	±	51	263	±	9
	Ca	56,9	±	37,7		n.d.		93,8	±	4,7	141	±	244
	Cd	0,77	±	0,24	0,37	±	0,20	0,13	±	0,22	0,03	±	0,04

	Element	Col 1	Col 2	Col 3	Col 4
	Cr	4,72 ± 0,40	3,22 ± 0,54	3,15 ± 0,69	0,67 ± 0,42
	Cu	3,42 ± 0,16	1,25 ± 0,31	1,55 ± 0,44	0,27 ± 0,48
	Fe	1359 ± 31	948 ± 24	1057 ± 19	285 ± 5
	K	54,5 ± 24,2	18,3 ± 8,9	6,40 ± 6,64	n.d.
	Mg	1187 ± 63	600 ± 102	690 ± 6	63,7 ± 12,3
	Mn	30,1 ± 0,3	26,7 ± 0,8	22,1 ± 0,2	7,75 ± 0,05
	Na	n.d.	n.d.	n.d.	n.d.
	Ni	7,05 ± 0,97	5,77 ± 0,08	4,85 ± 1,61	1,80 ± 1,15
	Pb	4,97 ± 1,86	1,32 ± 2,14	2,07 ± 3,79	1,07 ± 2,78
	Zn	6,82 ± 4,18	4,12 ± 4,56	5,25 ± 4,13	1,80 ± 1,73
(+1)	Al	36332 ± 777	22196 ± 1497	27130 ± 233	9080 ± 594
	Ca	3172 ± 1577	9607 ± 9170	2061 ± 343	270 ± 467
	Cd	2,57 ± 0,07	1,65 ± 0,09	2,00 ± 0,05	0,70 ± 0,04
	Cr	49,50 ± 1,10	31,53 ± 2,24	36,96 ± 0,50	14,6 ± 1,2
	Cu	30,69 ± 0,36	11,11 ± 0,85	17,11 ± 0,44	3,03 ± 0,34
	Fe	98589 ± 16726	58156 ± 4749	87252 ± 2136	12030 ± 3591
	K	21038 ± 1398	13044 ± 948	15033 ± 451	4266 ± 511
	Mg	18600 ± 411	8331 ± 227	13934 ± 544	4375 ± 754
	Mn	202 ± 4	148 ± 9	203 ± 4	123 ± 5
	Na	n.d.	n.d.	n.d.	n.d.
	Ni	19,8 ± 0,6	9,53 ± 0,45	14,5 ± 0,1	5,64 ± 0,22
	Pb	4,39 ± 0,12	2,29 ± 0,32	3,50 ± 0,55	1,28 ± 0,09
	Zn	62,7 ± 1,6	37,0 ± 1,9	47,4 ± 0,3	15,7 ± 1,2
pseudo total	Al	25426 ± 585	36620 ± 842	9735 ± 117	22428 ± 583
	Ca	37889 ± 1553	47745 ± 2483	506 ± 12	9174 ± 312
	Cd	2,03 ± 0,04	2,65 ± 0,03	0,84 ± 0,01	1,83 ± 0,05
	Cr	34,7 ± 0,9	52,37 ± 2,20	16,0 ± 0,7	33,44 ± 0,87
	Cu	17,1 ± 0,5	28,86 ± 0,66	3,74 ± 0,04	12,82 ± 0,44
	Fe	86117 ± 4478	106814 ± 3418	14587 ± 467	62932 ± 1636
	K	14454 ± 202	21983 ± 330	5469 ± 159	13130 ± 197
	Mg	16002 ± 192	24198 ± 48	5097 ± 138	9531 ± 181
	Mn	610 ± 7	644 ± 15	502 ± 13	622 ± 16
	Na	n.d.	n.d.	n.d.	n.d.
	Ni	21,6 ± 0,5	30,8 ± 0,4	7,38 ± 0,15	21,1 ± 0,5
	Pb	11,8 ± 0,1	15,4 ± 1,0	8,19 ± 0,17	11,1 ± 0,3
	Zn	47,9 ± 2,5	68,6 ± 0,8	18,7 ± 0,5	43,6 ± 1,1