Central European Journal of **Chemistry**

Sono-extraction as a pretreatment approach for the screening evaluation of element mobility of sediment samples

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Abstract: Application of economically important and time saving pretreatment for the screening element mobility evaluation of contaminated sediments is presented. Ultrasonically-assisted single-step extraction (USAE) was carried out by EDTA solution. The extraction time of USAE was optimized and obtained results were compared with results estimated by conventional (EDTA extraction) and by sequential extraction (modified BCR protocol). The original three step BCR protocol was modified by addition of the first step (water leaching) and the fifth step, total digestion of sediment residue (acid mixture with HF). Zn, Cu and Pb have been determined in extracts by ICP-OES. Good conformity of the ultrasonically-extracted element contents and sum of contents, extracted during first three steps (water-soluble, acid-extractable, reducible – *i.e.*, the most mobile fractions) of sequential extraction, was found. The sono-extraction reduced operating time of the first three steps of sequential extraction from 48 h to 15 min. Thus, USAE can serve as a rapid screening assessment of the mobile and potentially mobile element portions in sediments and other similar solid state environmental media. Analytical quality control was realized by comparison of the sums of element contents obtained at individual (five) extraction steps. Total element contents were also determined by an independent method (XRF).

Keywords: Environmental analysis • Extraction • Ultrasound • Screening of element mobility
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1. Introduction

Element contamination of sediments is a worldwide problem since it causes a disturbance of the normal functions of rivers, lakes and seas. Sediments, as the largest storage and resource of potentially toxic elements, play a rather important role in transformations of elements. In the aquatic environment trace and toxic elements are usually distributed as follows: water-soluble species, colloids, suspended forms and sedimentary phases [1]. Elements are associated to the sediments in various ways (chemical or physical sorption, precipitation, complexation, *etc*.), which exhibit different physical and chemical features. In some conditions, more than 99% of elements entering into the river can be stored in the river sediments in various forms [2]. The environmental

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Figure 1. Old mining works in the territory of Slovakia, with the marked location of sampling region [21].

behavior of potentially toxic elements depends critically on the forms in which they occur, and they influence the mobility, bioavailability, and the toxicity of the elements to organisms [3]. Elements could be released from the sediments or precipitated in accordance with the changes in the physicochemical conditions of the environment, *i.e.*, pH, redox potential, dissolved oxygen, presence of organic chelates, *etc.* For these reasons, the quantification of the total metal contents does not provide sufficient information about the potential interactions between biotic and non-biotic components in the environment [4].

Fractionation was defined as the process of classification of an analyte or a group of analytes from a certain sample according to physical (*e.g.* size, solubility) or chemical (*e.g.* bonding, reactivity) properties. It is usually performed by a sequence of the selective extraction steps, including the successive removal, or dissolution of these phases and their associated metals [5]. One of the objectives of fractionation studies is to characterize the degree of element mobility in sedimentary systems. The fractionation methods consist of the extraction procedure carried out under an operationally defined sequential scheme. Therefore, the fractionation using conventional sequential extraction methods gives the comprehensive information about the contamination [3], but also about the origin and geochemical behavior of the elements. However, this is a time consuming procedure [6].

Sonochemistry includes traditional applications such as synthesis [7], catalysis [8], fundamental studies of cavitation [9], electrochemistry, biotechnology [10] and material science [11,12]. Analytical chemists tend to use ultrasound for the improvement of the sample preparation [13,14] and analytical detection [15]. The ultrasound-assisted heterogeneous sample preparation includes many complex processes and it can lead to the total or partial dissolution of the samples [16,12].

The single-step extractions into the strong chelating agents (*e.g.* EDTA) are suitable for the evaluation of mobile and potentially mobile element contents, but these are quite lengthy in routine laboratory shakers.

For this purpose, the standard soil extraction with 0.05 mol L^{-1} $(NH_4)_2EDTA$ [17] was modified and ultrasonically accelerated [18] for the sediments from the studied area. A single-step extraction with 0.05 mol L^{-1} Na_2EDTA was used in the conventional as well as in the ultrasonically-assisted extraction procedures and the results were compared with results of the modified BCR protocol (the reference method) [19,20]. In this work BCR protocol [19] was slightly modified with respect to requirements of the regional pilot study [20]. Apart from the usual three steps of the BCR procedure [19], a first step (for elements extractable into the water phase) and a fifth step (the total digestion of the sediment residue) were added [20]. The single and the sequential extraction procedure were applied to sediment samples collected from an industrially polluted region of the Spišsko-Gemerské Rudohorie Mountains of Eastern Slovakia. The accuracy control of the analysis was realized by the comparison of the sums of contents of the extraction and digestion steps (sum of Cu, Pb, Zn contents, which were obtained at the individual four extraction steps and one digestion step) and the total element content analyses by an independent method (X-ray fluorescence spectrometry – XRF). As an additional independent quality control, a certified reference material (CRM-BCR 601, freshwater sediment) was used.

2. Experimental procedure

2.1. Sampling description and sample treatment
The sampling region (Spišssko-Gemerské Rudohorie Mountains) was industrially stressed in the long time horizon, because it was polluted from contact with mining

Table 1. Positions of the sampling sites.

Place of the sampling	Sediment	Geographic coordinates longitude / latitude	River / Stream
1 Rudňany – Markušovce	Sediment 1	20°38´ / 48°54´	Hornád
2 Slovinky	Sediment 2	20°45´ / 48°53´	Poráčsky jarok
3 Richnava	Sediment 3	20°50´ / 48°56´	Hornád
4 Jaklovce	Sediment 4	21°/ 48°53´	Hnilec

activity, see Fig. 1 [21]. The mining pollution dates back to the 13th century [22]. Geological characteristics of the region are mentioned in the text below and the list of sampling sites is described in Table 1 [20].

Rudňany – Markušovce: The bedrock and the sediments of the sampling place consist of gravels and loamy gravels of Pleistocene and Holocene age. The sandstones and sandy shales of Paleogene, and the carbonate material transported from the upper flow of the river, which comes from limestones of the Slovenský raj. Mountains are also present in this area.

Slovinky: The location of the stream (Poráčsky jarok) is characterized by metamorphosed rocks of the Gemericum of Gelnica Group (quartz-sericitic phyllite and sericite-chloritic phyllite), basic volcanic rocks (basic tuffs), metamorphosed basalts and amphibolites. In the upper layer there are also located the Triassic carbonate rocks of Galmus Mountains.

Richnava: The place is characterized by the rocks of the Gemericum of Krompachy group. Metamorphosed rhyolites, rhyolitic tuffs, shales and sandstones were also found.

Jaklovce: The bedrock is composed of metamorphosed rhyolite tuffs of the Gemericum of Krompachy group, shales, Wetterstein limestones and sandstones. The metamorphosed basalts of green shale facies are also present [23,24].

The sediment samples were collected from four individual sampling places in accordance with the Methodical Instruction of the Slovak Ministry of the Environment [25]: The fine-grained fluvial (oxic) sediments were taken. Such sediments provide sensitive indication of the accumulation through the deposition of suspended material of geogenic and anthropogenic character. The depth of physical and biological raise of the sediment is approximately 20 cm; therefore, a 20 cm thick layer was collected from the sediment surface. A grab corer was used for sampling.

Original samples consist of sand, silt and clay fractions. The sediments were dried at 40°C and passed through a 0.125 mm stainless steel sieve. Only the size fraction equal to or smaller than 0.125 mm was milled on an agate planetary treadmill to a grain size fraction under 0.09 mm. Portions of homogenized samples (0.5 g) were weighed for the assessment of extractable zinc (Zn), lead (Pb) and copper (Cu) contents.

2.2. Reagents and the preparation of extraction solutions

All standards and chemicals were obtained from the Sigma-Aldrich group and Merck (Darmstadt, Germany). Distilled water was additionally purified by reverse osmosis (Purelab Option R3, Elga) and on ion exchanger (Purelab Clasic, Elga). Deionized water was then used in all experiments. For the single-step extraction procedure, 0.05 mol L^{-1} Na_2EDTA solution (pH – varying within 3 and 7, adjusted with HCl and NH_4OH alternatively) was prepared. The initial pH of untreated 0.05 mol L^{-1} Na_2EDTA solution was 4.7. For the sequential extraction procedure (SEP), these solutions were used: 0.11 mol L^{-1} acetic acid, CH_3-COOH; 0.1 mol L^{-1} hydroxylammonium chloride, HO-NH_2.HCl; hydrogen peroxide, H_2O_2 (concentrated H_2O_2 was acidified with diluted nitric acid (1:1) to a pH value between 2 and 3); 1 mol L^{-1} ammonium acetate, CH_3-COONH_4.

2.3. Conventional single-step extraction with 0.05 mol L^{-1} Na_2EDTA

The standard soil extraction procedure with 0.05 mol L^{-1} $(NH_4)_2EDTA$ [18] was modified for the sediments from the studied area and a 0.05 mol L^{-1} Na_2EDTA solution was used. The original and modified conditions of the conventional and ultrasonic single-step extraction are given in Table 2. The solid sediment/solution extraction ratio (weight/volume ratio) of 1:150 (0.05 mol L^{-1} Na_2EDTA (75 mL) was added to the sediment sample (0.5 g) in a 100 mL polyethylene vessel). Tightly closed vessels were shaken for 6 h. The extract was separated by filtration and stored in a polyethylene vessel. This solution was then used for the determination of the extractable portions of Zn, Pb and Cu in the sample. The decomposition of the sediment residue was carried out by microwave heating, which is described below. The element determinations of sediment residues were realized by using atomic emission spectrometry.

Table 2. Standard and modified procedures of conventional and ultrasonic single-step extraction into 0.05 mol L^{-1} EDTA solution.

Standard procedure (conventional)1		Modified procedure (conventional)	Modified procedure (ultrasonic)
extraction agent	$(NH_4)_2EDTA$	Na_2EDTA	Na_2EDTA
time of extraction	1 h, pH = 7	6 h, without pH modification	15 min, without pH modification
temperature	20±2°C	20±2°C	20±2°C
solid sample/solution extraction ratio (w/v ratio)	1:10	1:150	1:150
acidity of extraction agent	pH = 7 (modified with NH_4OH)	pH = 4.7	pH = 4.7
extraction vessel	250 mL PE (washed by H_2O, 4 mol dm^{-3} HNO_3 and 0.05 mol L^{-1} EDTA-salt)		
filtration	Cellulose; particle size retention in liquid 3 μm, basis weight 80 g m^{-1}; Θ = 18.5 cm		

* The 1-hour conventional EDTA extraction is the standard procedure for extraction of the bioavailable element contents in the soils.

2.4. Ultrasonic single-step extraction with 0.05 mol L^{-1} Na$_2$EDTA and microwave decomposition of the sediment residue

Ultrasound assisted extraction (USAE) or ultrasound assisted leaching is the proper name for solid-liquid extraction by solubilization of target analytes. For partial dissolution of the samples and solubilization of the studied elements the ultrasonic probe was used. This means that sample preparation was carried out in the discrete US-assisted leaching system. The standard soil extraction procedure with 0.05 mol L^{-1} $(NH_4)_2EDTA$ was modified for the USAE of the sediments from the studied area. The sediment sample was weighed (0.5 g) in the extraction vessel and Na_2EDTA solution (75 mL) was added with a weight/volume ratio of 1:150. The extract was strained through the filtration paper with blue stripe (particle size retention in liquid 3 µm, basis weight 80 g m^{-1}; Θ = 18.5 cm) and stored in a polyethylene vessel at the temperature of 4°C in a dark place. The storage time of extracts was not longer than 6 hours to prevent chemical and photochemical degradation of some EDTA metal species or possible microbial degradation of the EDTA molecule. The untreated EDTA solution (0.05 mol L^{-1}) is weakly acidic (pH ≈4.7). Moreover, EDTA is the strong complexing agent and changes in the extracted element contents were not observed in the first 24 hours.

Decomposition of the sediment residue was carried out by the microwave (MW) digestion in an acid mixture of HF, HCl and HNO_3. A closed vessel device with temperature control of the MW heating was used. HNO_3 (7 mL), HCl (2 mL) and HF (2 mL) were added to the remaining solid residue. The digestion program was as follows: 1st step – time -10 min, temperature 200°C, MW power - 1000 W and 2nd step – time - 20 min, temperature 200°C, MW power - 1000 W. The cooled solution was transferred to a 25 mL volumetric flask, filled up to the mark with distilled water and used for the determination of the residual element contents. The element determinations were realized by using atomic emission spectrometry.

2.5. BCR sequential extraction

The method of sequential extraction used in this work has been modified in accordance with the requirements of the pilot study [20]. Apart from the usual three steps of the optimized BCR procedure [19], the first step, for elements extractable into the water phase, and the fifth step, total sediment residue digestion in the acid mixture of HF, HNO_3 and $HClO_4$, were added [20]. Each step of the sequential extraction was performed in a mechanical end-over-end shaker for 16 h (200 min^{-1}, temperature 20±2°C). Once the extraction was finished, the solution was centrifuged at 4000 min^{-1} for 20 min. The solutions obtained from the individual extraction steps were stored in the polyethylene vessels at the temperature of 4°C in a dark place. All results were obtained as the average values of five repeated extractions. The extractable portions of the chosen elements were determined from the solutions prepared in the way which was described in details in [20]. The cooled solution was transferred to a 50.00 mL volumetric flask, filled up to the mark with distilled water and transferred to the polyethylene vessel. The determinations of element contents were realized by using atomic emission spectrometry.

2.6. Instrumentation

The ICP OES spectrometer Varian-Liberty 200 with a Cetac ultrasonic nebulizer was used: Zn, wavelength λ=213.857 nm, limit of quantification, LOQ – 2 mg L^{-1}; Cu λ=327.396 nm, LOQ – 1 mg L^{-1}; Pb λ=220.354 nm, LOQ - 2 mg L^{-1}; background correction – dynamic; plasma conditions: power –1 kW; plasma flow: 12.0 L min^{-1}. The 10σ criterion for the LOQ calculation (means 3σ criterion for the LOD calculation) was used.

The conventional extraction was performed on a mechanical shaking machine (200 min^{-1}, temperature 20±2°C), model T22, Slovakia. The USAE was carried out using an ultrasound disintegrator, type Person-Ultragen UZD 500, Slovakia, equipped with titanium probe. The power of the disintegrator was 90% of the maximal power (P_{max}=500 W).

X-ray fluorescence spectrometry (XRF) was applied for the determination of total element contents in the studied sediments. The measurements were performed on a Spectro X-LAB 2000 spectrometer. The wax-pressed tablet analysis was used. The homogenized sample (5 g) and wax (1 g) – Hoechst wax C micro-powder was mixed in the agate mortar and pressed in the hydraulic press – p=140 MPa. The time of pressing was 14 s. Tablets were obtained with diameters of 40 mm. The experimental conditions of the XRF spectrometry were as follows: X-ray lamp, Rh with Be window; maximal power – P_{max}=300 W; X-ray generator, U=1–60 kV; I=1–80 mA; P=3.5 kW; detector–Si(Li), cooled by liquid nitrogen, resolution 150 eV; capacity of the vacuum pump 5 m^3 h^{-1}.

The analytical working ranges: 3–1320 µg g^{-1} of Zn, with precision 0.5–5.0%; 4–1162 µg g^{-1} of Pb, with precision 0.4–5.0%; 4–1230 µg g^{-1} Cu, with precision 1–14%. LOQ for Zn was 3 µg g^{-1}, LOQ for Pb–4 µg g^{-1}, and for Cu–4 µg g^{-1}. The recovery as the accuracy parameter of the method was for Zn 95.4–118.0%, for Pb 81.7–117.9%, and for Cu 83.0–115% (over the working ranges).

3. Results and discussion

3.1. Single-step extractions and BCR protocol: Optimization, evaluation and comparison

The optimization was realized for 10 regionally interesting elements. Three elements with medial (Zn, Pb) and higher (Cu) mobility were chosen for discussion about the element extractability of sediments of the investigated sedimentary subsystems. The statements, listed below, can be used for the evaluation of the next potentially mobile element contaminants of the studied region. All results of sediment 1 and 2 are given in Table 3 as numerical values. For the sake of clarity, the results of sediment 1, 2, 3 and 4 are processed into the column charts. The diagrams provide the comparison of the extraction ability of the techniques (Figs. 2a, 2b, and 2c), and information about the quality control of the analyses (Figs. 3a, 3b, 3c). The sequential extraction of the studied elements (marked as SEP or modified BCR protocol) shows their "mid-to-higher" mobility in the studied region. Significant portions of non-residual

element contents are extracted in the first three steps of the SEP (1st step - water soluble contents, 2nd - acid extractable contents, and 3rd - reducible contents of elements), in all studied samples, see Table 3 and Figs. 2a, 2b, and 2c. The sums of the first three steps of the sequentially extracted contents represent the most mobile and potentially mobile element forms in the sediments.

Table 3 provides results of Zn, Pb and Cu determination after five-step SEP, after conventional and ultrasonically assisted single-step (EDTA) extraction procedures, and the results of total content analyses performed by XRF (marked as *XRF* in Table 3 and Fig. 2). The extraction efficiency of the ultrasonically assisted EDTA extraction (15 min), marked as *EDTA-USAE*, and the conventional EDTA extraction (6 h), marked as *EDTA extraction*, was evaluated by the comparison of the extracted contents of the single-step extractions with the sum of the element contents extracted during the first three steps of the SEP, marked as *SEP Sum step 1-3*. See parameters *EDTA-USAE, EDTA extraction, SEP Sum step 1-3* and *XRF* in Table 3; see also columns *EDTA-USAE, EDTA extraction, and SEP Sum step 1-3*, in Fig. 2. This comparison informs about the element extractability of the most mobile and potentially mobile element forms into the EDTA in our experimental and local geological conditions.

All results presented in Table 3 are expressed with their expanded uncertainties. The estimations of uncertainties were realized by a (in-house) validation study.

Expanded uncertainties of the used analytical procedure yield10% in the concentration range of studied sediments and expanded uncertainties of the direct solid state analysis (by XRF) yield 5% or 1% (see discussion in chapter 3.2.).

Fig. 2 brings graphical illustration of the efficiency of *EDTA extraction*, *EDTA-USAE* – extraction, and also brings the results of total content analyses performed by *XRF*. Fig. 2 also provides a comparison of the extraction contents into EDTA (conventional and USAE) and summary contents of the first three steps of the SEP. With respect to measurement uncertainties of the analytical procedure, the summary contents and the contents of EDTA extractions for zinc and lead can be considered comparable:

The sums of first three steps of the SEP and the contents of conventional *EDTA extraction* show percentage differences in the range from 6 to 22%, for Zn, and from 1 to 22%, for Pb.

The comparison of the summary contents of the SEP and the new *USAE-EDTA* extraction shows percentage differences in the range from 0 to 16%, for Zn, and 1 to 10%, for Pb (Table 3, Figs. 2a, 2b).

Table 3. The comparison of the Zn, Pb and Cu determination after five-step SEP, after conventional and ultrasonically assisted single-step (EDTA) extraction procedures, and the results of total content analyses performed by XRF.

| | Mean content2 ± uncertainty (μg g^{-1}) | | |
	Zn	Pb	Cu
Sediment 1			
Extraction step			
1 (water soluble)	≤2	≤2	2.0 ± 0.4
2 (acid extractable)	59 ± 6	≤2	6 ± 1
3 (reducible)	63 ± 6	35 ± 4	42 ± 4
4 (oxidizable)	26 ± 3	4 ± 1	79 ± 8
5 (residual)	42 ± 4	6 ± 2	21 ± 2
SEP Sum	190 ± 19	45 ± 5	150 ± 15
SEP Sum step 1-3	122 ± 12	35 ± 4	50 ± 5
XRF	197 ± 2	46 ± 3	161 ± 2
Recovery SEP Sum /XRF (%)	96	99	93
EDTA extraction	105 ±11	39 ± 4	78 ± 8
EDTA residual	90 ± 9	6 ± 1	77 ± 8
EDTA sum	195 ± 20	45 ± 5	155 ± 16
Recovery EDTA sum /XRF (%)	99	98	96
EDTA-USAE	135 ± 14	33 ± 3	79 ± 8
EDTA-USAE residual	58 ± 6	14 ± 1	78 ± 8
EDTA-USAE sum	193 ± 19	47 ± 5	157 ± 10
Recovery EDTA-USAE sum /XRF (%)	98	103	98
Sediment 2			
Extraction step			
1 (water soluble)	≤2	≤2	2.0 ± 0.4
2 (acid extractable)	18 ± 2	≤2	3 ± 1
3 (reducible)	36 ± 4	21 ± 2	32 ± 3
4 (oxidizable)	16 ± 2	≤2	62 ± 6
5 (residual)	51 ± 5	9 ± 2	39 ± 4
SEP Sum	121 ± 12	30 ± 6	138 ± 14
SEP Sum step 1-3	54 ± 5	21 ± 2	37 ± 4
XRF	125 ± 1	35 ± 2	143 ± 1
Recovery SEP/XRF (%)	97	86	97
EDTA extraction	57 ± 6	20 ± 2	90 ± 9
EDTA residual	63 ± 6	11 ± 1	50 ± 5
EDTA sum	120 ± 12	31 ± 3	140 ± 14
Recovery EDTA/XRF (%)	96	89	98
EDTA-USAE	58 ± 6	20 ± 2	94 ± 9
EDTA-USAE residual	64 ± 6	13 ± 2	49 ± 5
EDTA-USAE sum	122 ± 12	33 ± 3	143 ± 14
Recovery EDTA-USAE/XRF (%)	97	94	100

† Mean content – the average of 5 times repeated extractions and 5 times repeated analyses.
(1) – parameters 1; 2; 3; 4; 5 – the individual steps of the SEP (modified BCR protocol); for Zn, Pb, Cu extracted contents;
(2) – parameter SEP Sum – the summary contents of the five-step SEP (modified BCR protocol);
(3) – parameter SEP Sum step 1-3 the sum of the first three steps of the SEP;
(4) – parameter XRF – the total content analysis by XRF;
(5) – parameter Recovery SEP/XRF – recovery – comparison of SEP Sum and XRF results;
(6) – parameter EDTA extraction – the conventional single-step EDTA extraction (6 h);
(7) – parameter EDTA residual – the totally digested sediment residue after conventional EDTA extraction;
(8) – parameter EDTA sum – the sum of the extracted and digested contents obtained in conventional EDTA extraction;
(9) – parameter Recovery EDTA/XRF – recovery – the comparison of EDTA sum and XRF;
(10) – parameter EDTA-USAE – the ultrasonically-assisted single-step EDTA extraction (15 min);
(11) – parameter EDTA-USAE residual – the totally digested sediment residue after ultrasonically-assisted EDTA extraction;
(12) – parameter EDTA-USAE sum – the sum of the extracted and digested contents obtained in ultrasonically-assisted EDTA extraction.

The uncertainties of the whole analytical procedure (in the concentration range of determined sediments) is 10%. Therefore, even a 16% difference can be considered acceptable, for the first screening evaluation of the element mobility changes in polluted areas.

Thus, the achieved contents of the sono-extraction (*EDTA-USAE*, in Fig. 2, and Table 3) show an acceptable compliance with the contents of the 1-3 steps of the SEP (*SEP Sum step 1-3,* in Fig. 2, and Table 3) , *and* conventional extraction (*EDTA extraction*, in Fig. 2, and Table 3).

In the case of the copper, the extracted Cu contents of all sediment samples were equivalent for the EDTA-USAE and the conventional EDTA procedure. The sequential extraction shows its higher mobility in the studied region. It demonstrates the extraction of copper into the water in the 1st step of SEP (Table 3) for the majority of the sediment and soil samples of the investigated region [26]. The higher mobility of copper is evident from the comparison of the summary content of 1-3 steps of the SEP and the EDTA extractions (conventional and ultrasonically-assisted). The ultrasonically improved EDTA extraction is also partially able to isolate the next oxidizable phase of the sediments of the studied region (parameters *EDTA-USAE*, and *SEP Sum step 1-3*, in Fig. 2c, and Table 3).

Nevertheless, the long term monitoring can provide first information of the Cu mobility changes in sediments. The ultrasonically and conventionally extracted Cu contents achieved higher values than the sum of the first three steps of the SEP (parameters *SEP Sum step 1-3* – for Cu, and *EDTA-USAE* in Fig. 2c, and Table 3). This fact reflects the higher mobility of Cu in the studied region and it is consistent with extractable copper contents of the wastewater, sludge, soils and plants collected in the sampling area [26,27].

The optimization process of the ultrasonically assisted extraction (USAE) is shown in the Fig. 4. It could be discussed as follows:

The optimal time of the ultrasonically assisted extraction (USAE) was 15 min (see Figs. 4a, 4c, 4e). The "fifteen-minute extraction" is the most appropriate not only due to the sufficiently extracted contents but also from the RSD's point of view. Figs. 4b, 4d, 4f documents the decreasing RSD values during the time optimization. The fifteen-minute duration of the USAE is sufficient for the extraction of the contents which correspond to the sum of the first three steps of the SEP (modified BCR protocol), see Figs. 2a, 2b, and 2c.

The 15 min USAE proved to be satisfactory for the separation of the mobile and potentially mobile Zn, Pb and Cu portions in all sediments samples, and it
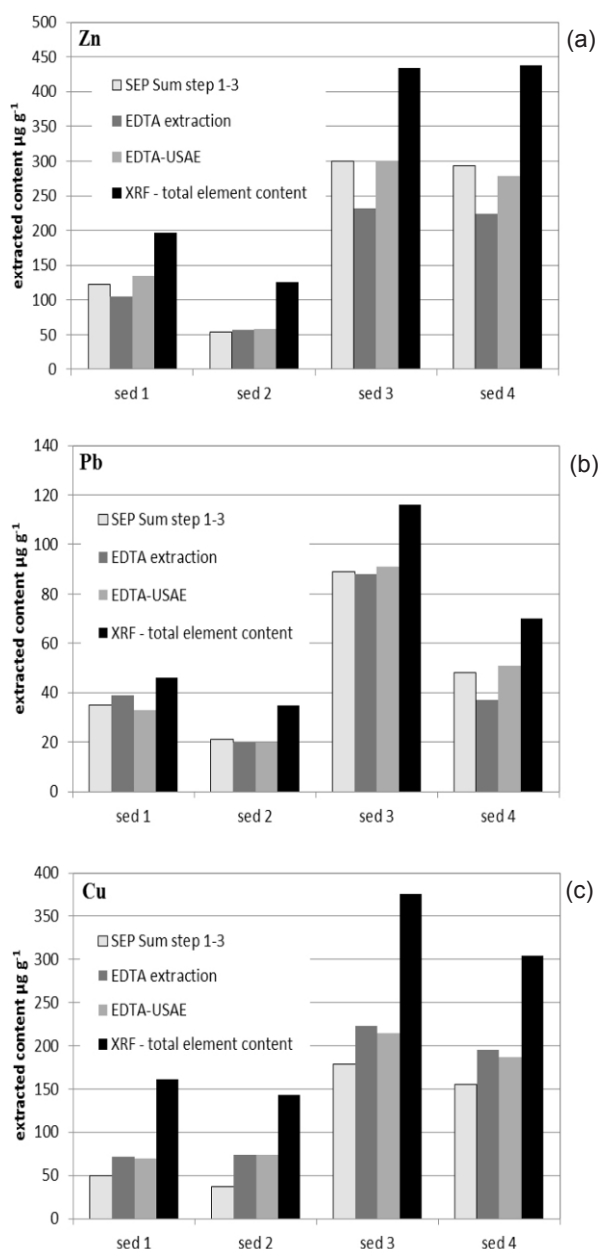
Figure 2. The comparison of the Zn, Pb and Cu determination of conventional EDTA extraction, EDTA-USAE (columns labeled – EDTA extraction, and EDTA-USAE) and summary contents of the first three steps of the SEP (column labeled – SEP Sum step 1-3). Results of total content analyses performed by XRF (column labeled – XRF-total element content).

delivers the screening information about the mobile and potentially mobile element portions in sediments in just 15 minutes.

The *EDTA-USAE* extraction brings acceptable results for all studied elements. The extraction time could be considered sufficient for the extraction of mobile and potentially mobile Zn, Pb and Cu portions, and as shown by further experiments, the (fifteen-minute) duration
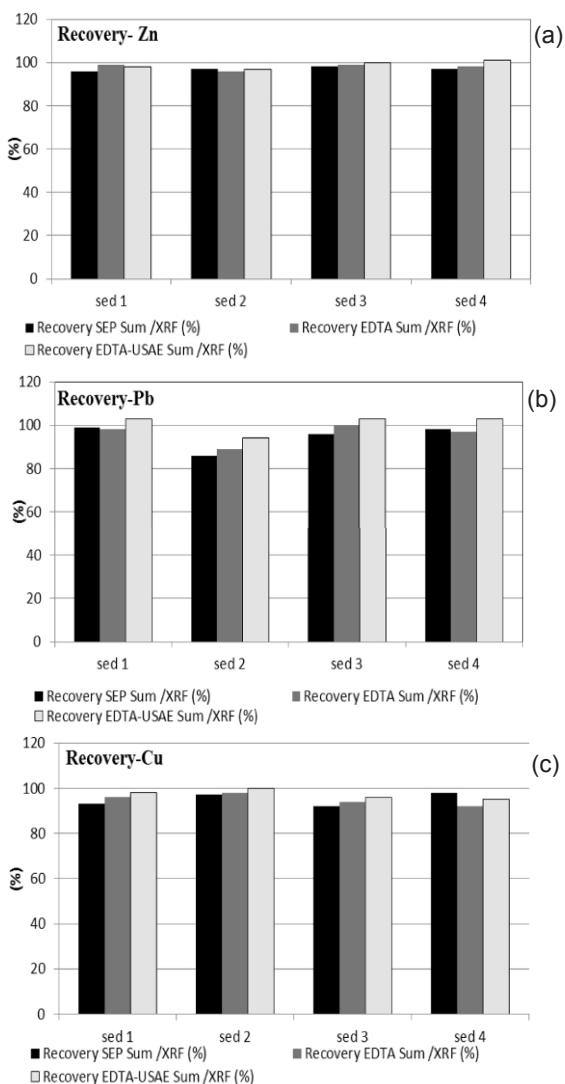
Figure 3. The comparison of the recoveries of the SEP (labeled as Recovery SEP Sum /XRF), conventional EDTA extraction (Recovery EDTA Sum /XRF), and ultrasonically assisted EDTA extraction (Recovery EDTA-USAE Sum /XRF).

is also suitable for the extractions of other element contaminants in sediments of investigated region.

This allows the use of this new ultrasonically assisted EDTA extraction for the "screening" element mobility evaluation in the regional conditions. It is also applicable for element mobility evaluation of various solid environmental samples of polluted area.

3.2. Quality control of the analysis

The accuracy of the determination by the conventional and ultrasonic single-step extractions was controlled by the comparison of the sum of the extracted and digested element contents, and the total element content analyses of sediments made by XRF method. The accuracy parameters expressed as recoveries are presented and

marked by the parameter *Recovery EDTA Sum/XRF* and parameter *EDTA-USAE Sum/XRF*, see Table 3, and Figs. 3a, 3b, 3c.

The recoveries of the ultrasonically assisted EDTA extractions, *EDTA-USAE Sum/XRF,* are between 97-101% for Zn, between 94-103% for Pb, and between 95-100% for Cu. See parameters *Recovery EDTA-USAE/XRF*, in Table 3, and Figs. 3a, 3b, 3c. All obtained recoveries of the conventional EDTA extractions are ranged from 89 to 100%, and in regard to the complexity of the sample preparation procedure, they could be evaluated as acceptable results.

The sums of the contents of individual extraction and digestion steps of the modified BCR protocol (5 steps) and the total element content analysis by XRF were also compared. The obtained recoveries are presented in the Table 3, and Fig. 3, as a parameter *Recovery SEP Sum/ XRF.*

The comparison has brought acceptable results, and the recoveries are ranged between 96 and 99%.

The running of all extractions has brought acceptable results, and satisfied the requirements on the analytical quality control for the complex sample preparation procedures.

All results listed in Table 3 are presented with their expanded uncertainties U, with coverage factor k = 2. For expanded uncertainty calculation, the combined standard uncertainty was used. The standard uncertainties of each component were used as follows:

$$U = k.u_c;.......k = 2;......u_c = \sqrt{u(p)^2 + u(q)^2 + ...}$$

They are expressed as standard deviations in [μg g^{-1}], see Table 3.

The estimations of uncertainties were realized by a (in-house) validation study, and all steps of the sample treatment were included in the validation process. Expanded uncertainties of the used analytical procedure (with extractions as the sample pretreatment) yield 10% in the concentration range of studied sediments and expanded uncertainties of the direct solid state analysis (by XRF) yield 5% (alternatively 1% - it depends on element concentration). The expanded uncertainties are usually expressed as individual RSD-values, for partial interval of concentration (*e.g.* 0-10 μg g^{-1} - uncertainty is 30%; 10-100 μg g^{-1} - uncertainty is 20%; *etc.*), in the validated working range. Validation of this method is a separate topic of another article.

The additional accuracy control of the extraction and analysis was performed by using CRM 601, which was extracted concurrently to the extraction of the four sediment samples discussed above (Table 4). The accuracy control by using CRM 601 is in accordance with the accuracy control by XRF. See the Cu, Pb
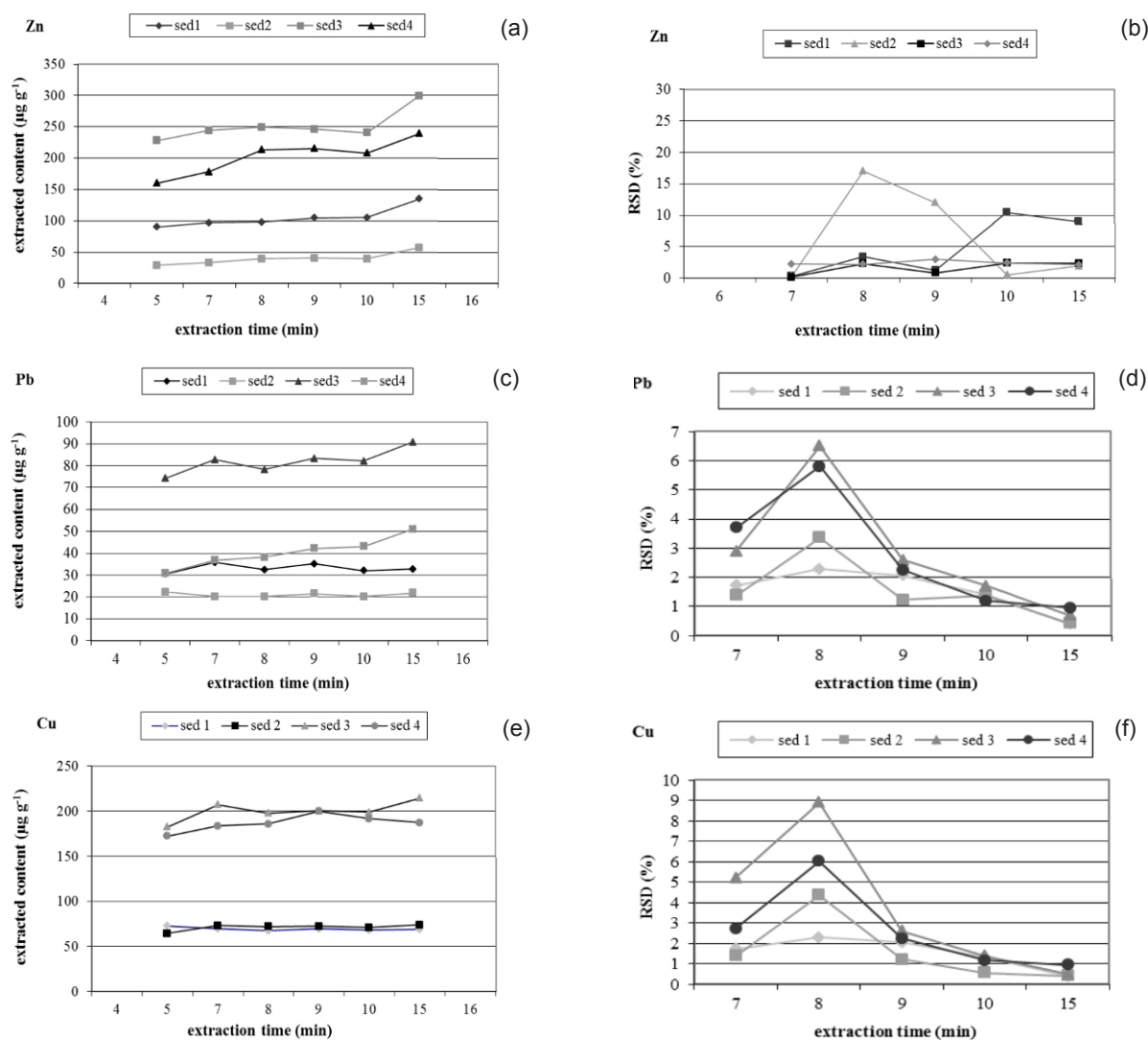
Figure 4. The optimization of the extraction time (USAE), the determination of (a) Zn, (c) Pb and (d) Cu extracted portions in the sediments and the relative standard deviation (RSDs) by time optimization for Zn, Pb, and Cu ((b), (d), and (f)).

analyses of extracted contents, and analyses of the total Cu, Pb contents listed in Table 4. The experiments have brought acceptable results, and they are comparable with the published results [19,28,29].

Detailed description and discussion of Table 4: The first column of Table 4 brings the experimentally obtained Cu and Pb contents of the individual extraction steps of the BCR extraction; the sum of the extracted and digested contents (labeled as the *SEP sum*); and the total content analysis (XRF), labeled as the *Total element content*. The first column also brings the comparison of the *Total element content* and the *SEP sum* for Cu and Pb contents. The comparison is expressed as a recovery, see parameter *Recovery SEP/Total element content*. This comparison, with regard to the relevant uncertainties yields practically identical results. The obtained recovery values are from 96 to 99%.

The second column presents the indicative Cu and Pb values of CRM 601 [28] and the results of the optimization experiments of BCR procedure from Sutherland and Tack (determination of the *residual* contents) [29] and Rauret *et al.* (determination of the *aqua regia contents – i.e.*, *pseudo-total digestion*) [19]. Estimation of the total element content in this study was performed by digestion of sediment residue in the mixture of HF, HNO_3 and $HClO_4$ as described elsewhere [20]. Total decomposition of sediment residue was used during the whole study because it allows a better control of accuracy of the experimental work.

Some authors tend to present the pseudo-total digestion and the comparison of the total and pseudo-total digestion [19,29]. In this case the consistency of the obtained and published results can also be stated. See

Table 4. Comparison of the obtained and published values of the Cu and Pb extracted contents in the CRM 601 after BCR extraction and the results of total content analysis performed by XRF.

Element	Isolated fractions	Obtained values ± SD ($\mu g \ g^{-1}$)	Indicative values ± SD ($\mu g \ g^{-1}$) [28]	Recovery (%)
Cu	acid extractable (1)	7.6 ± 1.5	10.5 ± 0.8	72
	reducible (2)	71 ± 7	72.8 ± 4.9	98
	oxidizable (3)	93 ± 9	78.6 ± 8.9	118
	residual	64 ± 6	60.4 ± 4.9 [29]	106
	SEP Sum	236 ± 12	222 ± 20	105
	Total element content	246 ± 93	230 ± 15 [19]4	107
	Recovery SEP Sum/ Total element content(%)	96	100	
Pb	acid extractable (1)	≤2	2.28 ± 0.44	-
	reducible (2)	199 ± 10	205.0 ± 11	97
	oxidizable (3)	25 ± 6	19.7 ± 5.8	127
	residual	37 ± 4	38.0 ± 8.7 [29]	97
	SEP Sum	261 ± 13	265 ± 27.0	99
	Total element content	264 ± 7[iii]	288 ± 52 [19][iv]	92
	Recovery SEP Sum/ Total element content(%)	99	92	

‡Presented experimentally obtained values are measured by independent analytical method, by XRF; §Presented experimentally obtained values are averages of 5 repeated extractions; pseudo-total digestion; the published recoveries comparing the total and pseudo-total digestion of Pb, Cu, in CRM 601 are: 107% for Cu, 106% for Pb [29].

Table 4 parameter *Recovery SEP sum/Total element content* in 2nd column [19,28,29].

The third column presents the comparison of the obtained and published (indicative) values of Cu and Pb for CRM 601, see parameter *Recovery.* The published recoveries comparing the total and pseudo-total digestion of Pb and Cu, in CRM 601 are: 107% for Cu, 106% for Pb [29]. It is possible to state that all results obtained in this study are in accordance with the XRF analyses and determinations of CRM 601 which were performed for analytical quality control.

3.3. ICP-OES and XRF determinations

Optimization of ICP-OES determination: All types of the possible interferences of the ICP-OES analysis-measurements were controlled and eliminated. The spectral interferences were eliminated by the appropriate choice of spectral lines and suitable background correction.

The non-spectral interferences (connected with nebulization, with high contents of dissolved compounds, and with the transport of sample into the plasma) were eliminated by the preparation of calibration solutions with analogical composition as the measured sample solutions. For the element determination in each extraction step a separate analytical calibration was prepared. The contents of the soluble components were tested by measurements of the diluted and undiluted samples. The results showed that the contents of dissolved salts do not affect the analytical signal (in the concentration range of the measured solutions).

Non-spectral interferences were also tested by using the method of standard additions. Comparison of the calibration of the standard additions method and the external calibration showed that these interferences were negligible in the concentration range of the sample extracts.

XRF determinations: The method for the reference determinations of the total element contents by XRF is validated throughout the calibration range. Obviously, the basic user calibrations are supplied by the manufacturer, based on the requirements of the laboratory. For each calibration 15 reference materials were used in the chosen concentration range. These included various types of samples (sediments, soil, silicates, granites, basalts, diorites, limestone, element oxides, ores, coal, *etc.*) and come from these sources: United States Geological Survey, USA (USGS); Canadian Certified Reference Materials Project, Canada (CCRMP); Centre Recherches Petrographiques et Géochimiques, France (CRPG); Bureau of Analysed Samples, UK (BAS); Geological Survey of Japan, Japan (GSJ); Institute of Geophysical and Geochemical Exploration, China (IGGE); Zentrales Geologisches Institut, Berlin

(ZGI); Bureau Comunitaire de Références, Brussels (BCR); South African Reference Material (SARM). The calibration can be extended by using the software of the XRF spectrometer. The software allows addition of the other CRM and LRM, or creation of completely new calibrations for different sample matrices [30].

4. Conclusions

The application of the ultrasound assisted single-step extraction procedure is very interesting from a time-saving point of view, and also gives acceptable information about the metal contamination in the environmental subsystems, and the first screening information about the most mobile portions in the sediment samples.

A good agreement between the element contents extracted into Na_2EDTA and the sum of the first three steps of the modified BCR protocol for the all studied elements was found in this study. Thus was achieved the basic aim of this study, namely: The optimization of the ultrasound assisted (EDTA) single-step extraction procedure for the releasing of the mobile and potentially mobile element forms from the solid and abiotic environmental samples. The extraction ability in optimal conditions was consistent with the extractability of the first three steps of modified BCR protocol. Whereas, ultrasonically assisted EDTA extraction can serve as a screening alternative of BCR procedure.

With respect to the execution of the presented experiments, it is possible to state that the fifteen-minute ultrasonically assisted extraction into a strong chelating agent releases mobile and potentially mobile metal forms from the solid and abiotic environmental samples. The use of the ultrasound assistance in the extractions is cost- and time- friendly method.

Therefore, it can be employed as a rapid screening evaluation of the mobile and potentially mobile element portions in the sediments, soils, and other solid state environmental matrices of the studied region.

Acknowledgements

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