An appraisal of conventional, microwave and ultrasound BCR extraction methods for the analysis of metals in sediments of Pančevo, Serbia

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Abstract. We use conventional, microwave and ultrasound assisted sequential extraction, of defined time and power, techniques for extractions of Cd, Cu, Cr, Ni, Pb and Zn in sediments and certified material. We did not change the conditions of extractions through steps, cause we what to see is there difference in extraction results for the certified material and sediments. We use lower powers and time from microwave and ultrasound extraction in order to avoid additional heating and boiling of the samples. Steps 1–3 of the BCR (Community Bureau of Reference), excluding the hydrogen peroxide digestion in step 3, were completed in 16 h in the conventional, in 120 s with 90 W power of microwave and in 30 min of 42 kHz of an ultrasonic frequency. Digestion of organic matter with hydrogen peroxide was performed the same for all techniques. The fourth step, the pseudo-total content, was performed the same on samples remaining after performing the extraction of the previous three phases either conventionally, microwave-assisted or with ultrasound. The precision and accuracy of the proposed procedures were evaluated using a certified reference material BCR701. Acceptable accuracy for most of the metals was observed for all three steps of BCR protocol applying a 16 h total shaking period. Metals were determined with an acceptable accuracy after the pseudo-total step; expect Cr. Results obtained after the application of different techniques on sediments were comparable with *ANOVA* test for the 95 % of confidence level.

Key words: Heavy metals, Danube alluvial sediments, BCR

Introduction

The total heavy metal content does not provide complete information about pollution of soils and sediments. From an environmental point of view, it is much more important to determine under which conditions some trace elements, including heavy metals, could be released and thus endanger the surrounding soil and waters. Metal fractionation into different chemical forms associated to matrix samples requires the application of sequential extraction methods (Pérez-Cid et al., 1999). Sequential extraction (SE) is an important and widely applied tool for gaining information on potential mobility (hence, potential bioavailability and toxicity) of potentially toxic metals in the environment. Application of the approach continues to expand and now encompass more elements and substrates than were probably ever envisaged by early workers in the field (Bacon and Davidson, 2008). In SE, metal partitioning depends on the extraction conditions, such as reagent temperature, extraction time, shaking, etc. The lack of a standard extraction method can make it difficult to compare the results obtained by different researchers. In order to harmonize the different fractionation scheme, the European Communities Bureau of References (BCR) proposed the three-stage SE protocol. Alternative energy sources (microwaves, ultrasound, electricity, etc.) are currently receiving a great deal of attention, with the emphasis on the reduction of treatment times and greater reproducibility (Castillo et al., 2011). If microwave heating techniques were applicable to the dissolution of total metals, microwave techniques could also be used to stimulate the rapid release of metals in each of the three binding fractions of sediments. The most known applications of microwaves are rapid solvent extraction and fast wet dissolution of different kinds of solid samples. It is known that exposure of solids to ultrasound leads to structural changes in their morphology. Some of authors

have achieved encouraging results using ultrasound probes to reduce the time required foe sequential extraction of metals from sediments. Ultrasound baths are less expensive than probes (Canepari et al., 2005). We used the ultrasound bath for shortening the time (to 30 min per step) of each BCR step. The main objective of this work was the application of the BCR three-step SE procedure plus determination of the pseudo-total metal content on certified materials and on sediments samples, by application of conventional mixing, microwaves and ultrasound. The trace metals considered included Cd, Cr, Cu, Ni, Pb and Zn. In this work, a microwave oven and ultrasound baths were employed as the energy source, with the goal of achieving faster metal extraction from the samples. In the analyses of certified materials, surface and buried sediments it was considered to determine how the microwaves and ultrasound of defined power and time influenced the extraction.

Materials and Methods

The metals were determined using an inductively coupled plasma/optical emission spectrometer iCAP 6500 Duo, (Thermo Scientific, United Kingdom). The detector was a RACID86 Charge injector device (CID). A microwave oven (Electrolux model 2100 S, 800 W power) was used as the microwave radiation source. For extraction with ultrasound we used an ultrasonic bath J.P. Selecta, with maximum power frequency of 42 kHz and an effective ultrasound power of 100 W, without heating.A centrifuge (Tehtnica, Železniki) was used for the separation of the extracts.

The extractant solutions were prepared from analytical-grade reagents (Carlo Erba). For calibration, external standard solutions were prepared from 1000 mg $L-1$ stock metal solutions. The extraction procedure was realized in closed 50 cm3 polyethylene tubes, in which 1000 ±1 mg of weighed samples were placed, and the required extract reagent was added. The ratio between the solid and solution was 1:40. Conditions that were applied in the three phases of the BCR extraction protocol and for the determination of the pseudo-total metal contents were presented in Table 1. For all three BCR extraction steps, we maintain power and time of microwave, where the temperature did not exceed 50 ^{0}C while in the case of USSE we maintain time (30 min). We used the ultrasound bath without heating, but because of the exposure of ultrasound waves on water, we checked temperature and it did not exceeds the 35 ^{0}C.

Precision is calculated as a percentage using the standard deviation divided by the mean of replicated measurements. Accuracy is determined by comparing the measured concentration with the certified value and is expressed as the percentage recovery. Satisfactory precision and accuracy are considered to be within ≤20%, and between 80% and 120% for all elements, respectively, which correspond to a 95% confidence interval.

Certified reference materials were supplied by The Community Bureau of Reference Sample (BCR): BCR-701. The materials were handled according to the supplier's specifications.

Thirty six soils and sediments from the Petrochemical Industry Pančevo and its surroundings, within 9 locations, were used in this study. Pančevo (44°52'15" north, 20°38'25" east) is an industrial town located in Vojvodina, the northern province of the Republic of Serbia. It is located 20 kilometers northeast of the capital Belgrade and lies on the left bank of the Tamiš River, 4 km from the Danube River. Composite samples consisting of four sediment sub-samples were collected within each sampling site. Sampling sites were: the Chlor-Alkali Plant (1); the Electrolysis Facility (2); along the road in the petrochemical complex (3); the area for mercury disposal (4); along the road around the petrochemical complex (5); Messer Industry (6); Vojlovica (7); Starčevo (8) and Pančevo City (9).

Results and Discussion

CSE extracted metals, Cd, Cu, Ni, Pb and Zn showed satisfactory accuracy after the first two BCR steps, and Cu and Ni after the third. Zn showed slightly higher accuracy value after the third step. The values for Pb and Cd did not match the reference values after the third extraction step in the CSE.

MWSE and USSE, applied in defined time and powers, showed lower accuracy for most of the metals after the all three BCR steps. In MWSE Pb was the only metal that showed satisfactory accuracy: after the first BCR step. In USSE Cd, Ni and Zn showed accuracy in the range of 80-120 % after the fist BCR step. The opposite of MWSE, the other metals (Cr, Cu and Pb) have higher values than the certificated ones.

Both of these techniques, MWSE and USSE, gave lower extracted concentrations after the second BCR step.

Similarity in the extracted vales after the second BCR step in MWSE and USSE was not case after the third step. MWSE extracted metals showed significantly higher values than the certificated once and significantly higher than CSE and USSE values. Cu, Ni and Zn obtained after the USSE showed satisfactory accuracy and value for Pb was closed to the higher level of the accuracy range, but generally the results were less reproducible than those obtained by CSE.

Cr was the only metal that showed accuracy less than 80 % after all extraction steps in all SE techniques, except after the first step in USSE where is above 120 %....

Cr, Cu, Pb and Zn showed the highest concentrations in the samples labeled 1 (the Chlor-Alkali Plant) in comparison to the other samples (Fig. 1). For Cr and Pb the higher values were obtained by USSE while for Cu and Zn by CSE. These higher values for Cr and Pb could be explained with significantly higher accuracy that these metals showed when the certificated material was extracted with ultrasound.

Table 1. Reagents and operating conditions required in the conventional (CSE), microwave (MWSE) and ultrasonic (USSE) BCR sequential extraction

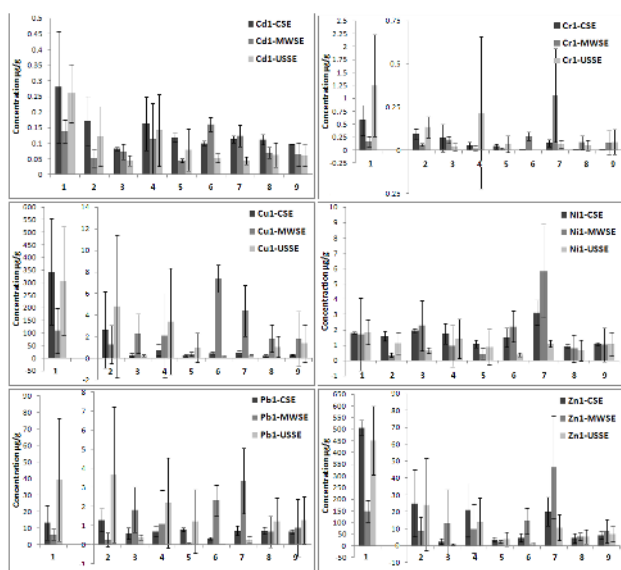| Step	Fraction	Reagens	CSE	MWSE	USSE
I	Exchangeable and acid soluble	40 cm^3 0.11 mol/dm^3 CH$_3$COOH	16 h (overnight), room temperature	120 s, 90 W	30 min, 42 kHz
II	Iron and manganese oxides	40 cm^3 0.5 mol/dm^3 NH$_2$OH·HCl (pH 1.5)	16 h (overnight), room temperature	120 s, 90 W	30 min, 42 kHz
III	Organic matter and sulfides	10 cm^3 8.8 mol/dm^3 H$_2$O$_2$	1 h (water bath), 85 °C	1 h (water bath), 85 °C	1 h (water bath), 85 °C
		10 cm^3 8.8 mol/dm^3 H$_2$O$_2$	1 h (water bath), 85 °C	1 h (water bath), 85 °C	1 h (water bath), 85 °C
		40 cm^3 1 mol/dm^3 CH$_3$COONH$_4$ (pH 2)	16 h (overnight), room temperature	120 s, 90 W	30 min, 42 kHz

Fig. 1. Distribution of metal concentrations with one standard deviation in sediments after the first phase of CSE, MWSE and USSE.

The conditions that were applied for microwave extraction in the first phase, although insufficient for the certified material, gave significantly higher concentrations of metals than those obtained by the CSE. *Anova* test that has been applied on of extracts of sediments from different locations produced by CSE, MWSE and USSE, were comparable according to the F value for a 95 % confidence interval.

After reductive dissolution of Fe and Mn-oxides, Cr, Cu, Pb and Zn showed significantly higher concentrations in the sediments labeled 1 (Fig. 2), as it was after the fist BCR step (Fig. 1). The difference is in abundance of extracted concentration tested techniques. After the second step dominant technique for Cr and Pb were CSE, while for Cu and Zn MWSE. There was significant difference between variance of Ni extracted in CSE and Ni extracted in MWSE and USSE on the other side. Anova test was comparable when was applied on of extracts of sediments produced by MWSE and USSE.

As was the case in the previous phases, the samples with the highest amount of organic and / or sulfide sorbed Cr,

Cu, Pb and Zn, were from the Chlor-Alkali plant (1) for all techniques (Fig. 3). MWSE was technique which gave the highest extracted concentrations of Cr, Cu and Zn, while CSE was for Pb. This is the SE step where are the differences among the behavior of the certified material with sediment samples significant. Based on the results for the certified material it should be expected that the highest extracted values should be gained by MWSE, which is not case in the most of sediments.

Conclusion

Main goal of this work is to show the differences or similarities in extracted metal concentrations obtained by CSE, MWSE and USSE in the certificate material and investigate sediments in defined time and power of microwaves and ultrasound. The conditions that were applied in MWSE, insufficient for the certificate material, gave significantly higher metal concentrations in sediments than those obtained by the CSE. *ANOVA* test which we used for all three techniques and for each metal gave the comparable values.
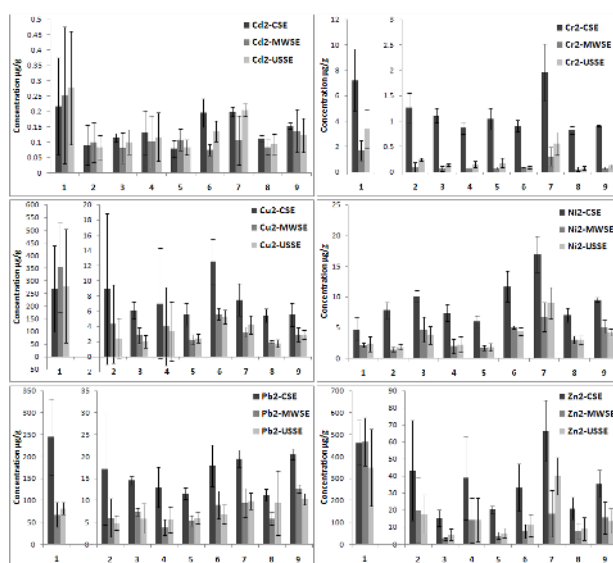

Fig. 2. Distribution of metal concentrations with one standard deviation in sediments after the second phase of CSE, MWSE and USSE.
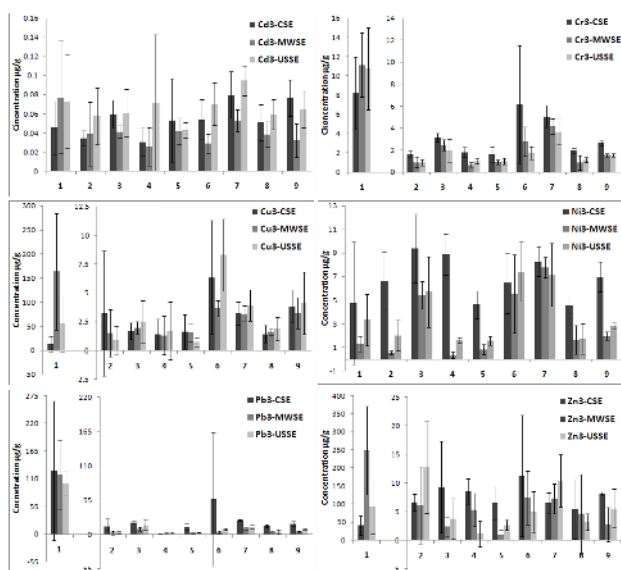
Fig. 3. Distribution of metal concentrations with one standard deviation in sediments after the third phase of CSE, MWSE and USSE.

In the second BCR step, in most of the sediment samples, the technique who gave the highest extracted concentration was CSE, and this is the only technique who gives satisfactory accuracy in applied extraction conditions. The obtained results indicate the need for stronger extraction conditions for MWSE and USSE.

In the third SE step, and based on the results of certificate material it should be expected that the highest extracted values should be gained by MWSE, which is not case in the most of sediments. CSE and USSE were techniques which gave the highest extracted metal concentrations in sediments and this is expected since with these two techniques the acceptable accuracy was obtained for most of the metals.

Acknowledgements

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