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MOBILITY TEST APPLIED TO A CERTIFIED REFERENCE MATERIAL BCR-483 – SEWAGE SLUDGE AMENDED SOIL

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Abstract. The aim of the study was to estimate the mobile forms of Cd, Ni and Pb from a certified reference material BCR-483, which is a sewage sludge amended soil. In the study were tested 4 extraction procedures, 2 of them were used by the BCR European Commission. The BCR certificate of analysis contains certified value for mobile fraction of Cd, Ni and Pb extracted with 2 different solutions: 0.05 M EDTA and 0.43 M CH_3COOH. The mobility tests include not only the values obtained with these 2 methods, but also the values obtained with another 2 single chemical extraction procedures, which used the following extractants: a buffer solution at pH = 7.3 of 0.005 M DTPA, 0.1 M TEA and 0.01 M $CaCl_2$, a mixture of 0.01 M EDTA and 1 M NH_4OAc at pH = 7. The contents of Cd, Ni and Pb were analysed with flame atomic absorption spectrometry (FAAS). The experimental tests applied to BCR-483 with BCR methods proved that both extraction and determination procedures can provide valuable data, comparable with the certified values for exchangeable fraction of Cd, Ni and Pb. The data obtained with the other 2 methods confirm the fact that the extractant type is very important in evaluating the mobility fraction of the metals (different concentrations of metallic elements obtained with different extraction procedures).

Keywords: metals, exchangeable fraction, single chemical extraction, certified value, soil, BCR-483.

AIMS AND BACKGROUND

Persistent and potentially harmful products have been widely dispersed and concentrated in different spheres of the environment (water, air, soil, sediment, living organism) as a result of human activities. Among the most dangerous are toxic metals. Such materials have been accumulated in materials dredged from waterways, harbours, in industrial sites, in landfills, in lake sediment, stream beds and deltas deposited. Some organisms have accumulated high enough level of metals to do harm to themselves or to human that use them as a food source[1].

Over the last decades scientists have became increasingly aware that determining total concentrations of metallic elements in soils provides very limited infor-

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mation about their mobility within the profile, bioavailability and toxic potential to ecological system.

The aim of the study was to estimate the mobile forms of Cd, Ni and Pb from a certified reference material (CRM) BCR-483 (Ref. 2), which is a sewage sludge amended soil. BCR is a registered trademark of the European Commision. According to Report EUR 17127 EN of BCR Reference Materials the certified reference material CRM-483 contains high quantity of mobile metallic elements. The sewage sludge amended soil has acid pH (5.4) that influences the mobility of metals to the environment (groundwater, surface water, plants).

The extraction methods tested were two standard methods (SR ISO 14870/99 (Ref. 3), NF X 31 – 120/92 (Ref. 4)), used in environmental study for evaluation and monitoring the mobile metallic species from soil, sediment and sludge[5–9] and two BCR methods for mobile metallic elements extracted from soil, proposed by Standard Measurement and Testing Program of the European Community[10].

The selected methods extract not only the mobile or exchangeable forms of metallic elements, but also the carbonate forms of metals (is the case of 0.43 M acetic acid extraction solution, method proposed by BCR).

EXPERIMENTAL

Materials and chemical reagents. All glassware were cleaned with 4 M HNO_3 and rinsed with distilled water. As reference materials were used standard solution traceable to SRM from NIST (1000 mg/l in 2–4% HNO_3, CertiPUR) for all metallic elements, acetic acid (96%), ammonium acetate, calcium chloride, triethanolamine, ethylenediaminetetraacetic acid disodium salt (EDTA) and diethylenetriaminepentaacetic acid (DTPA). All the chemicals used were of analytical reagent grade (Merck quality). Matrix of the solutions used for calibration curve were matching with the extraction solutions. Each standard solution used as reference material has a specificate uncertanty value.

Apparatus. Atomic absorption spectrometer THERMO scientific M series; Heidolph Promax 2020 shaker, analytical balance, filter paper 0.45 μm membrane filter, glassware[11].

Extraction procedure. The bottle (BCR-483) was manually shaken for 1 min to homogenise content. After than, 4 g of sample were taken for each experiment (Table 1) directly from the bottle. Operations were performed at 20 ± 2ºC. The sample portion was transferred into a glassware bottle in which was added the quantity of extraction solution according to the report in Table 1. The obtained mixture was shaken on an end-over-end shaker operating at precise number of rpm at 20ºC. The extracts were immediately filtered through a filter paper (porosity 0.45 μm capable of retaining particle of 2.7 μm size), rinsed with extraction solution followed by distilled water.

Table 1. Extraction solutions used for estimating the contents of Cd, Ni and Pb in CRM BCR-483 – sewage sludge amended soil

No	Method	Type of solution	pH	Extraction conditionss
1	SR ISO 14870-1999	0.005 M DTPA, 0.1 M TEA, 0.01 M $CaCl_2$	7.3±0.2	report (m/v)=1:10, 2 h at 30 rpm and 20ºC
2	NFX 31-120/1992	0.01 M EDTA, 1 M NH_4OAc	7.0±0.2	report (m/v)=1:10, 2 h at 40 rpm and 20ºC
3	Report EUR 17127 EN*	0.05 M EDTA	7.0±0.05	report (m/v)=1:10, 1 h at 30 rpm and 20ºC
4	Report EUR 17127 EN*	0.43 M acetic acid	2.5	report (m/v)=1:40, 16 h at 20ºC, end-over-end shaker

* Report of BCR reference materials.

Each experiment was performed 5 times, the final result represent the average of them. Blank extraction (i.e. without soil) was carried out for each set of analysis using the same reagents.

Determination procedure. The contents of Cd, Ni and Pb were detected by a flame atomic absorption procedure, using a THERMO scientific M series spectrometer with air–acetylene combustion mixture[11]. Before the process was started, the glassware volumetric flask was manually shaken for 5 min to re-homogenise the content.

The results were corrected to dry matter. This correction was performed on a separate portion of 1 g, which was taken at the same time with the experiments and was dried in an oven at 105 ± 2ºC for 3–4 h until constant mass.

Quality assurance (*QA*) *and quality control* (*QC*) *data*. The Analytical Laboratory of ECOIND is accredited by RENAR (Association for Accreditation of Romania) and follows the requirements of ISO 17025/2005 standard. The laboratory has certification with BVQI (Bureau Veritas Quality International) in accordance with ISO 9001 standard and participates periodically in internal and external audits.

The laboratory participates every year in tests for the evaluation of its capability by interlaboratory comparisons (IMEP Belgium, IAWD Germany, CALITAX Spain, Quality Infrastructure Danemark) for different groups of pollutants (organic compounds, metallic elements, inorganic compounds) from complex matrices (surface water, waste water, drink water, soil, sediment, sludge).

RESULTS AND DISCUSSION

In order to estimate the values of uncertainty for each concentration of mobile metallic elements, an uncertainty budget was developed. The different uncertainty sources and their influence on the expanded uncertainty are presented in the fol-

lowing formula (GUM method)[12]:

$$U_{expanded} = k\, u_{cs} = k\, (u_c^2 + u_v^2 + u_{rep}^2 + 1/u_{mass}^2 + 1/u_{rec}^2)^{1/2} \quad (1)$$

where k is a coverage factor, value 2 for 95% level of confidence; u_{cs} – combined standard uncertainty; u_c – concentration uncertainty (instrument calibration, flasks, pipettes, reference standard material); u_v – 50-ml volumetric flask (calibration, temperature); u_{rep} – repeatability uncertainty (mass, volume, absorbance, extraction recovery); u_{mass} – weight uncertainty (balance calibration, linearity); u_{rec} – extraction recovery uncertainty. The data on the certified and detected by EPTA and by acetic acid extractable contents of Cd, Ni and Pb in CRM BCR-483, sewage sludge amended soil are given in Tables 2 and 3, respectively. The results are expressed in mg per kg dry matter (mg/kg d.m.).

Table 2. Certified and detected by EDTA extractable contents of Cd, Ni and Pb in CRM BCR-483 – sewage sludge amended soil

No	Element	MU	Detected value		Certified value	
			value	uncertainty*	value	uncertainty*
1	Cd	mg/kg d.m.	22.7	0.4	24.3	1.3
2	Ni	mg/kg d.m.	27.3	0.8	28.7	1.7
3	Pb	mg/kg d.m.	205	7	229	8

*The value of uncertainty represents the half-width of 95% confidence interval of the mean of the data set (half of the expended uncertainty) = u_{cs}.

Table 3. Certified and detected by acetic acid extractable contents of Cd, Ni and Pb in CRM BCR-483 – sewage sludge amended soil

No	Element	MU	Detected value		Certified value	
			value	uncertainty*	value	uncertainty*
1	Cd	mg/kg d.m.	17.2	0.3	18.3	0.60
2	Ni	mg/kg d.m.	25.3	0.7	25.8	1.00
3	Pb	mg/kg d.m.	1.9	0.1	2.11	0.25

*The value of uncertainty represents the half-width of 95% confidence interval of the mean of the data set (half of the expended uncertainty) = u_{cs}.

To evaluate the efficacy of the experiments for each parameter were used the performance indicators *Z*- and ZETA-SCORE, according to the following equations:

$$Z = (x - X)/\Sigma \quad (2)$$

$$\text{ZETA} = (x - X)/(u^2_{det} + u^2_{ref})^{1/2} \quad (3)$$

where x is the mean of the results; X – certified value; Σ – standard deviation of the all results, including the results from the BCR Report EUR 17127 EN; u_{det} – combined standard uncertainty of the detected result; u_{ref} – combined standard uncertainty of the certified value.

Table 4. *Z* and ZETA-SCORE obtained for the each parameter

Element	*Z*-SCORE		ZETA-SCORE	
	EDTA 0.05 M	acetic acid 0.43 M	EDTA 0.05 M	acetic acid 0.43 M
Cd	–0.69	–0.98	–1.05	–1.64
Ni	–0.47	–0.32	–0.56	–0.29
Pb	–1.58	–0.56	–0.40	–0.78

According to the interpretation of the *Z* and ZETA-SCORE:

$$|Z, \text{ZETA}| < 2 \text{ satisfactory}$$

$$2 \leq |Z, \text{ZETA}| \leq 3 \text{ questionable}$$

$$|Z, \text{ZETA}| > 3 \text{ non satisfactory}$$

the data from Table 4 are satisfactory.

In Fig. 1 are shown the experimental data obtained in the extraction tests applied in accordance with Table 1 to CRM BCR-483. The highest values of mobile Cd, Ni and Pb were obtained with 0.05 M EDTA. For metallic mobile Cd and Ni the different values are in the same range, but for the exchangeable Pb the differences are major. 0.05 M EDTA extract the highest quantity of mobile Pb and the solution of 0.43 M acetic acid – the lowest quantity of mobile Pb.

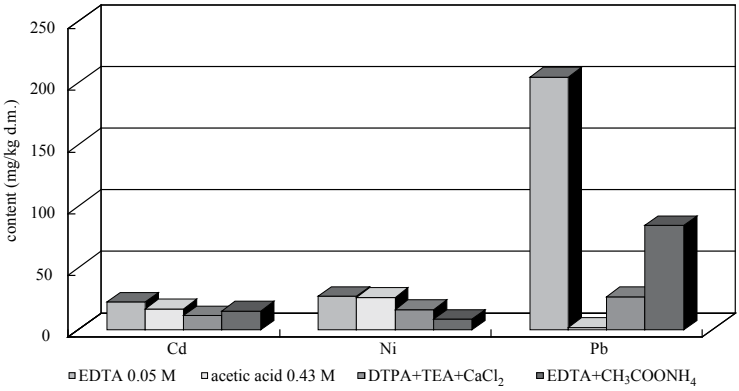

Fig. 1. Evaluation of the metallic mobile forms from CRM BCR-483 – sewage slugde amended soil – with 4 different extraction methods

In Figs 2–4 are presented the data obtained with 4 different extraction procedures applied to three matrices: a polluted soil collected from a mining site, sewage sludge from an industrial waste water treatment plant and another polluted soil sampled from a metallurgic plant. Extraction procedure with 0.05 M EDTA provides highest contents of Pb in both polluted soils. The quantity of mobile metallic Pb

obtained with the mixture of 0.01 M EDTA and 1 M NH_4Oac is lowest than the value from extraction with 0.05 M EDTA, but the data are in the same range.

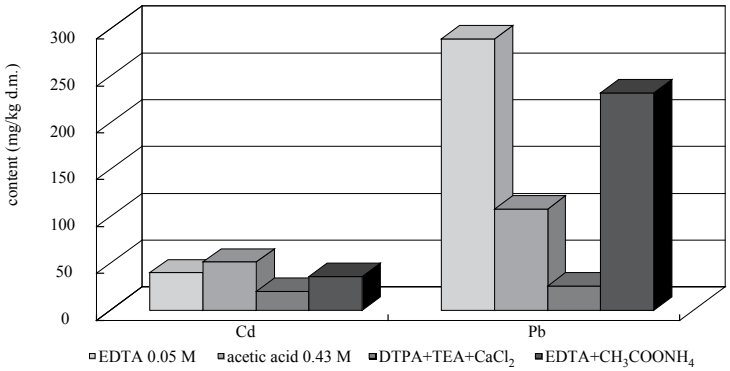

Fig. 2. Evaluation of metallic mobile forms from a polluted soil (metallurgic plant) with 4 different extraction methods

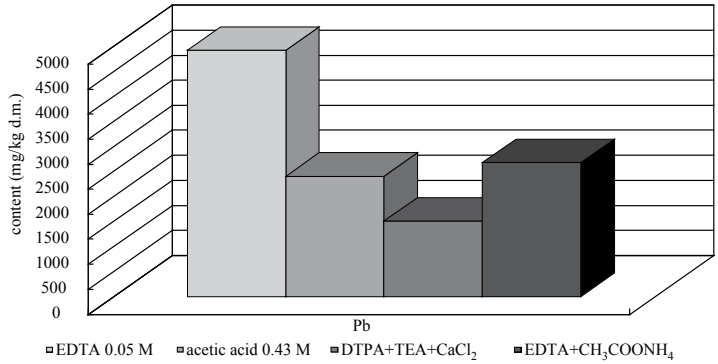

Fig. 3. Evaluation of metallic mobile forms from a high polluted soil (minig site) with 4 different methods

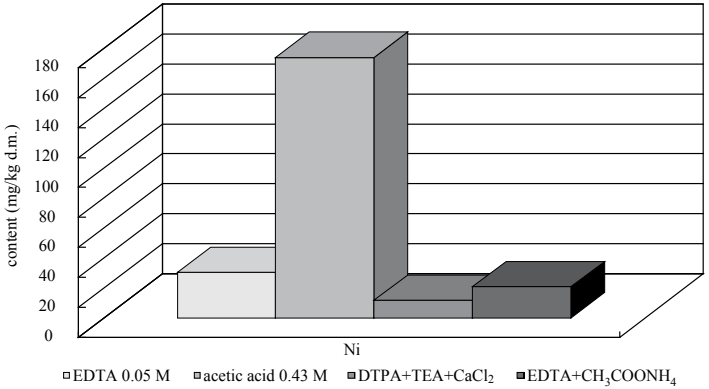

Fig. 4. Evaluation of metallic mobile Ni from a sewage sludge with 4 different extraction methods

In Fig. 4, the extraction with 0.43 M acetic acid applied to a polluted sewage sludge gives the highest quantity of mobile Ni. The values obtained with the other three methods are in the same range.

CONCLUSIONS

The extraction method with 0.43 M acetic acid applied to sewage sludge collected from industrial waste water treatment plant provides the highest quantity of mobile Ni. In this matrix, Ni was bounded not only in exchangeable forms, but also in carbonate forms that explains the differences in the value from the other 3 methods.

The extraction efficiency for mobile Pb increases in the order: DTPA + TEA + $CaCl_2$ < 0.43 M acetic acid < EDTA+CH_3COONH_4 < 0.05 M EDTA. If in the soil/sewage there are not carbonate forms of Pb metallic element, the extraction solution 0.43 M acetic acid is the last one in order of efficiency.

For mobile metallic Cd, all 4 extraction procedures can be successfully used to estimate the mobility of this element from polluted soils or sewage sludge.

The experimental tests applied to CRM BCR-483 with BCR methods proved that both extraction and determination procedures can provide valuable data, comparable with the certified values for exchangeable fraction of Cd, Ni and Pb.

The data obtained with the other 2 methods confirm the fact that the extractant type is very important in evaluating the mobility fraction of the metals (different concentrations of metallic elements obtained with different extraction procedures).

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