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Determination of Removable Portion of Some Elements in Stream Sediments of Spišsko-gemerské rudohorie Mountains*

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*Abstrakt.*The single extraction with 0,05 mol dm^{-3} EDTA recommended for leaching of soils was modified for this study. Information capacity (removal ability) of this single extraction was compared with operationally used sequential extraction procedure. Single and sequential extraction procedures were applied on four sediment samples coming from industrially polluted region of the Eastern Slovakia. This paper describes the preparation of samples, gives analytical results in each extraction step for Cd, Pb, Cu, Cr and Ni and brings comparison of these results with total element content analyses realized by independent spectral method.

Key words: fractionation analysis, sediments, environmental protection, single-step extraction, sequential extraction, AAS, ICP OES, XRF

Introduction

Actual geochemical research has skipped from total element contents observation to the study of elements forms in chosen systems of environment /water, soils, sediments/. Information about different degree of toxic effects of several element compounds on biological systems, gave birth to the effort of analytical resolution – fractionation of several element-binding forms in environmental and biological materials (Templeton, 2000).

The observation of chemical composition of stream sediments and phase distribution of element binding forms is useful in geological prospecting and environmental protection. Their influence on the environment is not limited on the stream bed. Quantification of chemical and binding forms of elements in sediments has given the basis for monitoring of bioavailability and mobility of contaminants in environment (Batley,1990). In comparison with a water analysis, "stream sediment samples" are more suited for a geochemical and environmental evaluation thanks to their good accumulative properties.

Fractionation analysis using sequential extraction like a method brings comprehensive information about potential mobility of metal contaminants but it is time consuming. Application of uniformed sequential extraction advances is necessary because of significance and comparability of extraction results.

In this work normative "soil extraction procedure" into 0,05 mol dm^{-3} EDTA (Ure,1995) for sediments was modified and compared with the results of operationally used sequential extraction procedure. Applied sequential extraction is a modification of BCR (Community Bureau of Reference) recommended extraction (Mackových et al., 2000) In this paper the results of this comparison is presented. The sediment samples from industrially stressed area of Spišsko-Gemerské rudohorie Mountains were studied and spectral methods like element detection are used.

Theoretical

The natural sediment is a full mixture of several phases, especially of weathering and erosion rests of clay materials, aluminosilicates, iron and manganese hydroxides, sulphides, carbonates, and particles coming from biological and industrial activities, which are transported through liquid phase. River sediment is a complicated dynamical system, which is chemically and biologically reactive. Time of element abidance in existing form is different, depends on element character, on physicochemical form, kind of chemical binding, mobility, and external conditions of systems. Precipitation and adsorption of metals from aquatic phase on sediment surface are seldom controlled by the formation of well-defined poorly soluble complexes (Hakansson, 1989).

For fractionation study of soils, sediments, and sludge many selective extractive advances were developed, which consist in consecutive-sequential leaching of element portion bound on main components of solid sediment phase. The most frequently used leaching advance was the method developed by *Tessier* (Tessier, 1988). It was applied and seriously tested by a great number of authors and the above-mentioned "BCR extraction" is a modification of Tessier scheme too (Fiedler et al., 1994). It deals with three-step sequential extraction.

In modified and here used extraction procedure except of the proposed extraction steps the first step for elements extractable at water phase and the fifth step for determination of element contents in sediment rest were

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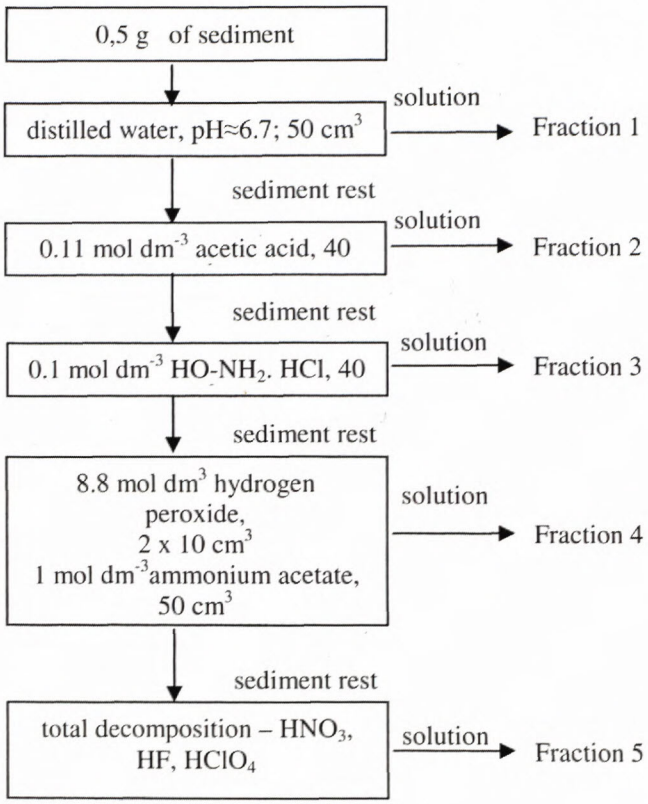
added. Detailed description of distribution of sediment fractions, formed during applied five-step extraction is listed in Reference (Vojteková et al., 2002) and final sequential extraction scheme is listed in Fig. 1.

Fig. 1. Description of the applied sequential extraction scheme (Mackových et al., 2000).



Experimental

The fluvial sediment samples were taken in industrially stressed region Spisško-Gemerské Rudohorie Mountains (Method. Instr.), four sampling places were chosen /Table 1/. Samples were dried at temperatures to 40 °C, then sieved and milled in agate planetary treadmill on fineness under 0.09 mm. For assessment of extractable element share of Cd, Cu, Cr, Pb and Ni 0,5 g of homogenized sample was weighted.

The original protocol for 0,05 mol dm^{-3} EDTA extraction of soils for sediments of chosen region was optimised. During optimisation were changed some conditions listed in table 2. Extraction ratio 1:50 means 0,5g of sample: 25 cm^3 of 0,05 mol dm^{-3} Na_2EDTA; 1:100 means 0,5g of sample: 50 cm^3 of 0,05 mol dm^{-3} Na_2EDTA and 1:150 means 0,5g of sample: 75 cm^3 of 0,05 mol dm^{-3} Na_2EDTA. Optimisation is shown for most contaminated sediment 3.

Sequential extraction (detailed conditions in Fig 1.) In each individual step was performed in a mechanical shaker for 16 h (number of vibrations 200 min^{-1}, temperature (20±2) °C). After finishing the extraction the solution was centrifuged by 4000 rpm, for 20 min. Solutions obtained from individual extraction steps were saved in

Table 1. Sampling Places of Chosen Region

Description of sample	Place of sampling	River / Stream
River Sediment 1	Rudňany - Markušovce	Hornád
River Sediment 2	Slovinky	Poráčsky jarok
River Sediment 3	Richnava	Hornád
River Sediment 4	Jaklovce	Hnilec

polyethylene vessels at temperature 4 °C. From the solution prepared in the described way, extractable shares of chosen elements were determined and results are average values of 5 repeated analyses.

For determination of studied elements in each leached fraction the following analytical methods were applied: for Cr, Cu, Pb and Ni – atomic emission spectrometry with inductively coupled plasma and ultrasonic nebulization of sample, for Cd – atomic absorption spectrometry with electrothermal atomization. AES measurements were carried out by spectrometer Liberty 200 (Varian) with ultrasonic nebulizer (Cetac) and AAS measurements by atomic absorption spectrometer Spectr AA-400 with electrothermal atomizer GTA-96 (Varian). For the determinations of total element contents in studied sediments roentgen-fluorescent spectrometry has been applied and measurements were realized by spectrometer Spectro X-LAB 2000.

Results and discussion

Optimisation of single-step "EDTA extraction" is possible to discuss as follows:

As shown in Fig. 2, 3, 4,5 and 6 the optimised extraction ratio for each sediment is 1:150 , optimised time of single extraction is 6 hours and the highest recoveries are observed in extraction medium with pH = 3, but pH =3 is not probable in real conditions of water-sediment system. There is more interesting optimise pH of "EDTA extraction" according to acidity of top water.

On the strength of comparison single and operationally used sequential extraction procedure about the removal ability of Na_2 EDTA is possible to state: Extraction into Na_2EDTA is after optimisation in good accordance with sum of 1^{st}, 2^{nd}, 3^{rd} and 4^{th} step of sequential extraction procedure. From the sediment matrix of chosen sampling areas with 0.05 mol dm^{-3} Na_2EDTA it is possible to extract shares corresponding to the first three /Fig. 7--10 for Ni, Cd, Pb, Cr, / or first four steps /Fig. 11 for Cu/ of sequential extraction. Into Na_2EDTA extracted contents and sum of contents extracted during 1^{st} 2^{nd} and 3^{rd} step of sequential extraction procedure are practically identical for Cd, Pb, Cr and Ni and higher for Cu. Extraction efficiency is (for chosen sediment samples) element-specific and dependent on the composition of sediment matrix.

Conclusions

Single-step leaching advance into Na2EDTA, or the other chelating agent, is able /after optimisation of extraction conditions according to regional geological particularities/ to release mobile and mobilizable metal forms

Tab. 2. Standard and modified procedure for single extraction of into 0,05 mol dm^{-3} EDTA-salt for the elements Cd, Pb, Cu, Cr, Ni and Zn

Standard procedure		Optimisation of standard procedure
extraction agent	$(NH_4)EDTA$	Na_2EDTA
time of extraction	1 hour	1-6 hours, without pH modification, pH=4,7 1 hour during optimisation of pH
temperature	20±2 °C	20±2 °C
extraction ratio	1:10	1:50, 1:100, 1:150
acidity of extraction agent	pH=7(modified with NH_4OH)	pH = 3 -7 (1 hour- extraction during optimisation of pH, modified with HCl, NH_4OH)
Extraction wessel	250 ml PE (washed by H_2O 4M HNO_3 and 0,05M EDTA-salt)	
Filtration	„paper with blue stripe" Θ = 18,5 cm	

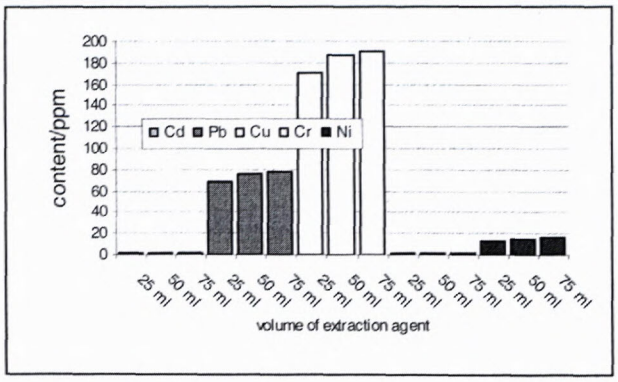


Fig 2. Optimisation of extraction ratio of studied elements-leaching agent 0,05 mol dm^{3} Na_2EDTA

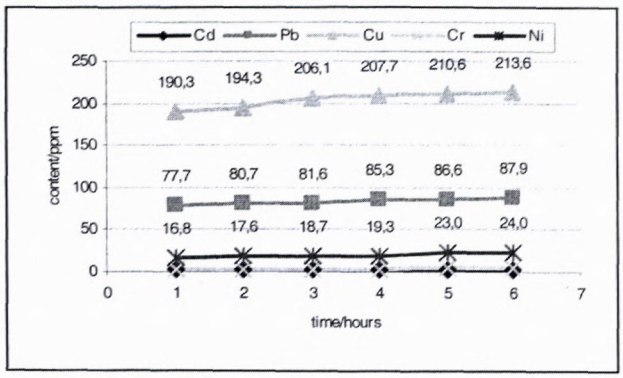


Fig 3. Optimisation of extraction time of studied elements, sediment 3- leaching agent 0,05 mol dm^{3} Na_2EDTA without pH modification (pH of dilluted Na_2EDTA = 4,7)

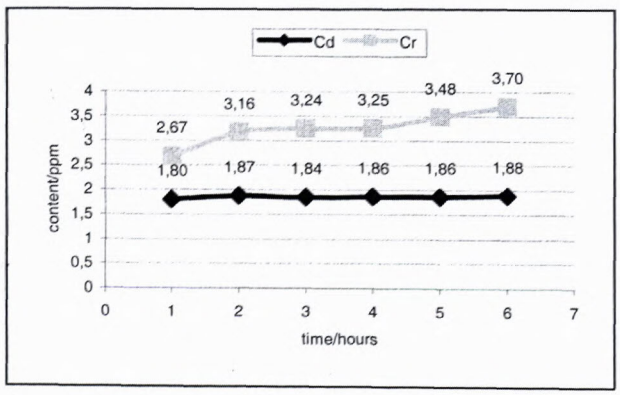


Fig 4. Optimisation of extraction time of studied elements, sediment 3,detail - leaching agent 0,05 mol dm^{3} Na_2EDTA without pH modification (pH of dilluted Na_2EDTA = 4,7)

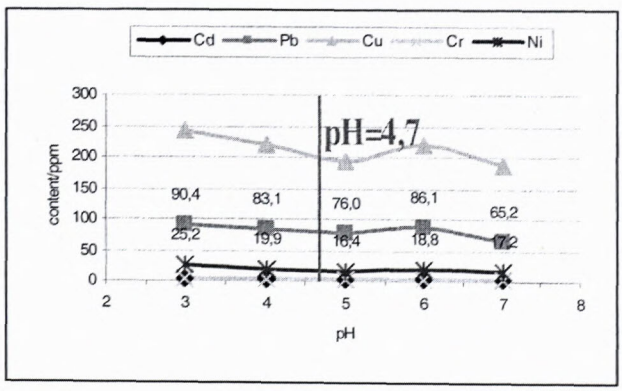


Fig 5. Extraction into 0,05 mol dm^{-3} Na_2EDTA, sediment 3 – optimisation of pH, pH = 4,7 – acidity of 0,05 mol dm^{-3} Na_2EDTA without modif

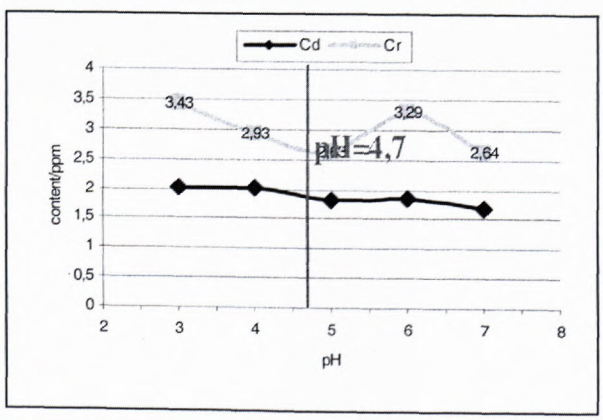


Fig 6. Extraction into 0,05 mol dm^{-3} Na_2EDTA, sediment 3, detail – optimisation of pH, pH = 4,7 – acidity of 0,05 mol dm^{-3} Na_2EDTA without modification

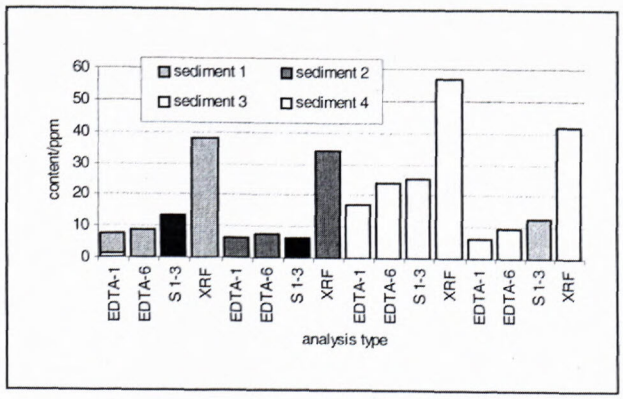


Fig 7. Comparison of Ni extracted shares during single and sequential extraction with total content analysis

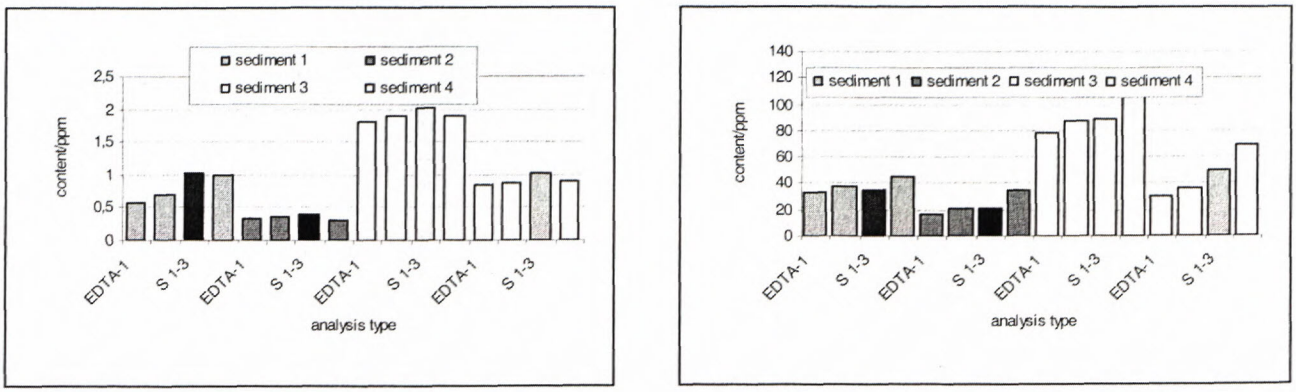


Fig 8,9. Comparison of Cd and Pb extracted shares during single and sequential extraction with total content analysis

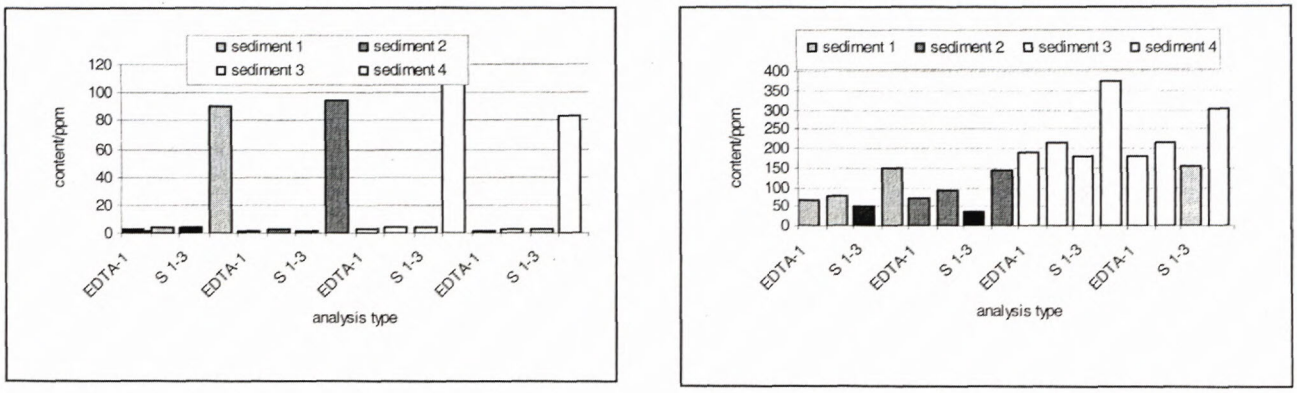


Fig 10, 11. Comparison of extracted shares of Cr and Cu during single and sequential extraction with total content analysis
Notice: EDTA - 1 -- extraction into 0,05M Na_2EDTA without modification of pH; pH= 4,7, time of extraction 1 hour, EDTA - 6 -- extraction into 0,05M Na_2EDTA without modification of pH; pH= 4,7, time of extraction 6 hour, S 1-3 -- sum of the first, second and third step of the five-step sequential extraction procedure, XRF -- total content analysis - control of accuracy of sequential extraction procedure by independent analytical method (XRF

retained in different modes and associated with specific sediment fractions.

Because of them "Na_2EDTA extraction" could be a form of the screening control of the sediments pollution /in local tested conditions - e.g. polluted regions of Slovakia/ and could be used like economically interesting and time saving supplementary test to recommended attested BCR sequential extraction procedures and fast alarm indication of element mobility changes in sedimentary systems.

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References

Batley G.E., *Trace Element Speciation: Analytical Methods and Problems.* CRC Press, Inc., Boca Raton , Florida, USA, 1990.

Fiedler, H. D., Lopez-Sanchez, J. F., Rubio, R., Rauret, G., Quevauviller, P., Ure, A. M., and Muntau, H., *Analyst 119,* 1109 (1994).

Hakansson, K., Karlson, S., and Allard, B., *Sci. Tot. Environ. 43,* 87 (1989).

Mackových et al.: *Method of determination of chosen toxic element binding forms,* Subproject 2, GAL/ŠVL/ČS/3-2000, Geological Survey of Slovak Republic (2000)

Methodical Instruction of the Slovak Republic Ministry of Environment from 27th August 1998 No. 549/1998-2, for risk evaluations of contaminated fluvial and bed-load sediments.

Templeton, D. M., Ariese, F., Cornelis, R., Danielsson, L.-G., Muntau, H., Van Leuwen, H.P., and Lobinski, R., *Pure Appl. Chem. 72,* 1453 (2000).

Tessier, A. and Campbell, P. G. C., *Anal. Chem. 60,* 1475 (1988).

Ure A.M., Davidson C.M., Thomas R. P., *Quality Assurance for Environmental Analysis.* Elsevier Science, Amsterdam, Netherlands,1995.

Vojteková, V., Mackových, D., Krakovská, E., Remeteiová, D., and Tomko J, *Chem. Pap. 57 (3), 179* (2002).