

## Optimalization of Sequential Extraction Method for Determination of Toxic Elements in Soils and in Stream Sediments

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**Abstract.** This study concerns the optimalization of sequential extraction method for the determination of Al, As, Cd, Cu, Cr, Hg, Pb and Sb in soils and stream sediments. These toxic elements were divided into five fractions: water soluble fraction, ion - exchange and carbonate fraction, reducible fraction, organic - sulphide fraction and residual fraction. Experimental results demonstrate that the precision of the determination was between 10 and 20 %. The quality was tested on a sediment reference material CRM 601. Experimental and certificated results show a good agreement. The time of extraction and tested stability of extraction solutions were optimized for each step of sequential extraction. Sequential extraction procedure gives useful information about geochemical forms of trace toxic elements in stream sediments and soils.

**Key words:** sequential extraction, stream sediment, soil, toxic element

### Introduction

Recently geochemical research has changed its aim from the monitoring of total concentrations of elements into studying of its forms in a given system. The total content of element in a sample is not an appropriate indicator of its biological availability. The toxicity of the element depends on its chemical form, mobility, transformation and biologically available for plants. Toxicologists' knowledge of a different scale of toxic effects of compounds of heavy metals and metalloids on living organisms led to efforts to analytical resolution of different forms of elements' bonds in the environmental samples and in biological materials. The quantification of chemical forms of elements in soils and sediments forms the basis for monitoring of bioavailability and mobility in the environment.

### Method selection and its optimalization

The method of the sequential extraction was chosen on the basis of results to the recommendation of Community Bureau of Reference (BRC) according to the methodology of Fiedler, H. D. and all, (1994). This methodology was tested and accepted by several European laboratories. It is a three-step sequential analysis. Certified reference material, which was prepared through the international laboratory test, is used to check accuracy and precision of analyses.

Except for the suggested steps of extraction we also added first step for extractible elements in water phase and last fifth step for the determination of element content in the residual bonded on silicate minerals.

The scheme of sequential extraction used in this study classifies metals into the following fractions:

a) **water soluble fraction (1)** - characterises trace elements dissoluble in water phase in the form of mostly inorganic salts,

b) **ion - exchange and carbonate fraction (2)** - characterises trace elements adsorbed on anorganic salts and carbonates, which are released into water if neutral conditions change into slightly acid conditions,

c) **reducible fraction (3)** - characterises elements associated with oxides of Fe and Mn, which are thermodynamically unstable and they release trace elements into water with a change of redox potential,

d) **organic - sulphide fraction (4)** - characterises the fractions of elements bonded in organic substance and in sulphides. These elements are released into water as the result of oxidation and a sequential degradation of organic substances and a decomposition of sulphides by the change of physical and chemical conditions,

e) **residual fraction (5)** - determines a fraction of elements bonded on primary and secondary minerals, which do not commonly release into water surroundings in nature.

### Extraction method

One gram of sample was used for the determination of extractible specific forms of elements - Al, As, Cd, Cu, Cr, Hg, Pb and Sb. The extraction was carried out in every step in a laboratory shaker during 16 hours, at 200 counts per one minute and at a temperature of  $20 \pm 2$  °C. The sample was kept in suspension during the extraction. The extract was separated from the solid residue by centrifugation and decantation of the supernatant liquid into polyethylene container and stored at 4 °C prior to analysis. The optimalization of this method was performed on five stream sediments and five soil samples. According to the concentrations of determined elements upper mentioned samples were chosen.

The following analytical methods were used for the determination of the tested elements:

**Al, Cr, Cu, Pb** atomic emission spectrometry with inductively coupled plasma

**Cd** atomic absorption spectrometry with electrotermic atomization

**As, Sb** atomic absorption spectrometry with hydride generation

**Hg** atomic absorption spectrometry

The total mineralogical composition of soils and sediments was measured by X-ray diffraction.

The total content of **Cr** in the sample was measured by the method of X-ray spectrometry (XRFS) on a spectrometer Spectro X - LAB 2000. The content of Cr was measured directly in extraction solutions (except in fraction 5). The content of Cr in fraction 5 was defined by subtracting from the total content of Cr in all four fractions measured by the method of XRFS.

Because of signal depression the method of calibration curve could not be used to measure **As** and **Sb** by hydride generation and **Al, Cr, Cu, Pb** by atomic emission spectrometry with inductively coupled plasma. The technique of spiked sample was used to determine and to eliminate interferences of matrix elements. Predetermined amounts of analyt were added into the sample solutions. The additions contained from 100% to 200% of the analyt in each sample. On the basis of experimental results of interferential influences during the determination of **As** and **Sb** in the environmental samples (Mackových, 1987), the influence of elements in solutions was monitored. Maximum acceptable concentrations of interferential elements are introduced in the table below.

The pilot samples of stream sediments and soils were used to test the technique of evaluation of an analytic signal by the method of a calibration curve or by the procedure of a standard addition. It was proved that extraction test solutions of the fractions did not have any influence on the intensity of the signal and on the effectiveness of a hydride generation. The results obtained by the method of a calibration curve and by the technique of a standard addition were identical. Therefore the method of a calibration curve was chosen for the evaluation of the signal.

**Hg** was measured by the method of AAS. The results of sequential extraction on standard samples show that the largest quantity of Hg was extracted in organic - sulphide fraction and that the residue left in the fraction 5. The oxidizing of Hg in organic - sulphide fraction (step 4) was performed by the influence of H<sub>2</sub>O<sub>2</sub>. By heating of the sample on approximately 85 °C Hg became a solution but with the loss of Hg in a form of vaporizable compounds. For this reason the content of Hg was extractible in the organic - sulphide fraction and it was determined in a solid residue after the extraction in step 4. The extractible amount of Hg in step 4 was determined by the formula introduced below:

$$C_{\text{Hg}(4)} = C_{\text{Hg}(T)} - C_{\text{Hg}(1)} - C_{\text{Hg}(2)} - C_{\text{Hg}(3)} - C_{\text{Hg}(5)}$$

$C_{\text{Hg}(T)}$  = total content of Hg

$C_{\text{Hg}(1)} \dots \dots (5)$  = content of Hg in the fractions 1 - 5

#### Extraction time optimization

Extraction time was an important indicator for suggesting an optimal method of sequential extraction not only for analytical but also for economical aspects. Pro-

posed extraction time was 16 hours. Extraction times of 6, 8 and 16 hours were chosen for this research. The experiments were done on two pilot stream sediments. After the extraction the solutions were separated and the trace elements were determined. The recovery of the extraction was evaluated on the basis of recovery. The value of analyt after sixteen - hour extraction in all steps was chosen as 100 % recovery. The recovery of extraction in second step for Cd was lowered. After six / eight hours about 70 % of Cd was extracted. The recovery of extraction was higher in step 3 of the value which had not extracted in step 2. For Cu the recovery of extraction was lower of 30 % in step 2 and lower of 10 % in step 3. Six - hour extraction was convenient for the other elements. On the basis of upper mentioned results 16 - hour extraction was used for all other experiments.

#### Precision

The precision was evaluated from the measured results of a monitoring sample 4Sp - 2364. This sample was analyzed 18 times. The precision of determination was calculated for each element in all five fractions. The results are introduced in table 2. The precision of determination is in a range of 10 -20 %. The values of RSD

#### Accuracy

Certified reference material of the stream sediment CRM 601 which was prepared by the Community Bureau of Reference was used for accuracy testing. This certified reference material was analyzed by 3 - step sequential extraction. The second, third and fourth steps of the extraction used in this study are identical with upper mentioned extraction.

Certified elements:      2nd step - Cd, Cr, Ni, Pb, Zn  
                                      3rd step - Cd, Ni, Zn  
                                      4th step - Cd, Ni, Pb

The recovery was evaluated for the following elements Cr, Cu, Pb and Cd whose content in reference material had been certificated. According to the results of the BCR comission of interlaboratory comparisons, the agreement among determined results is satisfactory if the difference of results is < 30 %, which was approached in all determinations except Cd. The content of Cd was determined 36 % higher in step 3 and 33 % lower in step 4. However it is not an important difference because of low contents of Cd. The results of determinations and recovery are introduced in table 3.

Analytical quality of elements determination in batch analyses was checked by a chosen monitoring sample - internal reference material which was analysed with every series of samples.

#### Stability testing of extraction solutions

The solutions obtained by 5 - step extraction were after the separation from solid residue kept in a refrigerator at approximately 4 °C. The stability of solutions was tested during two months. The solutions were analyzed

Table 1: Maximum acceptable concentrations of interferential elements

Analyt	Maximum concentration of interferent in a measured solution ( $\mu\text{g/ml}$ )									
	Fe	Ca	Co	Ni	Cu	Pb	Zn	As	Bi	Sb
As	1000	5000	1.0	1.0	5.0	1.0	7.5	-	1.0	0.2
Sb	1000	5000	1.0	1.0	5.0	1.0	2.0	0.2	0.5	-

Table 2: Precision of determination of elements in fractions 1 - 5

Fraction	Cu			Pb			Cr			As		
	Average	SD	RSD									
	$\mu\text{g/g}$	$\mu\text{g/g}$	%									
1	5	0.7	14	<2			<1			1.4	0.5	36
2	37	1.7	5	4	0.4	10	<1			<0.1		
3	137	11.7	9	85	6.4	8	4	0.5	13	22	2.4	11
4	120	7.9	7	8	1.9	21	6	0.9	15	4.8	1	21
5	46	3.4	7	13	1.8	14	101	5.5	5	50	3.1	6
$\Sigma$	344			111						78.2		
TOTAL	376			116			111			77		

Fraction	Sb			Cd			Hg			Al		
	Average	SD	RSD									
	$\mu\text{g/g}$	$\mu\text{g/g}$	%									
1	1.5	0.3	20	<0.01			0.003	0.002	67	21	6	29
2	0.5	0.2	40	1.63	0.44	27	0.009	0.002	22	82	12	15
3	1.5	0.2	13	0.38	0.12	32	0.011	0.002	18	1131	155	14
4	0.5	0.07	14	0.11	0.03	27	5.73	0.15	3	468	42	9
5	41.5	2.2	5	<0.5			2.12	0.13	6	56850	850	1
$\Sigma$	45.7			2.11						58552		
TOTAL	46			2			7.86			62600		

Table 3: Comparison of measured and certified values for elements in CRM 601

Fraction	Cr			Cu			Pb			Cd		
	A [mg/g]	B [mg/g]	R [%]									
2	<1	0.39	98	7.6	8.3	92	<2	2.28		4.1	4.14	99
3	10.4	10.6	86	71	72.8	98	199	205	97	4.2	3.08	136
4	17.3	20.1		93	78.6	118	25	19.7	127	1.4	1.83	77
5	128			64			37					
$\Sigma$	156			235.6			261			9.7		
Total	151	148	102	246			264	231	114	12.4		

A-measured value B-certified value R-recovery

straight after extraction, after one week, after one month and finally after two months. Any change of the concentrations of solutions were not observed during the whole period of our testing. The solutions are stable for at least 2 months if they are stored at temperature of 4 °C.

## Conclusion

The aim of this study was to test the new analytical methodology of determination of chosen toxic elements by 5 – step sequential extraction. The methodology of extraction was chosen on the basis of the recommendations of Community Bureau of Reference BCR. Sequential extraction does not only have analytical importance – it offers ability to compare results among laboratories and the use of reference materials, but the main reason of its importance is in comparing levels of contamination of different areas.

The optimization of analytic method was done on pilot samples of stream sediments and soils. Our attention was directed to the method of extraction, time stability of extracted solutions, precision, accuracy, recovery, frequency testing and long – term stability of analytical process.

On the basis of experimental results it can be stated that 5 – step sequential extraction is suitable for study of batch analyses of distribution of chosen toxic elements in stream sediments and in soils.

## References

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