Determination of Total Contents of Cd, Pb, Cr, Ni, As, Cu, Zn, Co, V, Mo in Some Slovak Soils

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Total soil metals can be used to estimate the degree of soil exposure to heavy metal pollution. The total contents of potentially dangerous elements were determined in 1996 in four monitored localities of Slovakia. The samples were taken from surface horizons of arable soils in Dvorníky, Topoľníky, Stakčín, and Macov and basic soil characteristics were determined. The results of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) analysis of the soil samples after microwave digestion with mixture of acids HF, HCl, HNO_3 are presented. We verify the accuracy using Certified Reference Materials: Soil Eutric Cambisols S-VM, Orthic Luvisols S-MS, and Soil Rendzina S-SP. A new sampling was made in the same localities in 2000 and analyzed using the ICP-AES method. Total metal contents in 1996 ranged from background levels to gross pollution in the locality Dvorníky. Other localities were mostly well due to topography and geological structure. When we compare the obtained results in 2000 with those obtained in 1996 we arrive to the statement that in the locality Dvorníky much higher content of all measured elements was found and the pollution by Pb, Zn, Cu, Cd, As was confirmed. This locality has been assigned to the location of an ore mine, which could explain these contents.

Trace elements are watched in soils most thoroughly, because they tend to accumulate in the soil and could penetrate into ground water and foodstuffs cycle. Many workers consider that sequential extraction of heavy metals from soils is a useful tool in differentiation between the various forms of heavy metals (exchangeable, carbonate forms). Such methods, however, do not provide direct characterization and identification of particular forms, but rather indicate chemical reactivity. The problems found by several authors [1—3] include limited selectivity of extractants, metal redistribution between phases during extraction, and overload of the chemical system if the content of metal is too high. Therefore in this work we used total decomposition of soil samples.

The risk trace element contents in most parts of Slovakia have been indicated under "A" hygienic limit [4]. In strongly contaminated soils the correlation between total contents of hazardous elements in soils and in plants is determined [5]. Therefore total soil metals can be used to estimate the degree of soil exposure to heavy metal pollution although this is not generally well-correlated with metal mobility and bioavailability [3, 6]. As the content of the trace elements depends on the soil unit and on the type of chemical bonding, the dissolution step requires some attention [7]. New decomposition methods in microwave oven can be advantageous because they are rapid, prevent losses of volatile elements and have reduced risk of contamination. Some authors dealing with total decomposition [8—11] suggest a mixture of acids HF, HCl, HNO_3, $HClO_4$, H_2O_2. The analytical method ICP-AES was used for the determination and following aspects were considered: choice of operating parameters, sample treatment, selection of analytical lines based on their sensitivity and on spectral interferences. Sampling was made according to ISO/CD 10381 in the depth 0.1 m (A horizon).

The aim was to elaborate a procedure for determination of total contents of microelements in some Slovak soils to confirm the known and add some new useful information about the soil quality. Soil pollu-

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Table 1. Fundamental Characteristics of Investigated Soils

Locality	Soil unit	Humus/%	Texture	pH_{KCl}	C_{ox}/%
Macov	Calcaric Chernozems	2.9	Medium heavy	7.77	1.73
Dvorníky	Eutric Fluvisols	1.8	Medium heavy	6.59	1.07
Topoľníky	Calcaric Fluvisols	1.9	Medium heavy	7.22	1.17
Stakčín	Eutric Planosols	1.7	Heavy	5.82	1.10

Table 2. Total Contents of Heavy Metals (i) in Certified Reference Materials (j) $m_{r,i,j}/(\text{mg kg}^{-1})$

Element (i)	CRM S-SP	Found	CRM S-VM	Found	CRM S-MS	Found
As	14.0 ± 1.5	14.20	13.6 ± 2.3	13.10	9.3 ± 0.5	8.30
Cd	0.3 ± 0.06	0.25	0.2 ± 0.04	<0.2	0.2 ± 0.03	<0.2
Co	15.6 ± 1.2	16.00	15.4 ± 1.2	15.00	11.9 ± 1.3	10.30
Cr	75.3 ± 3.2	76.30	79.8 ± 5.8	80.00	87.4 ± 10.4	90.00
Cu	30.9 ± 1.8	30.50	30.0 ± 2.1	28.90	21.2 ± 1.7	22.90
Ni	37.4 ± 3.3	38.20	30.8 ± 2.1	29.00	40.0 ± 2.5	39.20
Pb	41.3 ± 4.4	43.10	19.6 ± 2.2	21.30	18.9 ± 2.3	17.30
Zn	119 ± 6.0	120.00	88.8 ± 3.3	85.05	63.7 ± 4.3	65.00
V	89.7 ± 8.7	87.90	98.3 ± 9.8	101.00	–	–

tion is real situation in quality of soil cover of Slovakia. Therefore, new investigations are very welcome when we want to have more reliable data.

In the presented work we describe determination of microelements by the optical emission spectroscopy. We evaluate the commonly used method for digestion and determination of risk trace elements. The Certified Reference Materials (CRM) S-VM, S-SP, and S-MS, in which are various contents of hazardous elements, were analyzed and we obtained them from the Institute of Radioecology Košice, Slovakia. The results were compared with literature [12, 13] and the Slovak hygienic standard [14] and were in good agreement.

EXPERIMENTAL

The soil samples were collected in 1996 and 2000 from the topsoils of four key localities, which represent the most important agricultural arable soil types of Slovakia, by the Soil Science and Conservation Research Institute in Bratislava. These soils were classified according to the FAO system and had these soil units: Dvorníky – Eutric Fluvisols, Topoľníky – Calcaric Fluvisols, Stakčín – Eutric Planosols, and Macov – Calcaric Chernozems. The samples were dried and sieved through 0.125 mm screen, total organic carbon content (C_{ox}), humus content, and pH in KCl extract were measured. Basic soil properties were determined using commonly used methods and are given in Table 1.

The inductively coupled plasma atomic emission spectrometry analysis was performed using sequential spectrometer BAIRD ICP 2070 (USA). Ultrasonic nebulizer was used. Analytical spectral lines of λ(Cd) 214.438 nm, λ(Pb) 182.203 nm, λ(Cr) 267.716 nm λ(Ni) 341.476 nm, λ(As) 189.042 nm, λ(Cu) 324.754 nm, λ(Zn) 213.862 nm, λ(Co) 228.616 nm, λ(Mo) 202.03 nm, and λ(V) 311.07 nm with background correction were selected for the determination. Statistical treatment was proceeded with software ICP 2070. Multielemental standard solution of Cd, Pb, Cr, Ni, As, Cu, Zn, Co, Mo, V in concentration 1 mg dm^{-3} was used for calibration and the calibration standard solutions were spiked with the matrix elements to simulate the soil matrix (60 mg dm^{-3} Na and K, 140 mg dm^{-3} Ca, 380 mg dm^{-3} Fe, 680 mg dm^{-3} Al). The accuracy of the analysis was checked with CRM S-SP, S-MS, S-VM (Table 2) and was expressed with variation coefficient of less than 10 %. The relative standard deviation for five replicates ranged from 3—7 %.

For the decomposition microwave oven PMD PAAR (Graz, Austria) was used with mineralization according to the PMD program using two steps

Step 1
Power 400 W t = 10 min Low: 10 min High: 10 min
Step 2
Power 600 W t = 15 min Low: 10 min High: 15 min

0.2 g of soil sample was weighed into PTFE vessel and 1 cm^3 HNO_3 (65 %) + 2 cm^3 HF (40 %) + 3 cm^3 HCl (36 %) was added. After cooling the vessels were opened and samples filtered into 50 cm^3 calibrated flasks and diluted with 0.2 % H_3BO_3. Clear, slightly yellow coloured samples were obtained. The same procedure was used for preparing certified soils and blank solution.

RESULTS AND DISCUSSION

Sample preparation for trace analysis is very important and total decomposition is often difficult be-

Table 3. Total Contents of Trace Elements $m_{r,i}/(\text{mg kg}^{-1})$

Locality	Cd	Pb	Cr	Ni	As	Cu	Zn	Co	Mo	V
Sampling in 1996										
Dvorníky	9.0 ± 0.2	1005 ± 9	58 ± 5	11.5 ± 0.5	32 ± 1.6	102 ± 2	1100 ± 8	16 ± 1	2.2 ± 0.6	68 ± 4
Topoľníky	<0.2	19 ± 2	48 ± 4	23.5 ± 2	27 ± 1.5	22.5 ± 0.7	53 ± 3	9 ± 1	0.98 ± 0.6	38 ± 2
Stakčín	<0.2	25.5 ± 2.3	79 ± 6	18.5 ± 0.6	19 ± 1.4	23.5 ± 0.7	66 ± 3	16 ± 1.2	0.9 ± 0.3	45 ± 3
Macov	<0.2	20.5 ± 2.1	55 ± 5	20 ± 1.8	28 ± 1.2	42 ± 1.2	90 ± 4	10 ± 1.2	0.98 ± 0.4	28 ± 1
Sampling in 2002										
Dvorníky	8.5 ± 0.3	869 ± 6	42 ± 5	14 ± 0.5	33 ± 1.5	112 ± 2	975 ± 7	15 ± 1.5	2.8 ± 0.5	94 ± 4
Topoľníky	<0.2	20 ± 1.8	49 ± 4	22 ± 1.9	18 ± 1.8	23.3 ± 0.9	56 ± 4	11 ± 1	1.0 ± 0.3	39 ± 2
Stakčín	<0.2	32 ± 2.3	69 ± 5	26 ± 0.9	20 ± 1.4	28 ± 0.7	72 ± 6	16 ± 1.2	0.97 ± 0.3	38 ± 1
Macov	<0.2	23 ± 2.1	54 ± 4	23 ± 1.7	29 ± 1.9	50 ± 0.9	75 ± 5	10 ± 1	0.98 ± 0.4	99 ± 3

Table 4. Correlation between pH and Some Trace Elements Content

pH	m_r(V) / mg kg^{-1}	Corr.	m_r(Co) / mg kg^{-1}	Corr.	m_r(Zn) / mg kg^{-1}	Corr.	m_r(Cr) / mg kg^{-1}	Corr.	m_r(Pb) / mg kg^{-1}	Corr.
7.77	99	0.728	10	−0.993	75	−0.099	54	−0.868	23	−0.868
7.22	39		11		56		49		20	
5.82	38		16		72		69		32	

Table 5. Metal Ratio in Planosols (Stakčín) $m_{r,i}:m_{r,j}$

i	j		i	j		i	j		i	j	
Cu	Co	1:0.5	Zn	Co	1:0.2	Pb	Co	1:0.6	Cr	Co	1:0.2
	Cr	1:3.4		Cr	1:1.2		Cr	1:3.1		Ni	1:0.2
	Ni	1:0.8		Ni	1:0.3		Ni	1:0.7		Zn	1:0.8
	Zn	1:2.8		Pb	1:0.4		Cu	1:0.9		Pb	1:0.3
	Pb	1:1.1		Cu	1:0.35		Zn	1:2.5		Cu	1:0.3
	As	1:0.8		As	1:0.28		As	1:0.7		As	1:0.2
	Mo	1:0.02		Mo	1:0.01		Mo	1:0.02		Mo	1:0.01
	V	1:2		V	1:0.7		V	1:1.8		V	1:0.6
	Cd	1:0.01		Cd	1:0.002		Cd	1:0.006		Cd	1:0.002

cause sampling and homogeneity problems, critical reaction behaviour or volatile elements could occur. Mean values of determined hazardous elements are given in Table 3.

From the results it is evident that the highest contents were found in the locality Dvorníky. The refractory elements Mo and V are easily determined and for illustration there is shown in Fig. 1 signal of Mo (1 mg dm^{-3}) and Zn (1 mg dm^{-3}) without and with matrix elements. The analytical lines were tested by making scans around each line and for illustration there is in Fig. 2 scan around λ(As) 189.04 nm in soil sample (CRM S-SP, standard solution 0.25 mg dm^{-3} and blank). It is evident that certified material has similar spectrum as a soil sample. The detection limits were calculated (LOD 3σ) for microelements as follows: As 0.125 mg dm^{-3}, Zn and Cu 0.006 mg dm^{-3}, Mo 0.009 mg dm^{-3}, V 0.014 mg dm^{-3}, Cr 0.015 mg dm^{-3}, Cd 0.016 mg dm^{-3}, Ni 0.017 mg dm^{-3}, Co 0.0125 mg dm^{-3}, and Pb 0.050 mg dm^{-3}. Most important soil property controlling the content of trace elements in soils is soil acidity. Therefore pH in KCl was measured and correlation between pH and trace element contents was made (Table 4). Correlation between Co and pH was found – with lower pH the higher content was found. Low pH value as well as low clay and humus contents in Eutric Planosols (Stakčín) increase content of Pb, Cr, Ni, Co, and V in comparison with Calcaric Chernozems (Macov) or Calcaric Fluvisols (Topoľníky) and this is in agreement with literature [15]. The highest content of all elements was found in the locality Dvorníky (Eutric Fluvisols) in 1996 and also in the year 2000. pH Value is not low, but potential acidity could be emphasized by the slow acid flood. This could be also due to the presence of primary minerals of Pb, Zn (galenite, sphalerite) in this locality [13]. The distribution of Cd, Pb, Zn in soil profile close to the mine pointed to a relative accumulation of the total concentrations in the surface layer, which apparently did not depend on the other major chemical properties [2]. Total contents of microelements As, Cu, Zn in the locality Macov were

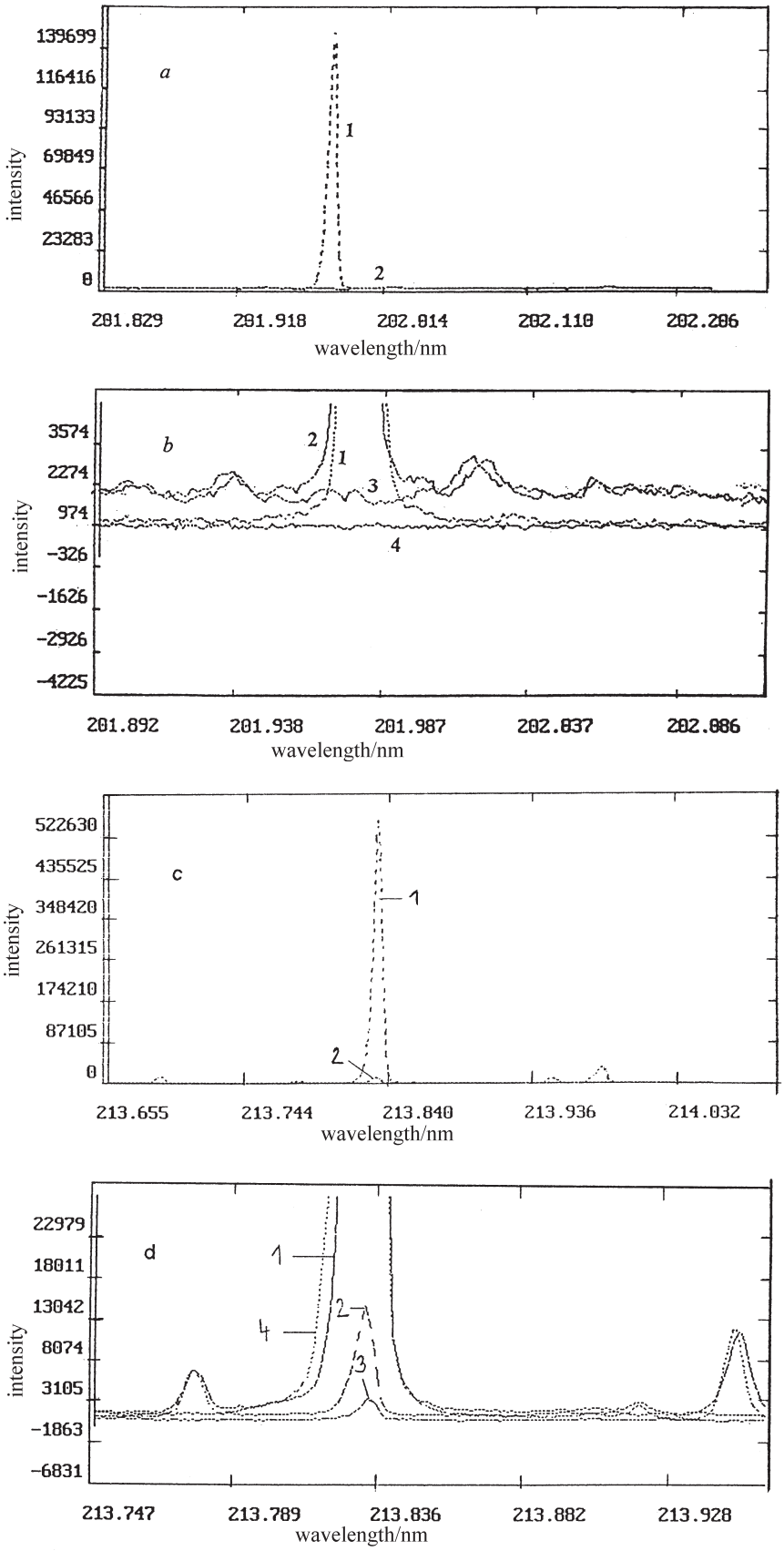

Fig. 1. Scan around λ(Mo) 202.03 nm and around λ(Zn) 213.856 nm. *a*) 1 – standard solution (1 mg dm^{-3} Mo), 2 – only matrix. *b*) 1 – standard solution (1 mg dm^{-3} Mo) without matrix, 2 – standard solution with matrix, 3 – only matrix, 4 – blank. *c*) 1 – standard solution (1 mg dm^{-3} Zn), 2 – only matrix. *d*) 1 – standard solution (1 mg dm^{-3} Zn) without matrix, 2 – only matrix, 3 – blank, 4 – standard solution with matrix.

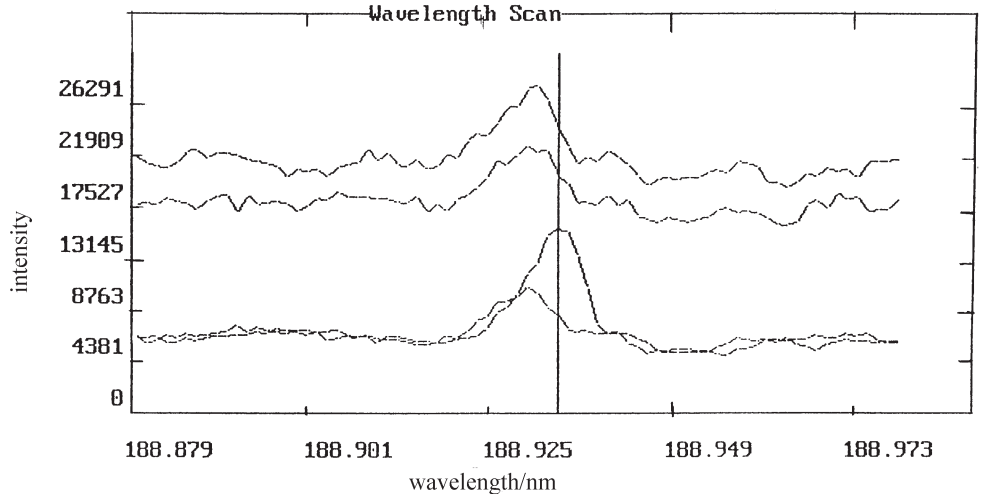

Fig. 2. Scan around λ(As) 189.04 nm. S-SP, sample Calcaric Fluvisol, standard (250 μg dm^{-3}), blank (from above).

higher than in Stakčín or Topoľníky in both years because of higher organic matter in Chernozems, which could bound trace elements with fulvic acids [16]. The results suggest that ICP-AES is a suitable method for studying microelements.

The hygienic limits were not overstepped even after four years [14] in the localities, except Dvorníky. We made also the metal content ratio (Table 5) between elements in Planosols (Stakčín). The reciprocal ratio is in geochemistry one of the most important indicators of changes in the system mineral—soil. In the environment the changes of reciprocal ratio between elements provide information about the contamination level. The results found in the locality Stakčín testify to no contamination in this region and were similar to that given by literature [12].

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