

Multielemental Determination of Cu, Zn, Mo, Mn, V in Soils by ICP-AES Method after Microwave Digestion

^aJ. LAŠTINCOVÁ*, ^aJ. VANOČAN, ^aD. OKTAVEC, and ^bE. KADEROVÁ

^a*Department of Analytical Chemistry, Faculty of Chemical Technology,
Slovak University of Technology, SK-812 37 Bratislava*

^b*Slovnaft a.s., SK-821 17 Bratislava*

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The development of ICP-AES came about due to the need for a fast multielement soil analysis. However, interferences do occur when there is a high concentration of any individual element in the soil.

The trace elements Cu, Zn, Mo, V, and Mn were determined by the ICP-AES method in a soil and interferences of macroelements Al, Ca, Fe, Mg, Na, K were studied. The limits of detection for trace elements were statistically calculated. The decomposition procedure for the soil samples was performed by popular microwave oven CEM. Modelled standard solution with matrix elements was used to obtain the calibration curve. Results were compared with the certified values of elements in certified reference material SO-2.

The suitability of the method for the determination of trace elements in soils must be taken into consideration, because the reliability of the results depends on the presence of the minor and major elements in the soil samples. The determination of trace amounts of Cu, Zn, Mo, V is difficult, because macroelements like Fe, Al, Ca, Mg, Na, K could interfere. Many papers deal with the determination of trace elements in soil and plant material [1–9]. AAS is a widely used method and in the last years also ICP-AES [10]. For the preparation of the soil samples new decomposition procedures may be advantageous, because they are rapid, prevent losses of volatile elements and have reduced risk of contamination [11].

We used the most recommended method: decomposition in microwave oven with a mixture of acids HF, HCl, HNO₃ in the closed vessel [12]. This step is required especially for determination of Mo and V which are bound on resistant minerals in the soil and by leaching we could not determine them [13–15].

The total content of hazardous elements in soils could be an indicator for the environmental monitoring studies. The regional contamination of soils occurs mainly in industrial regions where factories, motor vehicles, and municipal wastes are the most important sources of trace elements in the soils.

The scope of this work was to elaborate procedure for rapid determination of Cu, Zn, Mo, V, and Mn in the soil around Slovnaft a.s. Bratislava (Slovakia) by

ICP-AES. The aim of the study is the influence of Al, Fe, Ca, Mg, Na, K on the determination of Cu, Zn, Mo, V, Mn in the soil after microwave digestion. The assumed matrix was simulated to avoid interferences of macroelements. Because the level of these elements in real sample is high and in each type of soil their concentration varies, we would like to estimate the concentration from which it is necessary to simulate matrix in the analytical calibration. The interferences were also reduced by the selection of the analytical lines. The limits of detection were statistically calculated from 30 measurements of blank. Certified reference material of soil SO-2 was used in this work.

EXPERIMENTAL

The inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was performed using sequential atomic emission spectrometer BAIRD ICP 2070/USA/, equipped with Meinhard nebulizer, Scott-type spray chamber, peristaltic pump, and quartz torch for the plasma. Instrumental parameters for the determination are shown in Table 1. The microwave oven by fy CEM model MSD-2000/OS-22 SLAG/ was used for digestion of real samples. Program for normal 630 watt system is shown in Table 2.

The analytical lines available for measurement of the microelements were studied, bearing in mind their sensitivity [16]. The study of interferences was carried

*The author to whom the correspondence should be addressed.

Table 1. Instrumental Parameters for the Determination

Argon auxiliary gas flow rate	1.4 dm ³ min ⁻¹
Argon coolant gas flow rate	11 dm ³ min ⁻¹
Flow rate through peristaltic pump	4 cm ³ min ⁻¹
Argon carrier gas pressure	206.85 kPa
Power	900 W
Optical cell	Czerny—Turner
Optical length	1 m
Rapidity of scan	400 nm s ⁻¹
Diffraction grid	1800 grooves mm ⁻¹
Slit	0.01
Generator of radiofrequency	40.68 MHz
Detector	photomultiplier
Max. power	1500 W
Extent	190—800 nm

Table 2. The Heating Program for 5 Vessels

Stage	/1/	/2/	/3/	/4/	/5/
% power	100	0	0	0	0
p/kPa	900	0	0	0	0
t/min	30:00	0:0	0:0	0:0	0:0
tap/min	15:00	0:0	0:0	0:0	0:0
fan speed	100	100	100	100	100

out by making spectral scans around each of 3 lines of element in the presence of matrix and the best lines were chosen (Table 3).

The samples were taken of upper layer in the depth 10 cm and width 20 cm from the area around Slovnaft a.s. Bratislava:

Sample 1 is from the region Waste water treatment in Vlčie hrdlo.

Sample 2 is from the area around Slovnaft a.s. in Vlčie hrdlo.

Sample 3 is from the field in Vlčie hrdlo.

The rests of plants were removed and the soil was sieved (2 mm mesh). Then it was drained for 12 h at 110°C and homogenized in an agate mortar.

The soil certified reference material CRM SO-2 produced by Canadian Centre for Mineral and Energy Technology was used.

Chemicals

HNO₃ (65 vol. %) Suprapur (Merck), HCl (36 vol. %) Suprapur (Merck), HF (48 vol. %) Suprapur (Merck), H₃BO₃ (s) anal. grade (Lachema, Brno, Czech Republic). Stock Titrisol standard solutions of Ca, Fe, Mg (2000 mg dm⁻³, Merck) and one-elementary stock solutions of Cu, Zn, Mo, Mn, V, Na, K, Al (1000 mg dm⁻³) from the Slovak Institute of Metrology were used. Deionized water (conductivity 0.18 μS m⁻¹) was used for preparing all solutions.

Procedure

0.5 g of each sample was weighed into teflon vessel

and drenched with 10 cm³ of water. With precaution were added 5 cm³ HNO₃ (65 %) + 4 cm³ HF (48 %) + 1 cm³ HCl (36 %). After rustling the vessels were closed and put into microwave oven together with blank. The microwave digestion was performed using the program recommended by the manufacturer CEM Corporation (Table 2). After cooling the vessels were opened and 30 cm³ of saturated solution of H₃BO₃ was added and the closed vessels were heated again for 5 min at 100 % power. After cooling the sample solutions were transferred into 50 cm³ calibrated flasks and diluted to volume with deionized water. The same procedure was used for CRM SO-2.

For preparing multi-elementary calibration solution ($\rho = 1 \text{ mg dm}^{-3}$), aliquots were taken from stock standard solutions (Cu, Zn, Mo, V, Mn, 1000 mg dm⁻³) and diluted in deionized water and then (5 cm³ HNO₃ + 1 cm³ HCl)/100 cm³ were added. Simulated matrix solution was prepared by dilution of Ca, Fe, Mg (2000 mg dm⁻³) and Al, Na, K (1000 mg dm⁻³) to these concentrations: 700 mg dm⁻³ Al, 380 mg dm⁻³ Fe, 200 mg dm⁻³ Ca, 150 mg dm⁻³ K, and 60 mg dm⁻³ Mg, Na, which were taken from literature [7, 8] as the highest level expected in real samples.

RESULTS AND DISCUSSION

Selection of analytical lines which are given in Table 3 was carried out by making scans around each of the lines. For illustration scans of proper and improper lines of V and Cu are shown in Fig. 1. Based on studied interferences of simulated matrix, the most suitable lines were chosen for determination: Cu 324.754 nm, Mn 257.610 nm, Mo 202.030 nm, V 311.071 nm, Zn 213.856 nm.

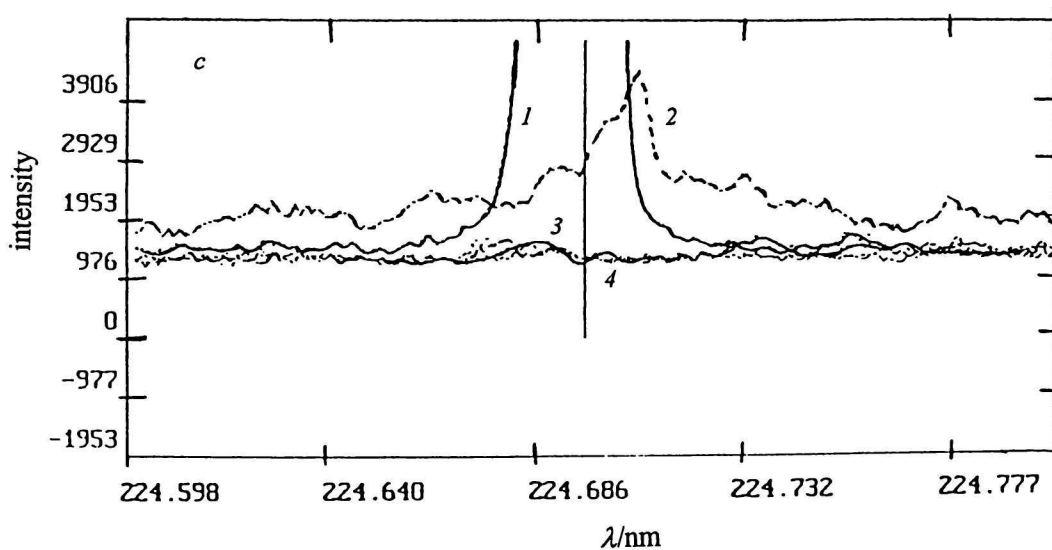
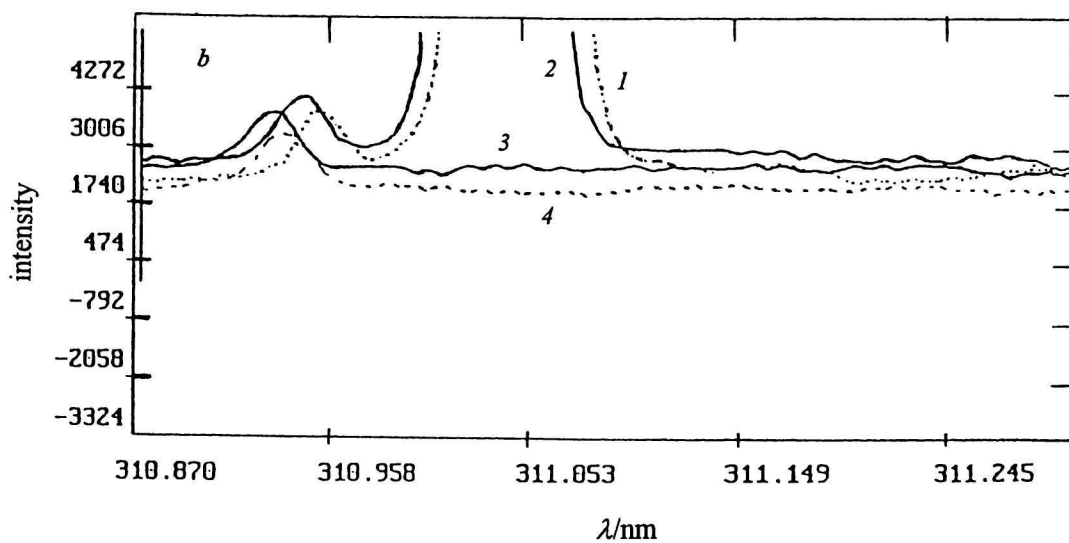
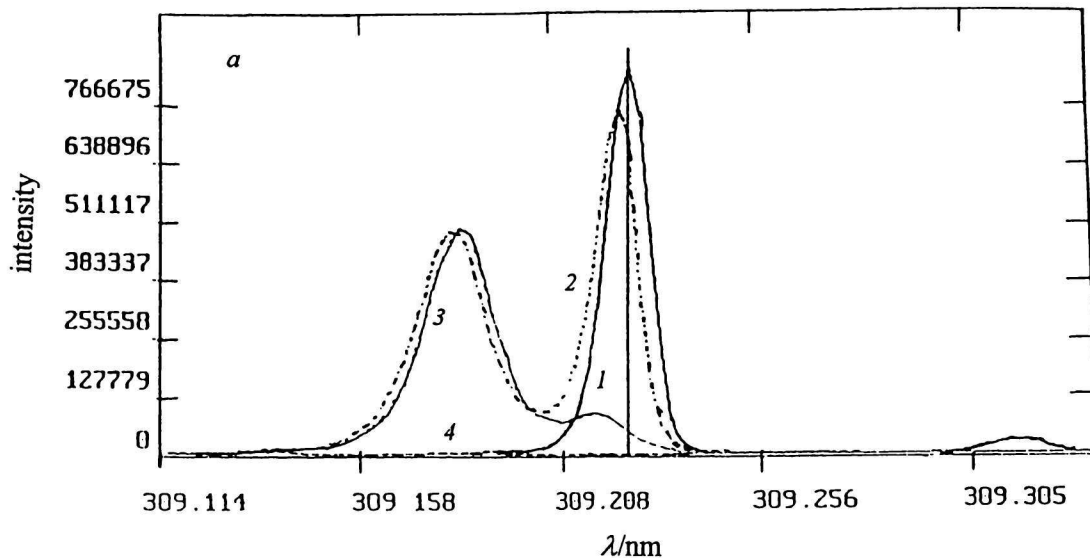
The limits of detection were statistically calculated for the trace elements: Cu 0.0066 mg dm⁻³, Zn 0.0058 mg dm⁻³, V 0.0147 mg dm⁻³, Mo 0.0092 mg dm⁻³, Mn 0.0056 mg dm⁻³.

The study of the influence of matrix elements on the determination was carried out by measuring the signals of 1 mg dm⁻³ concentration of Cu, Zn, V, Mo, Mn after gradual addition of macroelements from 10—200 mg dm⁻³ and these signals are shown in Fig. 2a—f.

Table 3. The Analytical Lines

λ/nm				
Cu	Mn	Mo	V	Zn
324.754 I	257.610 II	202.030 II	309.311 II	213.856 I
224.700 II	259.373 II	203.844 II	311.070 II	202.548 II
219.958 I	260.569 II	204.598 II	310.230 II	206.260 II

I — atomic line; II — ionic line.



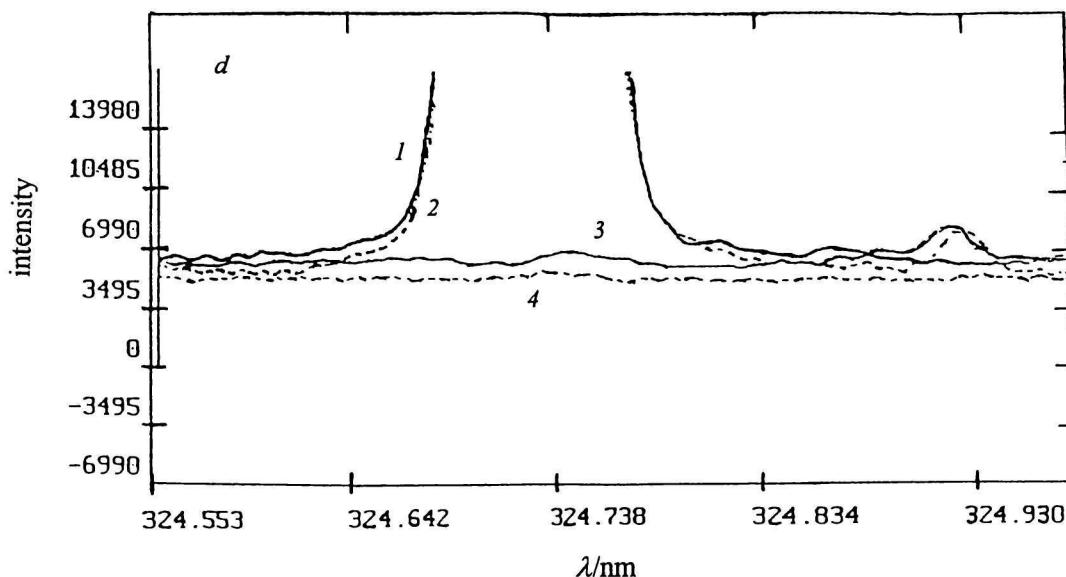


Fig. 1. a) Improper line $\lambda(V)$ 309.311 nm, b) proper line $\lambda(V)$ 311.071 nm, c) improper line $\lambda(Cu)$ 224.700 nm, d) proper line $\lambda(Cu)$ 324.754 nm. Intensity of the signal 1 mg dm^{-3} 1. without matrix, 2. with matrix, 3. only matrix, 4. signal of the blank.

Table 4. The Soil Analysis

Element	Soil 1/(mg kg^{-1})			Soil 2/(mg kg^{-1})		
	Total amount	SD	% RSD	Total amount	SD	% RSD
Cu	66.88	1.20	1.80	27.52	0.14	0.5
Mn	510.40	9.48	1.86	617.80	1.32	2.1
Mo	14.93	0.65	4.38	16.43	0.42	2.5
V	63.77	1.24	1.94	72.48	2.23	3.1
Zn	131.42	1.67	1.27	59.02	0.25	0.4

SD — standard deviation; RSD — relative standard deviation.

We checked linearity of calibration curve ($0-1 \text{ mg dm}^{-3}$) first without matrix and then after addition of matrix. The curves were linear, but the addition of macroelements shifted the calibration curves under or over the level of the aqueous solution without matrix. When the solution contained trace elements and macroelements the linear relation was obtained, however the off peak correction was needed in both cases.

It was found that Fe influenced the determination of Cu. The concentration of Mg and Al influenced the determination of Mo. The concentration of Ca and Mg most influenced Zn, Mn, and Mo and Na with K influenced all trace elements.

We suggest to simulate matrix in analytical calibration from concentration 200 mg dm^{-3} Al, Fe, 150 mg dm^{-3} Ca, K, 50 mg dm^{-3} Mg, Na. The influence is evident and for illustration increase of the signal of 1 mg dm^{-3} Mn in the presence of macro- and microelements is shown in Fig. 3.

If the presence of Al and Fe is too high (over 800 mg dm^{-3}) we cannot avoid the interferences and particular attention must be paid to the elimination or

correction of interferences so that reliable data can be obtained.

The results of the total content of microelements in the real samples are given in Tables 4 and 5. We did not find any accumulated metals in soils around Slovnaft a.s. to compare with literature [17]. Because of high level of matrix elements in the soil samples a "soil matrix" was simulated in calibration curves. Reliability and accuracy of this analysis was verified using CRM SO-2 and the results were satisfactory.

CONCLUSION

The total content of Cu, Zn, Mn, Mo, and V was determined in the soil samples by the ICP-AES method. The decomposition by acid mixtures containing HF in microwave oven was used.

In spite of the fact that the method ICP-AES was confirmed to be very convenient for multielemental determination, the precision for trace elements is influenced by the presence of matrix elements and the attention must be paid to the elimination or correction

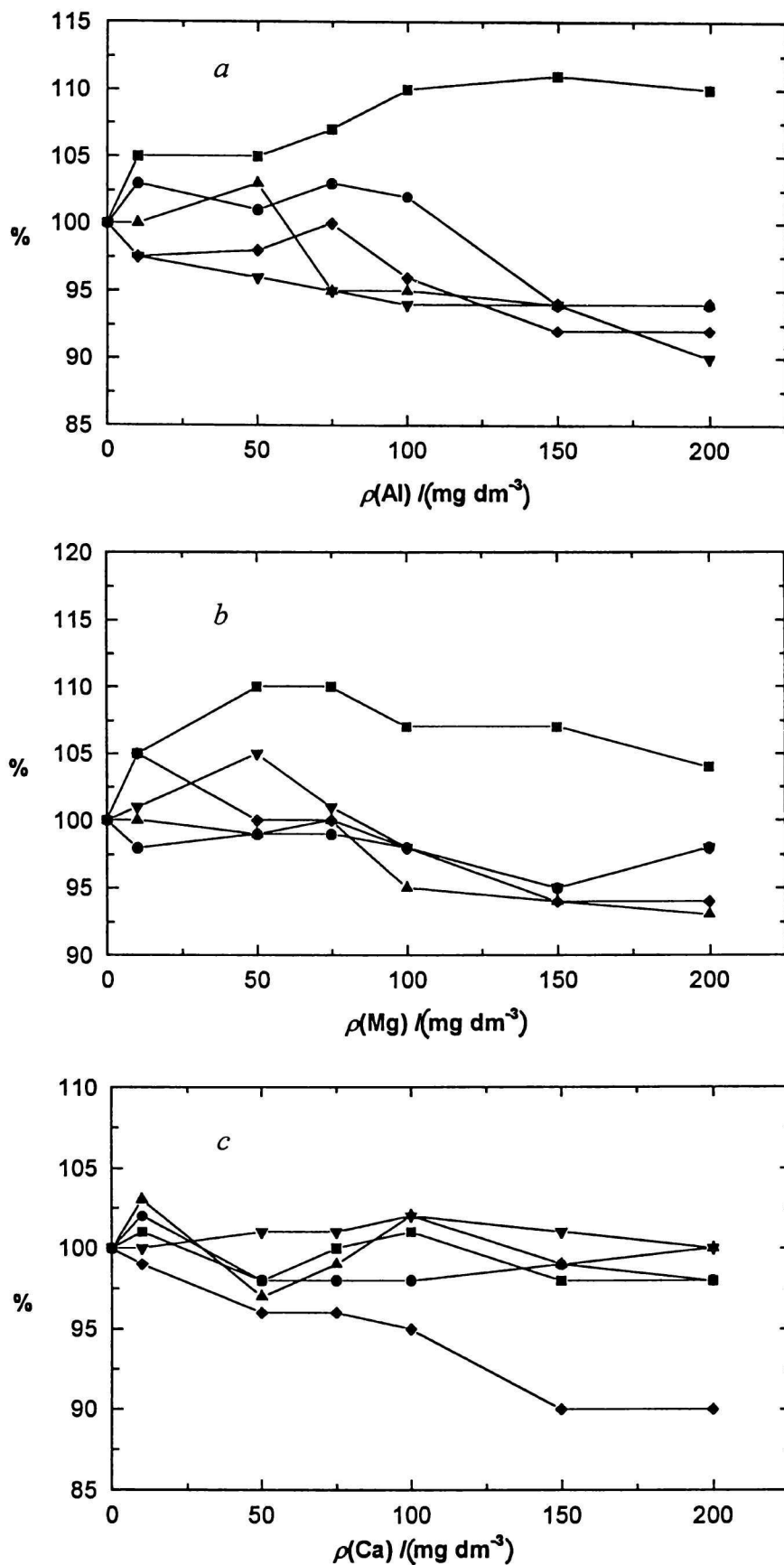
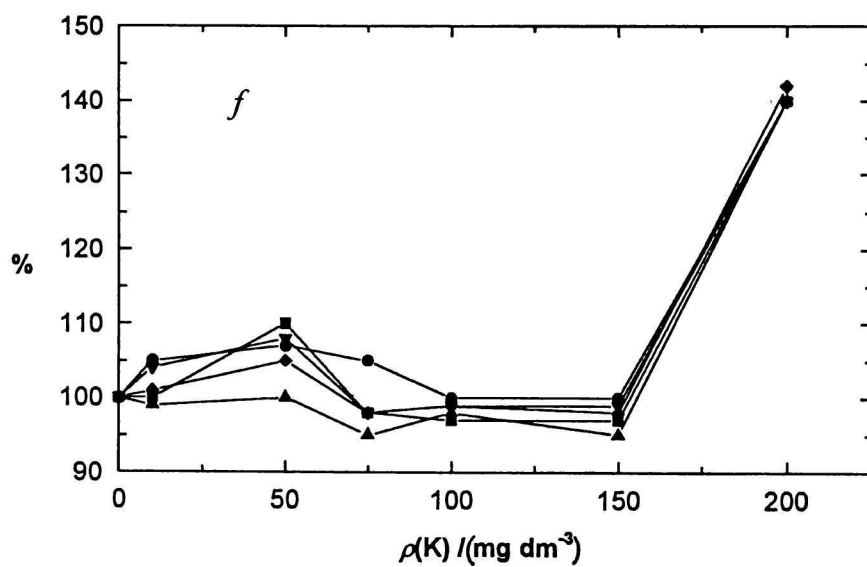
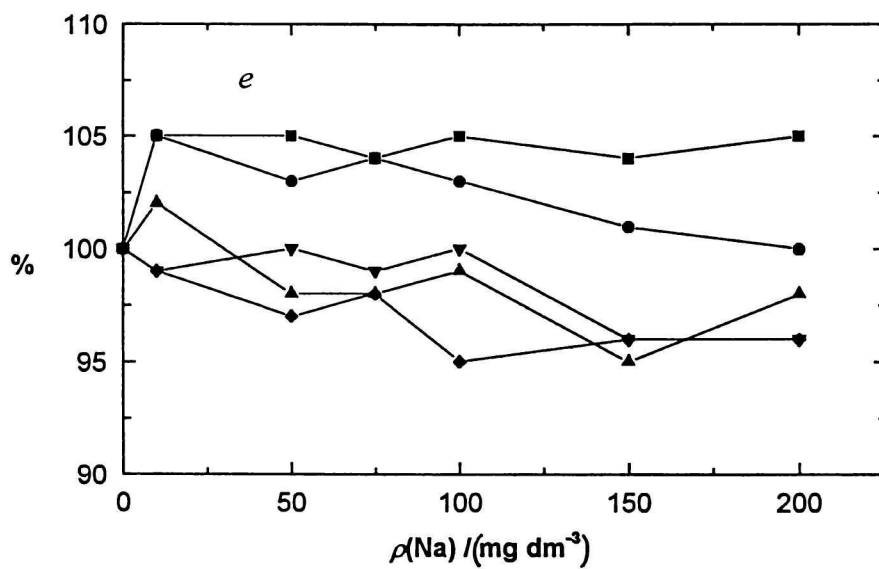
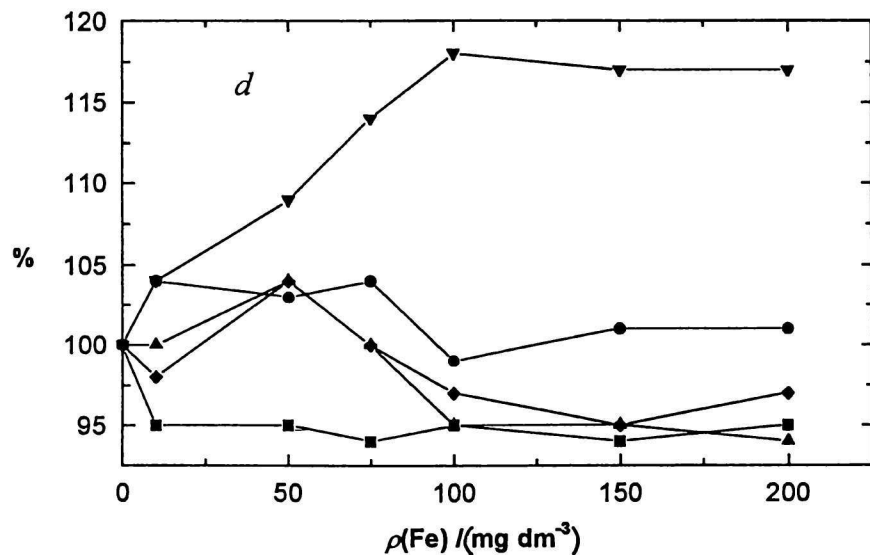


Fig. 2. The dependence of the intensity of the signal of microelements (concentration 1 mg dm^{-3}) on the concentration of Al (*a*),



Mg (b), Ca (c), Fe (d), Na (e), K (f) in the soil. ■ Mo, ● V, ▲ Zn, ▼ Cu, ◆ Mn.

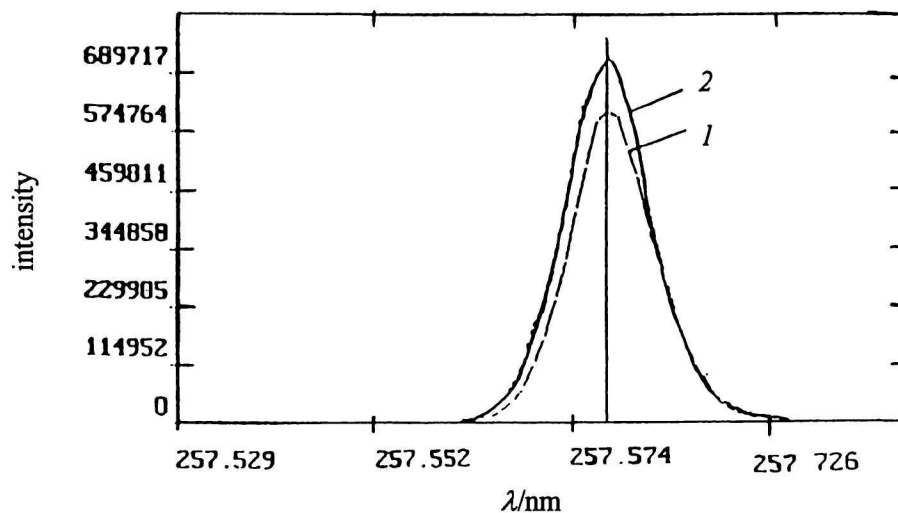


Fig. 3. Increasing of the signal of 1 mg dm^{-3} Mn in the presence of matrix elements /2/.

Table 5. The Soil Analysis

Element	Soil 3/(mg kg^{-1})			CRM SO-2/(mg kg^{-1})			
	Total amount	SD	% RSD	Found	SD	Certified	SD
Cu	33.09	0.56	1.68	8.00	0.75	7.00	1.00
Mn	518.80	1.30	0.25	679.80	13.00	700.00	20.00
Mo	11.21	0.08	0.72	2.60	0.68	2.00	
V	72.70	2.07	2.84	71.70	4.50	64.00	10.00
Zn	51.87	1.06	2.04	119.20	1.00	124.00	5.00

of interferences. We used the off peak correction, modelled matrix in calibration, and suitable lines for measurement to eliminate interferences. The results are in agreement with the literature. Analysis of CRM SO-2 was used to verify this method.

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