

Determination of High Zn and Pb Concentrations in Polluted Soils Using Energy-Dispersive X-ray Fluorescence Spectrometry

R. Sitko¹, B. Zawisza¹, J. Jurczyk^{1*}, F. Buhl¹, U. Zielonka²

¹Institute of Chemistry, Silesian University, Szkolna 9, 40-006 Katowice, Poland;

²Institute for Ecology of Industrial Areas, 40-833 Katowice, Poland

Received: 13 March 2003

Accepted: 5 May 2003

Abstract

A method of determination of high Zn and Pb concentrations by means of EDXRF (energy-dispersive X-ray fluorescence spectrometry) is presented. Zn and Pb concentration in soil samples from contaminated areas ranged within a limit of Zn: 800–2000ppm and Pb: 200–600ppm. Soil analysis was conducted directly after the samples had been dried and powdered, as well as in situ in polluted areas. Due to the absence of the certificate reference materials for soils with such high Zn and Pb concentrations, samples of soil with the Pb and Zn amounts determined using the AAS method were used to perform calibration. The obtained detection limits are 30ppm and 19ppm for Zn and Pb, respectively. Because of the high analytes concentration and material heterogeneity, the repeatability of the results was examined according to the sample holder's various positions in EDXRF analyzer; repeatability the of the results while putting into the sample holder and out of it, together with the repeatability of making the calibration. The results obtained using the EDXRF method were compared to these obtained using AAS and wavelength-dispersive X-ray fluorescence spectrometry (WDXRF).

Keywords: X-ray fluorescence spectrometry, zinc, lead, soil

Introduction

Many instrumental methods have found their implementation in trace elements determination in the soils: atomic absorption spectrometry (AAS) both with the use of a graphite furnace and flame [1, 2], inductively coupled plasma atomic emission spectrometry (ICP-AES) [3, 4], and inductively coupled plasma-mass spectrometry (ICP-MS) [5]. These spectroscopic techniques for soil analysis have been compared in [6, 7]. Another method used for soil analysis is neutron activation analysis (NAA). This method was used to determine Zn and Pb together with Al, Cr, Fe, Mn, Ni and Cu [8]. Preparation of the soil samples directly for analysis takes about 24 hours.

X-ray fluorescence analysis XRF allows analysis of solid materials with no need for digestion as in the AAS

or ICP-AES methods. The portable energy-dispersive X-ray spectrometer (EDXRF) with radioisotope excitation is very useful for determination of trace elements in situ on the analyzed area and it significantly reduces the sample number for the laboratory analysis by other methods. Soil samples can be directly analyzed by XRF method after drying and powdering of the material and pressing it up into a pellet with boric acid [9, 10]; pressed up into a pellet after samples were ashed [11]. The pressure pressing method was also used by the authors of the papers [12, 13] to estimate pollution with the metals in particular grain fraction after the soil had been sieved.

We have analyzed the polluted soils after drying and powdering, including in situ analysis with the portable energy-dispersive X-ray spectrometer implementation. Zn and Pb concentrations in the soil samples from contaminated areas reached the ranges: 800-2000ppm Zn and 200-600ppm Pb. The results

*Corresponding author; e-mail: jurczyk@us.edu.pl

Table 1. Energy of analytical lines.

Line	Energy (keV)	FWHM* (keV)
Pb L _β	11.9	11.7-12.0
Zn K _α	12.6	12.5-12.8
Fe K _α	6.40	6.28-6.51
Compton Ag K _α	-	20.3-21.1

* full width at half maximum height

Table 2. The loss in weight of the soils at 105, 300 and 900°C in relationship to the soils dried at room temperature.

Sample	105°C	300°C	900°C
Soil I	3%	8%	10%
Soil II	5%	5%	8%
Soil III	1.7%	1.5%	6%

were compared with AAS method results as well as with the wavelength-dispersive X-ray fluorescence spectrometry (WDXRF).

Experimental

We used a portable energy-dispersive X-ray analyzer X-MET 920 Metorex with radioisotope excitation (two sources ¹⁰⁹Cd and ²⁴¹Am) and a semi-conductor detector Si(Li) with 0.17keV resolution. Only ¹⁰⁹Cd source was used, because a high background with much worse detection and determination limits was achieved for ²⁴¹Am source. Pb determination was performed for Pb L_β line with a higher intensity (sensitivity) achieved rather than for the Pb L_α line. The aim of this analysis was fast Zn and Pb determination in soils (also in situ analysis), so the detection time was defined at 60s. Each sample has performed no fewer than three measurements. Other essential information has been included in Table 1.

Soils are analyzed directly in a form of powder samples. Preparation of the material for analysis entails several stages: sampling of the material at a depth of from 0 to 25cm in polluted areas; drying at room temperature in the time period related to soil humidity. Additional drying and roasting of the soil at 105, 300 and 900°C shows a few percent loss of mass (Table 2). Differences between the results obtained for the soils dried at room temperature and soils dried at 105°C can be neglected taking into consideration the small absorption of Zn and Pb fluorescent radiation by hydrogen and oxygen (H₂O contents below 5%), precision of EDXRF measurements, inhomogeneity of the analyte material and, most of all, requirements set according to the accuracy of the in situ analysis. After

soil drying at room temperature the material was powdered in an agate mortar and sieved through a round loop sieve of about 0.25 mm. Powdered soil was then inserted in a sample holder. The powder in the sample holder was pressed manually (pressure to 3kg per area of the sample – 6.6cm² does not influence the intensity of Zn and Pb fluorescent radiation).

The samples should obey the thick sample criteria, i.e. thickness should not be less than the critical layer thickness t_{min} emitting 99.9% of fluorescence radiation. Sample minimal mass corresponding to the critical layer thickness is given by the formula:

$$m_{min} = \pi r^2 \frac{4.6}{\bar{\mu}_{Ei}}$$

$$\bar{\mu}_{Ei} = \sum_{i=1}^n c_i \cdot \mu_{Ei} \quad \sum_{i=1}^n c_i = 1$$

where:

$\bar{\mu}_{Ei}$ - total mass absorption coefficient for the Ei energy of Zn K_α or Pb L_β radiation,
 c_i - element i concentration in a sample,
 μ_{Ei} - mass absorption coefficient for element i in a sample,
 r = 1.45cm - diameter of the sample holder.

To calculate sample minimal mass, the soil matrix element concentrations extending within wide ranges were taken from the soil catalogues (Glen Spectra Reference Materials Issue No. 3 and Reference Materials 2Theta 1997/98) with certified composition: GBW7407, GBW7411, GBW7401, GBW7404, GRSM/3 071-SO2, GRSM/3 071-SO3, GRSM/3 071-SO4. Total mass absorption coefficients for different soils ranged from 38 to 65cm²g⁻¹ for Zn K_α and from 26 to 37cm²g⁻¹ for Pb L_β. The calculated sample minimal mass m_{min} equals 1.2g, which corresponds to the critical layer thickness of 0.09cm. The sample mass should not be smaller than 1.2g, but for practical reasons (proportional location of the material in the sample holder), two times larger mass is recommended (i.e. about 2.5g).

Results and Discussion

Due to the lack of certificate reference materials of the soils with such high Zn and Pb concentrations, the soils analyzed by AAS were used as reference samples. Fig. 1 presents the calibration graphs (20 calibration samples) achieved for the EDXRF method. The following calibration equations were obtained: ppmPb=0.502·I-160 ($r=0.991$, RMS=11ppm) and ppmZn=0.632·I+84 ($r=0.991$, RMS=37ppm), where I - radiation intensity (counts per 60s). RMS (root of the mean square of the sum of the differences between the chemical value of the standard concentrations and the calculated values) is a standard deviation characterizing a dispersion point around the calibration line (residual error).

Table 3. The repeatability of results with different sample holder positions in the spectrometer chamber (two measurements were performed for each position).

Sample holder positions	Zn concentration (ppm)		Pb concentration (ppm)	
	Concentration for one measurement	Average for two measurements	Concentration for one measurement	Average for two measurements
0°	823	800	188	197
	778		206	
45°	783	771	184	194
	759		204	
90°	780	781	202	204
	781		206	
135°	761	777	213	207
	794		200	
180°	745	759	200	200
	773		200	
225°	830	811	209	219
	792		230	
270°	795	787	184	192
	780		201	
315°	779	777	221	202
	774		182	
360°	771	762	204	205
	752		207	
Average (p=0.95) std	781±11 22		202±6 12	

$$\text{RMS} = \sqrt{\frac{\sum (c_i' - c_i)^2}{n - 2}}$$

where:

c_i' - element concentration in the soil sample in ppm calculated from the calibration equation;

c_i - element concentration in the soil sample in ppm;

n - number of calibration samples.

The variable concentration of the matrix elements Ti, Ca, K, Si, Al, Mg, Na absorbing fluorescent radiation of Zn and Pb could be the source of certain errors. Enhancement effects can be neglected because of no enhancing elements or a very low concentration of them (trace heavy elements). Nevertheless, using scattered radiation (Compton scattered peak of Ag K_{α} line from ^{109}Cd source) as internal standard ($c_i = b_i + a_i \cdot I_i / I_{\text{compt}}$ [14]) to correct the absorption effects by the matrix light elements did not improve the results. In some soils, iron concentration was very diversified. Various

iron concentration can affect different absorption of Zn and Pb fluorescent radiation. For this type of soil, mathematical models that involved absorption of zinc and lead radiation by iron were applied: Lucas-Tooth and Price's model [15]:

$$c_i = b_i + I_i \cdot (a_i + \sum a_{ij} \cdot I_j)$$

and Mitchell and Hopper's model [16]:

$$c_i = b_i + I_i \cdot a_i + \sum a_j \cdot I_j + \sum a_{ij} \cdot I_i \cdot I_j + \sum a_{ijk} \cdot I_i \cdot I_k$$

where:

c_i - the determined element concentration,

I_i - radiation intensity emitted by the determined element,

I_j and I_k - radiation intensity emitted by the matrix elements,

b_i - constant characteristics of the background,

a_i - constant specifying the sensitivity for the determined element, if inter-element influences do not appear,

a_j, a_{ij}, a_{ijk} - inter-element influences coefficients.

Table 4. The repeatability of the results while the powdered soil is put into and out of the sample holder.

Number of measurement	Zn concentration (ppm)		Pb concentration (ppm)	
	Concentration for one measurement	Average for two measurements	Concentration for one measurement	Average for two measurements
1	796	791	215	202
	786		190	
2	761	774	199	201
	788		204	
3	811	816	208	211
	821		215	
4	806	790	222	216
	774		209	
5	817	809	206	203
	802		200	
Average (p=0.95) std	796±14 19		207±7 9	

The application of the models involving radiation absorption of the determined elements by iron did not significantly improve the results. The error being the result of the absorption by iron can thus be smaller than the errors resulting from the accuracy of AAS analysis, inhomogeneity of the materials or grain size effect. Thus, a linear regression was applied in further analyses.

The time drift was tested during the determination by means of EDXRF analyzer. Five measurements were made for a selected sample, and following results had been obtained of the average determined quantity: 761ppm Zn (std=15ppm) and 203ppm Pb (std=9ppm) and the results dispersion 745-783ppm for Zn and 194-214ppm for Pb. Consequently, the measurements were repeated for the same sample after 5 hours of work. The obtained results of five measurements were as follows: 757ppm Zn (std=26ppm) and 214ppm Pb (13ppm) and

the results dispersion 715-784ppm for Zn and 201-228ppm for Pb. The average of these five measurements calculated within 5 hours time distance do not differ statistically (the differences are smaller than a single standard deviation). A statistical comparison of the standard deviations – Test F ($F = s_1^2/s_2^2$) admits the fact that the differences between them are irrelevant ($p=0.95$; the number of independent variables 4) both for Pb and Zn. To ensure counting precision with a portable EDXRF analyzer, the number of measurements should not be smaller than three.

Due to inhomogeneity of the analyzed soils and their direct analysis in the form of powdered samples, the following parameters were tested: result repeatability while putting them in and out of the sample holder, and result repeatability with different sample holder positions in the spectrometer chamber. The latter parameter is crucial in

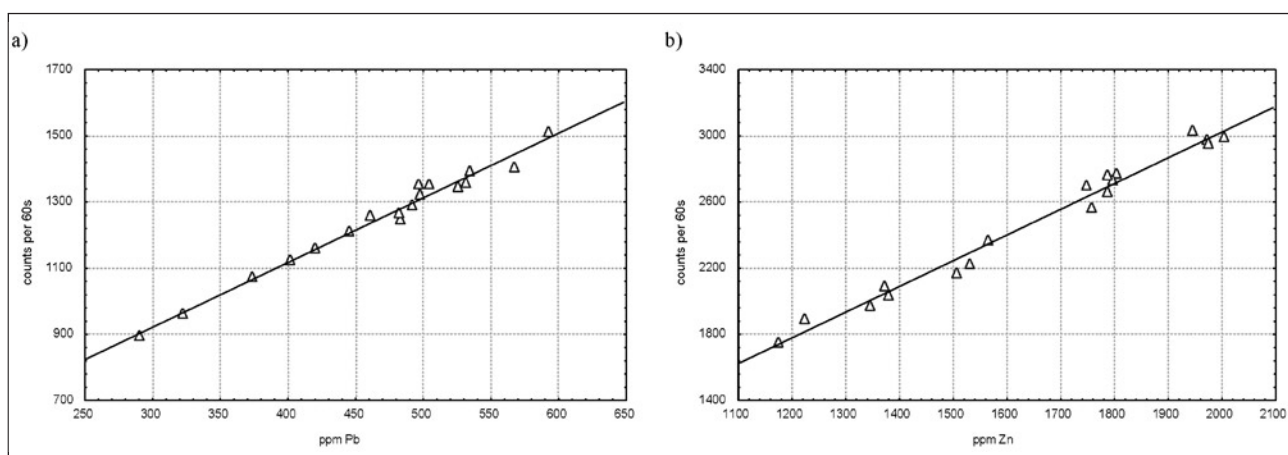


Fig. 1. The calibration graphs obtained for a) lead and b) zinc by EDXRF method.

Table 5. Comparison EDXRF results with AAS and WDXRF results.

Method	Element	Equation	r	RMS (ppm)
AAS	Pb	$\text{ppmPb(EDXRF)}=0.982 \cdot \text{ppmPb(AAS)}+8.4$	0.991	10.6
	Zn	$\text{ppmZn(EDXRF)}=0.982 \cdot \text{ppmZn(AAS)}+29.3$	0.991	35.4
WDXRF	Pb	$\text{ppmPb(EDXRF)}=1.004 \cdot \text{ppmPb(WDXRF)}-0.31$	0.984	18.9
	Zn	$\text{ppmZn(EDXRF)}=0.943 \cdot \text{ppmZn(WDXRF)}+83.7$	0.997	23.1

the case of the portable X-MET 920 analyzer because of no rotation of the sample. The sample holder was turned at a 45° angle (0°, 45°, 90° ... 315°) and for each position two measurements were performed. The results are presented in Table 3. The confidence interval for the sample holder without taking it out of the spectrometer chamber for p=0.95 and n=5 reach 779.7±41.5ppm (738.2-821.2ppm) for Zn and 197.6±15.7ppm (181.9-213.3ppm) for Pb. Measurement results for the sample rotated by a 45° angle fall into the same interval (except for Pb measurement, 225° -219.45ppmPb). So the sample position

does not affect the results of analysis as far as measurement precision is concerned. The repeatability of the results while putting the sample into and out of the sample holder was checked in the following way: two measurements were made for the “unmoved” sample, then the powdered sample was taken out; and again the sample put into the holder was measured twice. The cycle was repeated five times (Table 4). The measurement results for the sample being put into and out of the sample holder fall into the confidence interval of the sample which was not taken out of the holder (exception being no 4 input for

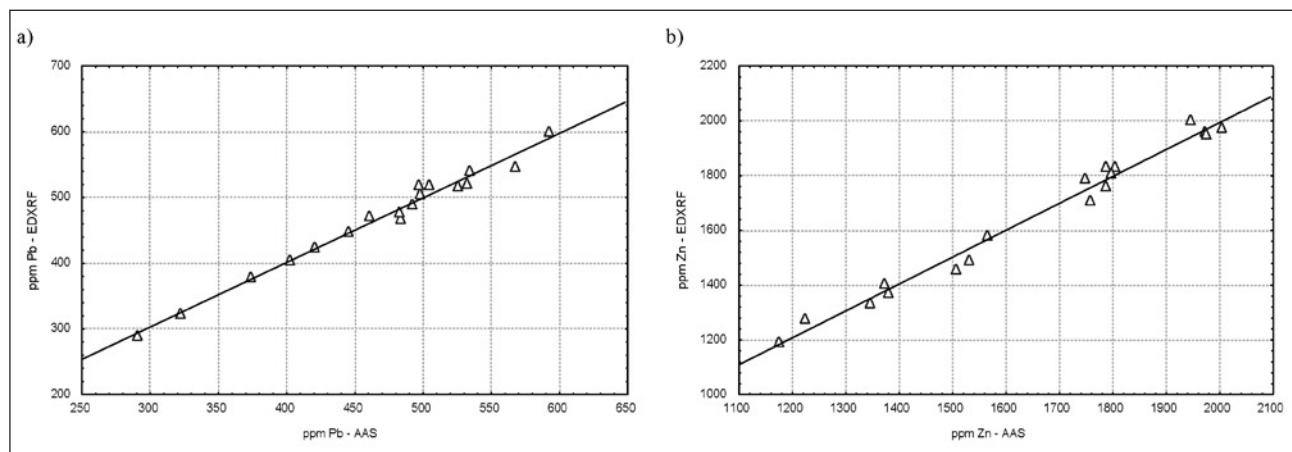


Fig. 2. Comparison EDXRF and AAS results for a) lead, b) zinc.

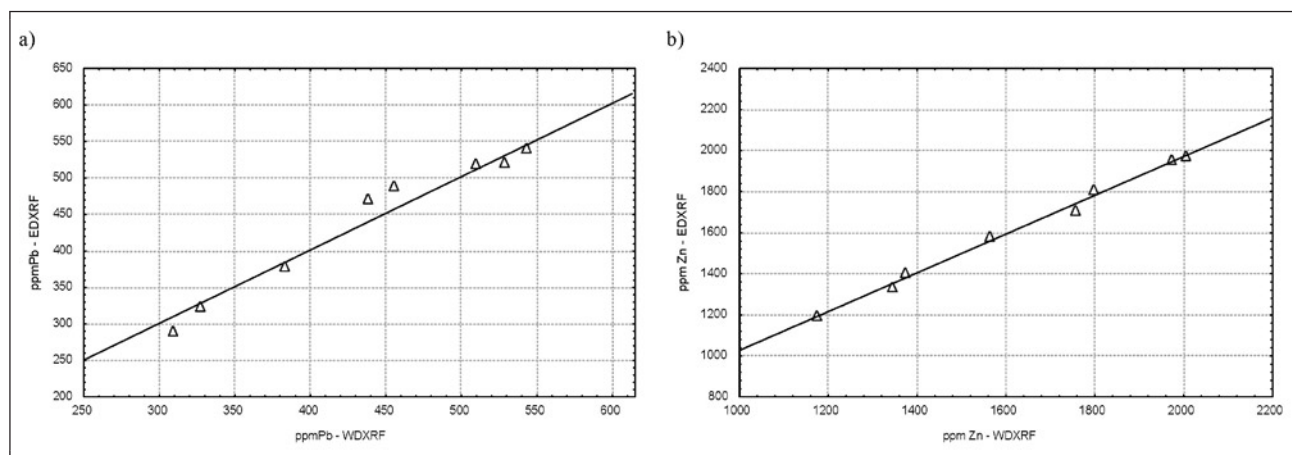


Fig. 3. Comparison EDXRF and WDXRF results for a) lead, b) zinc.

Pb). The procedure for putting the powdered sample in a holder does not affect the analysis results as far as measurement precision is concerned.

The obtained results of EDXRF were compared to AAS (Fig. 2) and to the WDXRF results (Fig. 3). In the second method, a wavelength-dispersive sequential X-ray spectrometer with molybdenum target X-ray tube was used. The other WDXRF measurement conditions: 50kV, 40mA, analyzing crystal LiF200; fine collimator, rotation of the sample, flow and scintillation counter, detection time 40s and 100s for Zn and Pb respectively. For WDXRF analysis soil samples were prepared in the same way as for the EDXRF and the same sample holders were used. Comparison of EDXRF with AAS and WDXRF results are presented in Table 5. The slope of the straight line of the above relationships is characteristic for the systematic proportional error, while the free term in the equation is characteristic for the systematic constant error. Taking into account the dispersion point around the straight lines (the residual error RMS), the differences between the results obtained by EDXRF, WDXRF and AAS methods are insignificant. To determine the detection limits, the following criterion was accepted:

$$C_0 = 3\sqrt{N_b}/k$$

where: $\sqrt{N_b}$ is the standard deviation of the background and k - is the slope of the calibration line to characterize the method's sensitivity.

The obtained detection limits for EDXRF method are (the measurement conditions in Table 1): 19ppm Pb and 30ppm Zn. The detection limits for WDXRF are lower and reach approximately 2ppm for both elements.

Conclusion

The portable EDXRF spectrometer with radioisotope excitation is very useful for determining trace elements in situ on the analyzed industrial or post-industrial area and it significantly reduces the sample number for laboratory analysis by other methods. Sample preparation is restricted to drying (dry air) and powdering of the analyzed soils. This preparation significantly reduces the whole analytical process, especially in situ element determination, which permits estimating pollution of a large area. Nevertheless, the measurements performed in situ are approximate and require correction due to the soil conditions (i.e. "a raw sample" its granularity, humidity or certain mechanical contaminations initial sieving through "thick sieves").

References

1. HODREJARV H., VAARMANN A. Pseudo-total analysis for metallic elements in siliceous soil by acid digestion and

- flame atomic-absorption spectrometry, *Anal. Chim. Acta.* **396**, 293, **1999**.
2. FYTIANOS K., KATSIANIS G., TRIANTAFYLLOU P., ZACHARIADIS G. Accumulation of heavy metals in vegetables grown in an industrial area in relation to soil, *Bull. Environ. Contam. Toxicol.* **67**, 423, **2001**.
3. RYBAK M. E., SALIN E. D. Direct determination of metals in soils and sediments by induction heating-electrothermal vaporization (IH-ETV) inductively coupled plasma-optical emission spectrometry (ICP AES), *Appl. Spectrosc.* **55**, 816, **2001**.
4. BETTINELLI M., BEONE G. M., SPEZIA S., BAFFI C. Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis, *Anal. Chim. Acta* **424**, 289, **2000**.
5. MOOR C., LYMBEROPOULOU T., DIETRICH V. J. Determination of heavy metal in soils, sediments and geological materials by ICP AES and ICP MS, *Mikrochim. Acta* **136**, 123, **2001**.
6. ANDERSON P., DAVIDSON C. M., LITTLEJOHN D., URE A. M., GARDEN L. M., MARSHALL J. Comparison of techniques for the analysis of industrial soils by atomic spectrometry, *Int. J. Environ. Anal. Chem.* **71**, 19, **1998**.
7. BETTINELLI M., BAFFI C., BEONE G. M., SPEZIA S. Soil and sediment analysis by spectroscopic techniques. Part I: Determination of cadmium, cobalt, chromium, copper, manganese, nickel, lead and zinc, *At. Spectrosc.* **21**, 50, **2000**.
8. SHTANGEEVA I., VUORINEN A., RIETZ B., CARLSON L. Combination of ICP-AES and instrumental neutron activation analysis as effective methods for studying distribution of elements in soil and plants, *Geostand. Newsl.* **25**, 299, **2001**.
9. DOS ANJOS M. J., LOPES R. T., DE JESUS E. F. O., ASSIS J. T., CESAREO R., BARRADAS C. A. A. Quantitative analysis of metals in soil using X-ray fluorescence, *Spectrochim. Acta Part B* **55**, 1189, **2000**.
10. OLUWOLE A. F., AJAYI O., OJO J. O., BALOGUN F. A., OBIOH I. B., ADEJUMO J. A., OGUNSOLA O. J., ADEPETU A., OLANIYI H. B., ASUBIOJO O. I. Characterization of pollutants around thin mining and smelting operations using EDXRF, *Nucl. Instr. and Meth. in Phys. Res. A* **353**, 499, **1994**.
11. SOMOGYI A., BRAUN M., POSTA J. Comparison between X-ray fluorescence and inductively coupled plasma atomic emission spectrometry in the analysis of sediment samples, *Spectrochim. Acta Part B* **52**, 2011, **1997**.
12. HORVÁTH T., SZILÁGYI V., HARTYÁNI Z. Characterization of trace element distribution in soils, *Microchem. J.* **67**, 53, **2000**.
13. HARTYÁNI Z., DÁVID E., SZABÓ S., SZILÁGYI V., HORVÁTH T., HARGITAI TÓTH A. Determination of the trace elements distribution of polluted soils in Hungary by X-ray methods, *Microchem. J.* **67**, 195, **2000**.
14. ANDERMAN G., KEMP J. W. Scattered X-ray as internal standards in X-ray emission spectroscopy, *Anal. Chem.* **30**, 1306, **1958**.
15. LUCAS-TOOTH H. J., PRICE B. J. A mathematical method for the investigation of interelement effect in X-ray fluorescent analysis, *Metallurgia* **64**, 149, **1961**.
16. MITCHELL B. J., HOPPER F. N. Digital computer calculation and correction of matrix effects in X-ray spectroscopy, *Appl. Spectrosc.* **20**, 172, **1966**.