

Determination of some heavy and toxic elements in plants and soils with ED-XRF using americium-241 excitation source

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The conditions for the determination of Co, Cr, Fe, Mn, Ni and Pb in plant materials and As, Ba, Fe, Pb, Sr, Rb and Zr in soils by energy dispersive X-ray fluorescence analysis with americium-241 as excitation source are discussed. The applicability of the proposed method is tested by the analysis of certified reference materials and of two plant biomonitors.

Introduction

The determination of the heavy and toxic elements in plants and soils permits the study of their distribution, of the pollution level as well as the risk assessment in the investigated ecosystems. Undoubtedly, the most popular methods for this purpose at present are atomic absorption spectrometry (AAS) [e.g., Refs 1–3], inductively coupled plasma – atomic emission spectrometry (ICP-AES) [e.g., Refs 4–6], and instrumental neutron activation analysis (INAA) [e.g., Refs 7–8]. The closing of many research nuclear reactors, necessary for INAA, and the necessity to dissolve soils and plants for AAS and ICP-AES, however, stimulate the interest towards ED-XRF in ecological investigations. The method is purely instrumental and multielement and is already used for the determination of some heavy and toxic elements in environmental matrices.^{9–15}

Although more elements and better detection limits may be achieved with X-ray tubes as excitation source and by total reflection ED-XRF,¹⁶ serious attention is also paid to the radioisotope excitation sources¹⁷ mainly because the intensity of the irradiation is very stable, depending only on the half-life of the radionuclide on the one hand, and because they are much more cheaper than the tubes, on the other.

One of the excitation sources rarely used in environmental investigations is ²⁴¹Am though it has extremely long half-life ($T_{1/2}=433$ y) and is cheaper than other radioisotope sources. The reason is that ²⁴¹Am is generally suitable for the determination of elements of $31 < Z < 69$, whereas most of the environmentally interesting elements are just below ($Z=24–33$) or above ($Z=82$ for Pb) and the respective concentrations are rather low, especially in plants. Therefore, optimization of the conditions for analysis is necessary.

The aim of the present study was to investigate the possibilities for the determination of some heavy and toxic elements in plants and soils using ²⁴¹Am excitation source in ED-XRF.

Experimental

Materials and sample preparation

In the present paper the following certified reference materials have been used: IAEA-Soil 7, IAEA-SDN-1/2, NIST-SRM-1575 (Pine Needles), NIST-SRM-1573 (Tomato Leaves), NIES-3 (Chlorella), NIES-6 (Tea Leaves).

About 0.25 g from the samples were mixed with 1 g H₃BO₃ (spectroscopy grade) and pressed into a pellet of 25 mm diameter and 2 mm height. The conditions for the preparation of the pellets were experimentally standardized.

Method of analysis

The pellets were measured using Ortec Si/Li detector (175 eV energy resolution at 6.4 keV, thickness of the Be window = 0.0254 mm) coupled to a MCA Canberra 35 Plus. As excitation source ²⁴¹Am (3.7 GBq) with ring geometry is used.

For the estimation of the concentration of elements to be determined in plants and in soils as standards NIST-SRM-1571 Orchard Leaves and IAEA-Soil 5 were used, respectively.

Precision, trueness and accuracy

For the assessment of the quality of the analysis the following criteria are used: detection limit: the true net signal level which may be a priori expected to lead to detection according Currie;¹⁸ precision: the closeness of

agreement between results by applying the same procedure several times under the prescribed condition;¹⁹ accuracy: the term covers precision and trueness in the new ISO definition.²⁰ The accuracy is calculated according to the SR – criterion, developed by MCFARREN et al. from the Analytical Reference Service, Ohio:²¹

$$SR = \frac{|C_x - C_w| + 2\sigma}{C_w} \cdot 100$$

where C_x is the experimental value, C_w is the true value and σ is the standard deviation of C_x .

On the basis of this criterion that methods were divided into three categories: $SR \leq 25\%$ – excellent, $25 < SR \leq 50\%$ – acceptable, $SR > 50\%$ – unacceptable.

Results and discussion

Measurement geometry

Sample preparation for the determination of trace elements by ED-XRF generally involves the mixing of the sample with a binding agent and compressing the mixture in the form of pellets. In choosing a binding agent two conditions must be considered: (1) low absorption coefficient of the binding compound, and (2) good homogeneity. The use of loose powder is not preferred for the precision of the method for the determination of trace elements is not good enough. According RASHETTI and WEGSCHEIDER²² the relative standard deviation when using loose powder is higher than for pellets, especially for those elements which peaks are growing on the slope of the low energy region, where the intensity of the scattered exciting radiation increases.

By choosing an appropriate thickness of the pellets, the detection limits for different elements can be improved.

For the present investigation: Li_2CO_3 , H_3BO_3 , starch, and cellulose binding agents were tested. H_3BO_3 was found the most suitable for the investigated materials. Different concentration ratios between binding agent and sample were tested. Pellets with good mechanical quality were obtained at ratio sample/ H_3BO_3 = 1:5. The dilution of the samples with H_3BO_3 helps to reduce the matrix effects like absorption and enhancement. The precision of the sample preparation was tested by parallel experiments and for plants it was below 5%. For the soil samples the precision of the sample preparation was below 10%.

Spectrometric conditions

The optimal measurement conditions used in this study are presented in Table 1 together with the detection limits achieved. In all measurements the K_{α} lines have been used but for As and Pb. The measurement time for soils is 1000 seconds, for plants 1500 seconds but for Co and Pb. On the basis of the experimental work the following considerations for the separate elements may be done.

Arsenic: The use of $K_{\alpha 1}$ at 10.53 keV for the determination of As is practically not possible since it overlaps with the Pb $L_{\alpha 1}$ at 10.55 keV. The As $K_{\beta 1}$ at 11.72 keV is interfered strongly by Br $K_{\alpha 1}$ at 11.9 keV. Therefore, in plant matrices where the concentration of Br exceeds usually by an order of magnitude the concentration of As, its determination is not possible. In soil samples the use of As, $K_{\beta 1}$ permits the correct determination without problems if the concentration ratio As/Br is more than 1.5 and the concentration of Br does not exceed 15 ppm.

Table 1. Spectrometry conditions and detection limits for determined elements

Element	Analytical line, keV	Measurement time for plants, s	Measurement time for soils, s	L_c , ppm	Interferences (E), keV
As	$K_{\beta 1}$ (11.72)	–	1000	10	Br $K_{\alpha 1}$ (11.9)
Ba	$K_{\alpha 1}$ (32.06)	–	1000	10	–
Co	$K_{\alpha 1}$ (6.92)	1000	–	0.1	Fe $K_{\beta 1}$ (7.05)
Cr	$K_{\alpha 1}$ (5.41)	1500	1000	1	–
Fe	$K_{\alpha 1}$ (6.39)	1500	1000	15	–
Mn	$K_{\alpha 1}$ (5.89)	1500	–	7	Cr $K_{\beta 1}$ (5.94)
Ni	$K_{\alpha 1}$ (7.47)	1500	–	2	Fe $K_{\alpha 1}$ (7.11)
Pb	$L_{\alpha 1}$ (10.55)	2000	1000	6	As $K_{\alpha 1}$ (10.53)
Rb	$K_{\alpha 1}$ (13.37)	–	1000	8	–
Sr	$K_{\alpha 1}$ (14.14)	–	1000	6	–
Zr	$K_{\alpha 1}$ (15.74)	–	1000	28	–

Table 2. Results from the analysis of plant certified materials (in µg/g)

Element	NIST-SRM-1573		NIST-SRM-1575		NIES-6		NIES-3		Overall SR, %
	Our result	Certified	Our result	Certified	Our result	Certified	Our result	Certified	
Co	0.54 ± 0.04	(0.6) ^a	0.12 ± 0.01	0.10	0.10 ± 0.01	0.12	0.52 ± 0.05	0.87	>25
Cr	4.47 ± 0.30	4.50	2.50 ± 0.18	2.6	<1	0.15	<1	–	<25
Fe	696 ± 0.30	690	215 ± 15	200	118 ± 8	116	1646 ± 11	1850	<25
Mn	228 ± 4	238	629 ± 9	675	722 ± 11	700	65 ± 1	69	<25
Ni	3.4 ± 0.1	3.1	3.9 ± 0.2	3.5	6.4 ± 0.2	6.5	2.3 ± 0.1	2.6	<25
Pb	6.2 ± 0.2	6.3	10.5 ± 0.3	10.8	<6	0.8	<6	0.6	<25

^a Information value.

Cobalt: The determination of Co ($K_{\alpha 1}$ at $E=6.92$ keV) is hindered not only by the fact that its peak grows on the slope on the low-energy region but also is highly influenced by the presence of Fe, which $K_{\beta 1}$ line (7.07 keV) interferes with the Co $K_{\alpha 1}$. Therefore, in soils where the concentration of Fe is in the percentage range the determination of Co has been impossible. Analysing plant materials different measurement times have been tested aiming to optimize the ratio background/peak. Best results have been obtained for measurement times 500 or 1000 seconds (all other elements in plants are measured at least 1500 seconds). Above 1000 seconds the ratio increases rapidly and the correct determination of Co is not possible.

In spite of higher concentration of Co in IAEA-Soil 7 and IAEA-SDN-1/2 than in the investigated plant materials, its determination with ^{241}Am is not possible. The reason is that Fe $K_{\beta 1}$ line with $E=7.05$ keV overlaps with Co $K_{\alpha 1}$ line with $E=6.9$ keV.

Chromium and iron: The determination of both elements has been possible both in plants and soils. However, the detection limit for Cr is rather high and obviously not enough for its determination in all types of plants (see Table 2).

Manganese: The detection limit (Table 1) permits its determination in plants in all investigated CRM's. In soils however this has not been possible. The reason is the considerably higher concentration of Cr (in comparison to plants) whose $K_{\beta 1}$ overlaps with the Mn $K_{\alpha 1}$.

Nickel: The determination of Ni in soils has not been achieved due to the interference of the Fe K_{abs} . In plants this effect has not been observed.

Lead: The influence of As $K_{\alpha 1}$ at 10.53 keV in the determination of this elements must be considered. For analysis of plants the influence of the concentration ratio As/Pb was investigated. The correct X-ray fluorescent determination of Pb in plants was possible for concentration of Pb higher than 6 ppm and concentration ratio As/Pb<0.5 ppm. The optimal measurement time was 2000 seconds. It is clear that this

limits the analysis of Pb only to plants from polluted regions but not from normally background stations.

In soils a strict dependence As/Pb has not been observed. Because of the higher concentration of Pb in soils the optimal measurement time was smaller than for plants – 1000 seconds.

Barium, rubidium, strontium, and zirconium: For the determination of Ba, Rb, Sr and Zr their $K_{\alpha 1}$ were used. The detection limits of the method for determination of these elements are not low enough and because of this reason results for the investigated plant materials were not obtained. Correct results for soils have been obtained without any spectrometric problems.

Results

Tables 2 and 3 present the results from the analysis of the investigated plant and soil CRM's. Each value is a mean of three independent determinations and the respective standard deviations are presented, together with SR-criterion for accuracy evaluation.

The results for the determined elements in the plant certified materials are excellent ($SR<25\%$) with exception for Co. The reason is that the concentration of this element in the investigated plants is near the detection limit of the method (0.1 ppm).

The results from ED-XRF analysis for the elements: As, Ba, Fe, Pb, Sr, and Zr in IAEA-Soil 7 and IAEA-SDN-1/2 are excellent. For Rb and Cr the results are acceptable ($SR>25\%$).

The use of more radioisotope sources generally does not lead to determination of more elements (e.g., Ref. 24) although better precision and detection limits are usually achieved.

The applicability of the method for the determination of the elements discussed above is tested by analysis of two plant spices: *Taraxacum Officinale* and *Populus Nigra* which are already accepted biomonitors.^{25,26} The samples were analyzed parallelly by INAA and AAS. It is worth mentioning that the investigated samples were collected in highly polluted areas. The results from ED-XRF determination show good agreement with the results by INAA and AAS.

Table 3. Results from the analysis of IAEA-Soil 7 and IAEA-SDN-1/2 (in µg/g)

Element	IAEA-Soil 7		IAEA-SDN-1/2		Overall SR, %
	Our result	Certified	Our result	Certified	
As	12.2 ± 1.2	13.4	47 ± 5	50	=25
Ba	163 ± 7	159	304 ± 13	289	<25
Cr	53 ± 9	60	–	–	>25
Fe, %	2.63 ± 0.18	2.57	3.17 ± 0.22	3.64	<25
Pb	59 ± 6	60	115 ± 12	120	<25
Rb	48.3 ± 6.7	51	75.7 ± 10.5	74.2	>25
Sr	104.2 ± 7.3	108	286 ± 20	291	<25
Zr	171 ± 10	185	342 ± 40	327	<25

Table 4. Results from the analyses of *Taraxacum Officinale* and *Populus Nigra*

Element	<i>Taraxacum Officinale</i> – A			<i>Taraxacum Officinale</i> – B			<i>Populus Nigra</i> – C			<i>Populus Nigra</i> – D		
	ED-XRF	INAA	AAS	ED-XRF	INAA	AAS	ED-XRF	INAA	AAS	ED-XRF	INAA	AAS
Co	0.30 ± 0.01	0.29 ± 0.02	–	0.20 ± 0.01	0.36 ± 0.03	–	0.92 ± 0.02	0.98 ± 0.05	–	0.12 ± 0.01	0.13 ± 0.01	–
Fe	327 ± 22	381 ± 19	–	218 ± 14	253 ± 13	–	262 ± 18	228 ± 11	–	440 ± 22	467 ± 23	–
Mn	58 ± 1	–	57 ± 5	67 ± 1	–	58 ± 5	153 ± 3	–	135 ± 11	217 ± 5	–	252 ± 20
Ni	1.7 ± 0.6	–	1.7 ± 0.2	4.8 ± 0.2	–	4.9 ± 0.1	0.9 ± 0.1	1.0 ± 0.1	–	2.7 ± 0.2	–	2.6 ± 0.1
Pb	38 ± 1	–	33 ± 2	17.2 ± 0.5	–	18.8 ± 0.9	12.5 ± 0.4	–	11.2 ± 0.5	23.6 ± 0.7	–	18.5 ± 0.9

– Not determined.

A – Industrial pollution (chemical plants).

B – Industrial pollution (chemical plants).

C – Urban pollution.

D – Urban and industrial pollution.

Conclusions

A method for ED-XRF determination of some heavy and toxic elements in plants and soils using ^{241}Am as excitation source has been proposed. The suggested procedure for sample preparation is simple. The optimal measurement conditions permit the determination of elements, which peaks are growing on the low energy region.

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