

Nondestructive multielement analysis of environmental samples by the radionuclide X-ray fluorescence method

I. Determination of heavy metals in plant material

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The radionuclide X-ray fluorescence method has been shown to be an effective technique for multielement analysis of plant tissues. In the present paper the simultaneous determination of heavy metals content in above- and underground parts of plants is described. Employed X-ray measuring system consisted of a radionuclide source ^{238}Pu exciting K X-rays of Mn, Fe, Ni, Cu, Zn as well as L X-rays of Pb, and Si/Li semiconductor detector connected to the multichannel X-ray analyzer. All the measurements were performed in noncoaxial geometrical arrangement of source, sample, and detector.

Показаны возможности применения метода рентгенорадиометрического анализа для исследования и определения содержания тяжелых металлов в над- и подземных частях растений. Источником служил радионуклидный излучатель ^{238}Pu , эффективно возбуждающий линии всех определяемых элементов, т.е. K-линии Mn, Fe, Ni, Cu, Zn как и L-линию Pb. Для детекции был использован полупроводниковый Si/Li детектор. Все измерения были проведены в геометрических условиях с боковым помещением источника, пробы и детектора.

Regional environment pollution is an old problem, but now — caused by human activity — the worldwide increase of trace elements in our environment is of general interest. The analysis of plants for certain elements is interesting for environmental research. In highly polluted areas plants show increased concentration of elements specific for impurities in air and water, and thus can serve as a long-term monitor of environmental pollution. An advantage of these bioindicators is that they are stationary, commonly available in large numbers and give relatively equal reactions.

Employment of plants as indicators of environmental pollution depends on various factors, of which the most important are: the physical and chemical state of pollutant (particles size, solubility of solid impurities, type and form of chemical compounds, their reactivity, etc.), plant species (physiology and morphological structure), part of plant to be analyzed (root, stem, leaf), plant age, vegetation period, climatic and meteorological conditions, distance from source of pollution, various soil properties, etc. [1, 2].

Our investigation we have oriented to the simultaneous determination of heavy metals in plant material. It is evidenced that heavy metal dust can affect the plant by the deposited particulate matter on the surface and by contamination of the soil. Adsorbed trace elements are not uniformly distributed throughout the plant, so that different organs may vary in their ability to concentrate heavy metals. Particularly in roots of some plants the cell wall is important in acting as a heavy metals accumulator. In leaves and stems, however, the cell vacuole system is the main place for heavy metals deposition. When washed plant material is used for analysis, then detected amounts of metals are mostly larger in roots than in aboveground parts of plant; this fact can be explained by long-term effects of pollutants on roots by soil [3].

Experimental

Instrumentation

For simultaneous determination of heavy metals in dried plant material we have developed a nondestructive X-ray fluorescence method (XRF). In order to excite the characteristic and *L*-fluorescent radiations of elements to be determined a low-energy gamma-ray source ^{238}Pu with the activity of 3.7×10^8 Bq, energy of 12–22 keV (U_L X-rays)

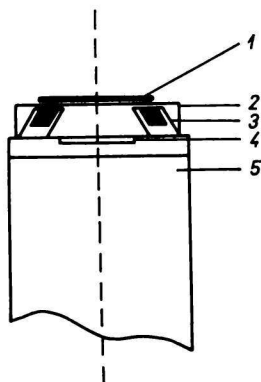


Fig. 1. Scheme of the used geometrical arrangement.
1. Sample; 2. carrier of sample; 3. radionuclide source;
4. detector window; 5. detector.

and half-life of 86.4 years was used. Energy of this radionuclide source permits the effective excitation of *K* X-rays of elements ranging from *K* to *As* (having the absorption edges of 3.607—10.543 keV) as well as *L* X-rays of elements the energies of which occur in the mentioned energy range (especially *Pb*, *Hg*, *Au*, and lanthanoides).

For the detection a *Si*/*Li* semiconductor detector with a beryllium window of 0.25 mm thickness, 12 mm in diameter, and of 300 eV resolution for *Fe K* line was employed; it was connected to the multichannel X-ray analyzer 8100 Canberra. The samples were analyzed for 1000 s using the noncoaxial geometrical arrangement of source, sample, and detector. The scheme of the used X-ray measuring system is shown in Fig. 1.

Preparation of samples and standards

Samples of plant material to be analyzed were prepared in two different ways:

- by pressing the ash left after combustion of plants,
- by pressing the dried and pulverized plants.

More detailed description is done in our previous papers [1, 4]. Using both these methods of sample preparation we have obtained a sample in form of pellet having 30 mm in diameter, 1 mm thickness and mass per unit area of about 99 mg cm⁻².

The great source of error is, however, the combustion of the sample due to nonreproducibility of combustion efficiency and loss of elements by volatilizing; moreover, this way of

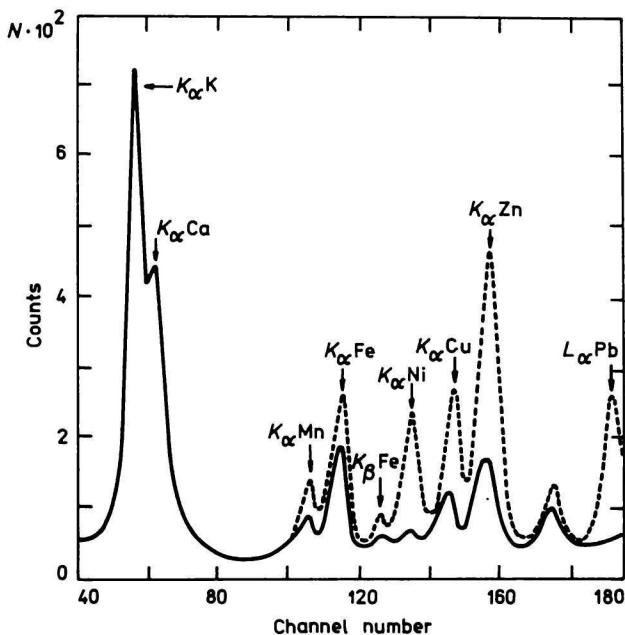


Fig. 2. Spectrum of analyzed sample No. Š-HB/8 (rye) (—), and of multi-element internal standard (---), obtained by a radionuclide source ²³⁸Pu and *Si*/*Li* semiconductor detector.

sample preparation requires a relatively large amount of material to be analyzed. For these reasons it seems that the best method of plant sample preparation from the point of view of X-ray fluorescence analysis is to present it as a pellet made of dry pulverized plant. Ashing is very difficult to control and leads to considerable and not systematic error.

As an example the spectrum of plant sample (rye) excited by radionuclide source ^{238}Pu is shown in Fig. 2.

Detailed data concerning the whole set of analyzed plant material — e.g. plant species, part of plant to be analyzed, collection locality and date, weather conditions — are summarized in Table 1. For purposes of comparison samples No. Š-HB/6—9 were analyzed also by atomic absorption spectrometry with the results given in Table 2.

Besides improper sampling, the weakest procedure in most analytical systems — including XRF method — is standardization. Identification of elements according to the related energy lines present in a measured spectrum using known standards makes no

Table 1

Detailed data concerning the plant material to be analyzed

Sample No.	Plant species	Part to be analyzed	Date and locality of collection	Weekly weather
Š-HB/1	Grass	G – aboveground part	9/7/80 Vysoká	Showers
Š-HB/2	Rape	Ra – aboveground part	9/7/80 Havlíčkův Brod	Showers
Š-HB/6	Red clover	7—17 cm of C – aboveground part R – roots	22/5/80 E-15 Jihlava	Dry weather
Š-HB/7	Wheat	20—25 cm of W – aboveground part R – roots	22/5/80 Sv. Kříž	Dry weather
Š-HB/8	Rye	45 cm of Y – aboveground part R – roots	22/5/80 Lípa	Dry weather
Š-HB/9	Rape	Ra – aboveground part (in flower) R – roots	22/5/80 Habry	Dry weather
Š-HB/12	Potatoes	P – bulb A – aboveground part	29/8/80 Kámen	Cloudy
Š-HB/13	Potatoes	P – bulb A – aboveground part	29/8/80 Šmolovy	Cloudy
Š-HB/14	Turnip	T – bulb A – aboveground part	7/10/80 Havlíčkův Brod	Cloudy
Š-HB/15	Cabbage	C – leaves S – stem	7/10/80 Havlíčkův Brod	Cloudy

Plant samples were collected by The Central Control and Experimental Institute of Agriculture, Havlíčkův Brod.

Table 2

Contents of Mn, Fe, Cu, Zn, and Pb in plant samples
No. Š-HB/6—9 (underground parts of plants) obtained by atomic absorption spectrometry

Sample No.	Content in $\mu\text{g g}^{-1}$				
	Mn	Fe	Cu	Zn	Pb
Š-HB/6	50.4	452.8	24.1	23.8	6.8
Š-HB/7	149.5	201.9	22.3	43.8	2.9
Š-HB/8	19.7	79.1	15.6	11.8	4.1
Š-HB/9	17.3	116.9	9.6	45.8	5.5

problems; their quantitative evaluation, however, is more difficult and lengthy. Much of the difficulty lies in the fact that suitable standards of known composition which are of the same character as the unknown (real sample) are not available. In our department we have used the so-called "internal standard" prepared as follows: the solution of known content of elements to be determined ($38.0 \mu\text{g Ni}$, $39.4 \mu\text{g Fe}$, $29.0 \mu\text{g Mn}$, $31.6 \mu\text{g Cu}$, $35.6 \mu\text{g Zn}$, and $35.9 \mu\text{g Pb}$) was deposited onto a pellet of pressed plants to be analyzed utilizing a "drop-by-drop" technique wherein drops of standard solution were placed in an array on a pellet using a micropipette; after drying at room temperature this pellet was pressed again. The solution was pipetted onto the pressed pellet of analyzed plant material in order to have the standard substrate the same as for real samples.

The analytical signal (count rate at time unit) of the prepared multielement standard we have obtained as the differential count rate between counts of standard sample and of real sample measured in selected energy ranges. The spectrum of a multielement standard (rye formed its matrix) excited by a radionuclide source ^{238}Pu is shown in Fig. 2. On the basis of the above-mentioned spectrum the energy calibration was made, e.g. for each element to be determined the measuring energy line (given in number of appropriate channels) was chosen to be:

Energy line	Channel number
$K_{\alpha}\text{Mn}$	101—107
$K_{\alpha}\text{Fe}$	112—118
$K_{\alpha}\text{Ni}$	131—137
$K_{\alpha}\text{Cu}$	141—147
$K_{\alpha}\text{Zn}$	152—158
$L_{\alpha}\text{Pb}$	188—194

In these energy regions the analytical signal was measured being proportional to the mass fraction of element present in the sample. This proportionality was checked by measuring a standard sample set prepared in concentration ranges ($\mu\text{g g}^{-1}$) of 0—200 for Mn, 0—1000 for Fe, 0—30 for Ni and Cu, 0—200 for Zn, and 0—20 for Pb, respectively. The accuracy of sample preparation technique and measurement was estimated by standard deviation. In

case of sample No. 8 (rye) of which 15 samples (pellets) were prepared the standard deviation was found to be (in %): for Mn 4.00, for Fe 3.54, for Cu 5.3, for Zn 4.53, for Ni 5.96, for Pb 4.18.

Results and discussion

All the plant material reported in Table 1 was analyzed for Mn, Fe, Ni, Cu, Zn, and Pb by X-ray fluorescence method with the use of the above-mentioned multielement internal standard and the results are presented in Table 3.

Table 3

Determination of Mn, Fe, Ni, Cu, Zn, and Pb in plant material by XRF method using internal multielement standard

Sample No.	Distance from road m	Content in $\mu\text{g g}^{-1}$						
		Mn	Fe	Ni	Cu	Zn	Pb	
Š-HB/1	0	134.3	161.0	7.6	23.1	32.7	9.4	
	10	75.7	128.2	9.6	20.3	31.4	8.8	
	50	60.2	76.0	2.6	21.0	24.4	5.3	
	100	101.3	90.2	7.1	21.2	28.4	8.4	
Š-HB/2	0	28.0	89.9	5.7	19.6	24.5	8.3	
	10	16.9	105.8	4.2	15.4	24.3	8.5	
	50	34.8	78.3	5.8	17.5	34.9	8.0	
	100	20.1	78.1	8.9	22.1	27.6	9.7	
Š-HB/6	20	C	83.1	458.0	13.2	30.0	35.6	4.7
		R	181.3	2173.2	—	32.1	34.0	15.0
Š-HB/7	20	W	175.1	183.3	4.7	23.2	43.7	1.4
		R	513.2	5395.1	—	13.8	69.0	39.3
Š-HB/8	15	Y	31.0	102.1	3.7	18.4	14.6	4.5
		R	341.7	5025.5	—	6.0	16.3	17.6
Š-HB/9	50	Ra	39.1	78.5	5.9	18.5	17.4	2.7
		R	81.3	1195.6	—	18.3	91.4	6.6

Table 3 (Continued)

Sample No.	Distance from road m		Content in $\mu\text{g g}^{-1}$						
			Mn	Fe	Ni	Cu	Zn	Pb	
Š-HB/12	0	P	28.5	210.5	10.2	23.6	15.5	4.4	
	10	P	19.0	113.0	8.4	23.5	13.0	3.7	
	50	P	17.9	66.4	8.1	20.1	13.7	1.6	
	100	P	21.1	61.0	7.9	23.1	12.7	5.4	
	0	A	188.9	1463.1	—	34.6	40.6	13.2	
	10	A	132.5	1147.7	—	27.9	24.9	4.8	
	50	A	143.5	1203.3	—	30.6	25.8	8.6	
	100	A	163.8	1940.9	—	20.7	20.5	11.1	
	Š-HB/13	0	P	16.4	66.1	7.1	19.9	17.0	2.2
		10	P	14.5	52.5	10.2	26.2	17.2	3.7
50		P	8.7	83.5	6.6	21.9	11.8	4.8	
100		P	18.2	68.0	5.1	19.7	11.7	2.5	
0		A	322.2	983.0	—	35.9	48.7	16.2	
10		A	245.9	739.3	—	52.0	64.9	9.8	
50		A	167.3	984.6	—	41.3	37.4	8.4	
100		A	293.7	775.5	—	35.2	41.2	2.7	
Š-HB/14		0	T	22.4	93.0	5.0	23.2	18.9	4.8
		10	T	39.8	106.2	6.4	26.1	33.2	5.5
	50	T	31.1	105.3	6.5	24.5	16.8	3.1	
	100	T	9.5	84.7	3.5	21.5	16.3	3.1	
	0	A	50.1	272.0	6.8	19.4	21.5	4.3	
	10	A	71.2	182.7	5.9	17.8	21.7	4.9	
	50	A	24.8	155.4	5.9	20.8	14.6	5.2	
	100	A	41.7	172.9	8.8	22.3	20.4	6.9	
	Š-HB/15	0	C	17.1	55.0	4.7	18.0	12.8	2.8
		10	C	14.0	38.3	7.8	17.9	10.0	4.0
50		C	33.5	39.6	11.7	18.8	11.4	4.0	
100		C	21.1	22.9	3.4	14.9	15.4	1.8	
0		S	39.3	127.3	7.8	17.8	16.8	4.9	
10		S	28.8	107.1	8.8	21.7	16.7	4.9	
50		S	33.2	69.1	14.0	17.2	13.5	3.5	
100		S	51.2	105.6	6.4	18.9	23.5	3.1	

Let us observe the results obtained for samples No. 6—9. All these samples were collected at the same sunny day; for analysis both above- and underground parts of plants were taken. The results show the higher amounts of Mn, Fe, Zn, and Pb in roots of analyzed plants; especially iron content in underground parts of corn, wheat and rye was found to be much times higher than that in aboveground parts of these plants. As concerns Cu, in roots of corn a significant decrease was observed, whereas in clover and rape approximately the same content in both above- and underground parts was found. Due to the large amounts of Fe in roots causing the spectral interferences between K_{β} X-rays of Fe and K_{α} X-rays of Ni, the determination of Ni in roots could not be realized. Nickel contents in the aboveground parts of plants were found to be of the order of $\mu\text{g g}^{-1}$ dry matter.

Samples No. 1, 2, 12—15 were collected from the selected localities at four various distances from the road. As to this set of samples, it is seen from the results obtained that the amounts of Mn, Fe, Zn, and Pb vary according to distance of collection place from the road; Ni content in the whole set of samples varied in the range up to $10 \mu\text{g g}^{-1}$ dry matter and Cu content was $20 \mu\text{g g}^{-1}$ (except for its elevated amount in samples of potatoes aboveground parts).

Of interest are the data obtained from samples No. 12 and 13 (potatoes). In potatoes with the utilized underground parts the contents of the determined elements are in aboveground parts significantly higher than those in proper potato bulb.

Conclusion

The developed multielement radionuclide X-ray analysis proved to be a useful analytical method for the determination of elemental composition of environmental samples. The nondestructive nature of this technique has obvious attractions for environmental monitoring, in view of the need to preserve sample. In case of plants material, it allows the simultaneous trace metals measurements in organic matrix with sufficient accuracy and represents an attractive method in the design of an efficient and cost-effective monitoring system.

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