Air Pollution Monitoring Using the Radionuclide X-Ray Fluorescence Analysis

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The radionuclide X-ray fluorescence method has been shown to be an effective technique for multielement analysis of air samples. In the present paper the simultaneous determination of Fe, Zn, Pb, and Br in air samples originating from three cities (Prague, Bratislava,Trenčín) is described. Used analytical system consisted of a radionuclide source ^{238}Pu and a Si-Li semiconductor detector connected to the multichannel analyzer.

The high concentration of impurities in the atmosphere is a very serious contemporary probiem and the future of human population depends on solving it. The first step towards solving this problem is to make a detailed analysis and evaluation of impurities in the air, to determine their degree of harmfulness and the mechanism of their action on the human body.

For analysis of environmental samples, especially for monitoring the elemental composition of particulate matter in air, many methods have been proposed. Recent developments in this field have been oriented to the automated procedures utilizing instrumental analytical techniques which can give rapid and accurate information about a wide scale of elements. One of the suitable methods is the radionuclide X-ray fluorescence (RXRF) analysis [1].

Present paper describes the multielement radionuclide X-ray fluorescence analysis of urban atmosphere, which is illustrated on the samples collected from three cities – Prague, Bratislava, Trenčín.

EXPERIMENTAL

Samples were obtained by passing a defined volume of air through a nitrocellulose membrane filter Synpor 4 (produced by East-Bohemian Chemical Works Pardubice, ash content 0.03—0.05 %, max. elements content: 0.01 % Ca, 0.01 % Al, 0.01 % Cu, 0.001 % Si, Hg and trace amounts of Na, K, and Fe). Samples were collected considering the current Czech and Slovak Recommendations, *i.e.* a pump was located at 2 m distance from the road at the height of 1.50 m (the head of a walking man), the volume of collected air ranged from 1 to 10 m^3, the sample density did not exceed 0.3 mg m^{-3} (air particulates collected on a filter formed a thin-layer sample).

Characteristic radiations of elements to be determined were excited by a radionuclide source ^{238}Pu (activity of 740 MBq) the UL_x energy lines (13.613—20.163 keV) of which occur above the absorption threshold of these elements (for Fe 7.111 keV, for Zn 9.660 keV, for Pb 13.044 keV, for Br 13.475 keV) and they efficiently excite their characteristic as well as *L*-fluorescent radiations. The relatively long half-life of ^{238}Pu (86.4 y) allows the measurements to be made without activity correction.

The analytical signal was registered using a Si-Li semiconductor detector (produced by the Institute of Nuclear Research, Řež near Prague, the Czech Republic) connected to a multichannel analyzer 8100 Canberra (USA).

Standardization and Energy Calibration

For energy calibration and also for final quantitative evaluation of samples, it is necessary to use standards. A series of standard solutions of elements to be determined were prepared and calibration curves for each element were constructed. Then, a multielement standard was made by applying standard solutions directly onto the filter Synpor 4 in order to have the same matrix composition as real sample. The spectrum of this standard (containing 5.12×10^{-6} g Fe, 2.91×10^{-6} g Zn, 5.96×10^{-6} g Pb, and 6.24×10^{-6} g Br) is shown in Fig. 1 (measuring time 1000 s). As it is seen, the energy lines of all determined elements are effectively excited and also well separated from each other as well as from the scattered radiation of primary radionuclide source. The resolving power of the Si-Li detector used was 180 eV for ^{55}Fe. The accuracy of measurement and the reproducibility of standard and sample preparation was estimated by the standard deviations, the values of which were < 5 % (Fe 4.68 %, Zn 2.19 %, Pb 2.04 %, Br 2.78 %).

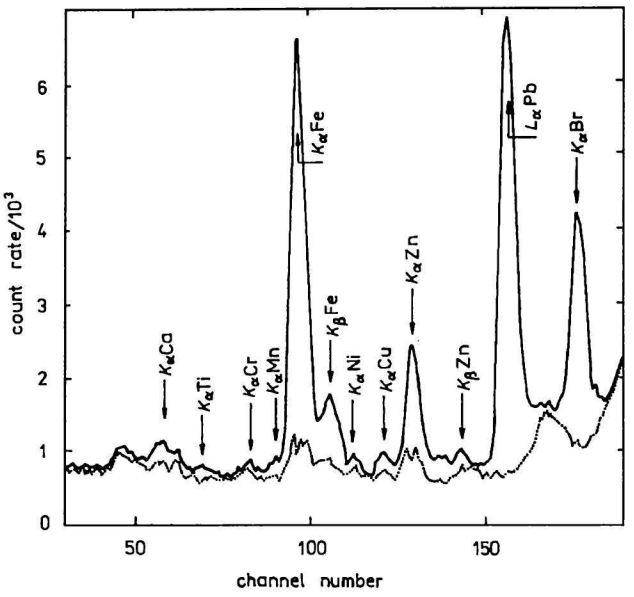

Fig. 1. Spectrum of the air sample (———) and of the sample carrier — Synpor 4 (·····) excited by a radionuclide source ^{238}Pu.

Measurement of Analytical Signal

The choice geometric conditions of measurements, *i.e.* a mutual arrangement of the radionuclide source, sample, and detector, depended on the diameter of the used disc source (14 mm), and also on the size of the Si-Li detector used. The samples were analyzed using the reflection noncoaxial geometry, the optimum angle between detector and source was found experimentally to be 60°, and the distance of sample from detector was 12 nm. To keep constant conditions of measurements the sample was placed on a Mylar foil with marked ring for sample. This foil was fixed in a plexiglass holder above the detector window.

The multielement RXRF analysis of air samples for Fe, Zn, Pb, and Br requires: to measure the spectrum of sample to be analyzed excited by the radionuclide source ^{238}Pu; to differentiate the analytically important energy lines from the remaining ones; to determine the area of peaks (corresponding to the analytical lines of elements to be determined); to obtain the integral sum of the peak area; to obtain the integral sum of the background value (nonanalytical signal below the peak); to calculate the content of determined elements using the formula (*1*). (In the given formula, the Compton scattered radiation correction is included [2, 3].)

$$m_F = \frac{I_F - I_{F(\text{real})}}{I_s - I_{s(\text{real})}} \cdot \frac{I_{c(s)}}{I_{c(F)}} m_s \qquad (1)$$

where I_F is the count rate of characteristic (*L*-fluorescent) radiation of element to be determined, $I_{F(\text{real})}$ the background count rate for real sample, I_s the count rate of characteristic (*L*-fluorescent) radiation of standard, $I_{s(\text{real})}$ the background count rate for standard, $I_{c(s)}$ the count rate of simple Compton scattered radiation for standard, $I_{c(F)}$ the count rate of simple Compton scattered radiation for sample, and m_F, m_S is the mass of elements determined in sample and in standard, respectively.

RESULTS AND DISCUSSION

This developed method was used for analysis of a large series of air samples, which have been collected for a long time at various localities in Prague, as well as for evaluation of atmospheric pollution of Bratislava and Trenčín. For comparison, some air samples were analyzed also by other methods (AAS, NAA) and the obtained results showed a good agreement [4].

As illustration, some examples of results are given in Table 1, whereas Table 2 contains the estimation of analyzed samples sets.

The determined content of elements allows to conclude that the results of analysis are highly influenced by the conditions and the localities of sam-

Table 1. Results of RXRF Analysis of Air Samples Collected in Prague, Bratislava, Trenčín. Determination of Fe, Zn, Pb, and Br

Locality	$\rho_l/(10^{-6}$ g m$^{-3})$				Locality	$\rho_l/(10^{-6}$ g m$^{-3})$				Locality	$\rho_l/(10^{-6}$ g m$^{-3})$			
	Fe	Zn	Pb	Br		Fe	Zn	Pb	Br		Fe	Zn	Pb	Br
Prague	1.29	0.24	0.83	0.35	Bratislava	4.21	0.75	3.35	2.04	Trenčín	6.65	0.25	2.18	0.59
	2.44	0.27	1.69	0.81		7.49	1.14	3.71	1.45		6.75	0.89	1.86	0.27
	2.09	0.50	3.46	1.44		9.33	1.04	4.58	1.24		5.27	0.53	2.17	0.47
	0.56	0.44	1.07	0.61		9.32	0.67	1.51	1.76		1.91	0.16	0.94	0.23
	2.65	0.34	2.18	0.56		12.96	1.29	3.46	0.75		1.72	5.29	3.69	0.07
	2.63	0.30	1.87	0.69		5.74	1.07	5.03	1.73		6.67	0.43	1.58	0.39
	2.68	0.59	1.83	0.77		6.82	1.13	3.85	0.98		0.76	0.13	0.17	0.02
	4.71	1.71	5.92	1.25		5.50	1.27	6.03	2.14		2.96	1.45	6.00	2.56
	3.36	1.39	9.95	2.16		4.52	1.22	5.99	2.90		0.70	0.33	1.60	0.52
	4.65	0.78	4.27	1.33		27.98	6.24	16.08	2.60		2.30	1.46	6.37	2.08

ple collecting. High amounts of all the chosen elements (Fe, Zn, Pb, Br) in air samples from Bratislava confirmed the known considerable atmospheric pollution of this town.

Results of our analyses showed the great differences also inside each set of samples. This fact confirms that besides the collection locality, the elements content in air samples is influenced by numerous other factors of which the most important are: traffic volume, weather (bright sky, cloudy, rain, wind), time interval of sample collecting (day of the week, day or night), *etc.* We have investigated these factors in detail using a set of air samples from Prague. The examples of results are given in Table 3.

When comparing the determined content of Pb and Br with the traffic density, the highest values of these elements (samples 4P, 7P, 9P) are in a good correlation to the observed heavy traffic in the time of sample collecting (*i.e.* increased traffic on Friday — departure to week-end as well as on Sunday evening and Monday morning — arrival from week-end resulted in the increased Pb content in air samples).

When evaluating the day-time and night-time samples, the obtained results demonstrated a direct dependence of Pb content on the traffic density, too: sample 1P — day, sample 2P — night. Analogous correlations were found in all series of analyzed samples.

Table 2. Evaluation of the Whole Sets of Analyzed Samples

Locality	Element	$\rho_i/(10^{-6}$ g m$^{-3})$			
		minimum	maximum	arithmetic mean	median
Prague	Fe	0.56	4.71	2.71	2.64
Bratislava*		4.21	12.96	7.32	6.82
Trenčín		0.70	6.75	3.57	2.63
Prague	Zn	0.24	1.71	0.66	0.47
Bratislava*		0.75	1.29	1.06	1.13
Trenčín		0.13	5.25	1.09	0.48
Prague	Pb	0.83	9.95	3.31	2.03
Bratislava*		1.51	6.03	4.19	3.85
Trenčín		0.17	6.37	2.66	2.02
Prague	Br	0.35	2.16	0.99	0.79
Bratislava*		0.75	2.90	1.66	1.73
Trenčín		0.02	2.56	0.72	0.43

*The last sample from Bratislava with extremely high values of Fe, Zn, Pb, Br has been omitted.

Table 3. Evaluation of Some Factors which Affected the Results of Analysis of Air Samples from Prague

Sample	Weather	Collection data	Traffic volume (veh/hour)	$\rho_i/(10^{-6}$ g m$^{-3})$ Fe	Zn	Pb	Br
1P	cloudy	Tuesday (D)	825	0.85	0.25	1.22	0.31
2P	cloudy	Tuesday (N)	202	0.59	0.14	0.42	0.001
3P	half-covered sky	Sunday (D)	543	2.16	0.42	1.79	0.55
4P	half-covered sky	Sunday (N)	1465	5.17	0.43	3.01	1.02
5P	cloudy	Saturday (D)	748	4.39	0.59	1.15	0.15
6P	cloudy	Saturday (N)	214	2.54	0.29	0.57	0.01
7P	cloudy	Monday (D)	1514	21.92	0.79	4.27	3.90
8P	cloudy	Monday (N)	387	2.54	0.43	1.60	1.33
9P	half-covered sky	Friday (D)	1444	5.68	0.56	3.13	1.09
10P	half-covered sky	Friday (N)	462	0.96	0.28	1.02	0.37

(D) = samples collected from 7 a.m. to 7 p.m.
(N) = samples collected from 7 p.m. to 7 a.m.

REFERENCES

1. Tölgyessy, J., Havránek, E., and Dejmková, E., *Radionuclide X-Ray Fluorescence Analysis with Environmental Applications*. Elsevier Publishers, Amsterdam, 1990.
2. Havránek, E. and Bumbálová, A., *Chem. Zvesti 35*, 57 (1981).
3. Havránek, E., Dejmková, E., and Bumbálová, A., *Acta Fac. Pharm., Univ. Comenianae 39*, 39 (1983).
4. Krečmer, F., *Dissertation*. Institute of Agriculture, Prague, 1983.

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