

Multielement analysis of air samples

Determination of iron, zinc, lead, and bromine content by the radionuclide X-ray fluorescence analysis

E. HAVRÁNEK and A. BUMBÁLOVÁ

*Department of Analytical Chemistry, Faculty of Pharmacy,
Komenský University, 880 34 Bratislava*

Received 11 July 1980

In this work, the radionuclide X-ray fluorescence analysis for nondestructive determination of Fe, Zn, Pb, and Br content in air samples collected on nitrocellulose membrane filter Synpor 4 is described. A radionuclide source ^{238}Pu for the excitation and a semiconductor Si/Li detector for the detection of characteristic and *L*-fluorescent radiation of the above elements were used. A correction method based upon the measurements of simple or multiple Compton scattering for compensation of varying mass per unit area values in sample deposits was theoretically proposed as well as experimentally checked. The results obtained both with and without the use of this correction method were compared and a good agreement with those given by atomic absorption spectrometry was observed.

В статье описано определение Fe, Zn, Pb и Br в воздухе методом рентгенорадиометрического анализа. Источником излучения служил излучатель ^{238}Pu и для детекции был использован полупроводниковый Si/Li детектор. В качестве материала для фильтровки воздуха был применен мембранный фильтр Synpor 4. На основе комптоновского рассеяния разработан метод для коррекции влияния т. наз. матричного эффекта. Полученные результаты хорошо коррелируют с результатами, достигнутыми с помощью абсорбционного спектрофотометрического анализа.

About half of all air pollutants are particulates or aerosols. In order to investigate the origin, the behaviour, and the ecological and health effects of particulates, analysis of large numbers of samples is necessary for as many elements per sample as possible. A suitable analytical technique must be sensitive, rapid, multielement, and adequately accurate. In addition, the ability to measure more elements than just listed pollutants without specially raising analysis costs greatly increases the usefulness of multielement signatures in identifying specific pollution sources, and reduces the changes of missing unsuspected pollutants.

The work reported herein has shown that X-ray fluorescence analysis (XRF) is a suitable method for simultaneous determination of air pollution particulates. It is

sensitive enough to perform quantitative trace element analysis on milligram amounts of material, it requires little or no sample preparation, and is fast enough to analyze several samples per hour.

For this purpose it is very important to have a detector with high degree of resolution allowing to display a well-resolved spectrum corresponding to the characteristic X-rays of a number of elements in a single sample. The advent of solid state detectors with an energy resolution better than 400 eV promises to extend the use of X-ray fluorescence technique to a fast, simultaneous multielement analysis with low detection limits. This makes environmental monitoring and research possible on a large scale.

In the present work, the radionuclide X-ray fluorescence analysis is used for the determination of Fe, Zn, Pb, and Br content in air samples. Some of the naturally occurring concentrations of these elements are given in Table 1 [1].

Table 1

Amount of iron, zinc, and lead normally found in the environment

Environmental component	Fe	Zn	Pb
Mineral soils	0.5—10%	20—300 $\mu\text{g g}^{-1}$	2—20 $\mu\text{g g}^{-1}$
Organic soils	0.2—0.5%	10— 50 $\mu\text{g g}^{-1}$	
Soil extractions	500—1000 $\mu\text{g g}^{-1}$	1— 40 $\mu\text{g g}^{-1}$	
Plant materials	40— 500 $\mu\text{g g}^{-1}$	15—100 $\mu\text{g g}^{-1}$	0.05—3 $\mu\text{g g}^{-1}$
Animal issue	100— 400 $\mu\text{g g}^{-1}$	100—300 $\mu\text{g g}^{-1}$	0.1 —3 $\mu\text{g g}^{-1}$
Rainwater	5— 150 $\mu\text{g l}^{-1}$	1— 15 $\mu\text{g l}^{-1}$	
Fresh water	50—1000 $\mu\text{g l}^{-1}$	5— 50 $\mu\text{g l}^{-1}$	2—20 $\mu\text{g l}^{-1}$

The observed increase in concentration of the above given elements in atmosphere relates to their emissions associated with the manufacturing or processing of materials and goods. However, studies of trace elements emitted from mobile sources (primarily directed toward automobiles) have shown that these elements are also derived from automobiles using leaded gasoline. It is now well established [2] that automotive exhaust particulates contain the concentration ranges of these elements as follows: 0.4% Fe, 0.14% Zn, 40% Pb, 7.9% Br.

Experimental

The measurement of the characteristic and *L*-fluorescent radiation intensity of Fe, Zn, Pb, Br has been carried out in a measuring system composed of a 30 mm² Si/Li semiconductor detector with a beryllium window of 0.12 mm thickness, connected to the multichannel

X-ray analyzer 1024 Canberra. In order to excite X-rays of elements to be determined a radionuclide source ^{238}Pu (activity of 3.7×10^8 Bq, energy of 12–22 keV, and half-life of 86.4 years) was employed. Taking into account the size of radionuclide source used all the measurements were performed in noncoaxial geometrical arrangement of source, sample, and detector.

Air samples collected under defined constant conditions [3] as well as prepared standards were deposited onto a 35 mm in diameter membrane filter Synpor 4 having an average pore size of $0.55 \mu\text{m}$ and an average mass of 3 mg, respectively. The main reasons for choosing Synpor 4 as a carrier are its thinness and low mass, low hygroscopicity, sufficient strength, and also the fact that the aerosol penetrates a considerable distance (max. down to $20 \mu\text{m}$) into this filter during sample collecting.

Synpor 4 is a cellulose based filter with ash content ranging from 0.03 to 0.05% (ash consists of max. 0.01% Ca, 0.01% Al, 0.01% Cu, 0.001% Si, Mg, and of Na, K, Fe traces). The amount of other impurities present in this filter was determined by activation analysis made at the Institute of Nuclear Research at Řež near Prague; the values obtained were $50 \mu\text{g}$ Cl, $3.5 \mu\text{g}$ K, $1.4 \mu\text{g}$ Al, $1.2 \mu\text{g}$ Na, $0.9 \mu\text{g}$ Zn, $0.005 \mu\text{g}$ Mn, $0.025 \mu\text{g}$ Br, $0.01 \mu\text{g}$ As, $0.008 \mu\text{g}$ Mg, $0.005 \mu\text{g}$ Fe, $0.003 \mu\text{g}$ Ca, and $0.001 \mu\text{g}$ La. The spectrum of a membrane filter Synpor 4 excited by a radionuclide source ^{238}Pu is shown in Fig. 1.

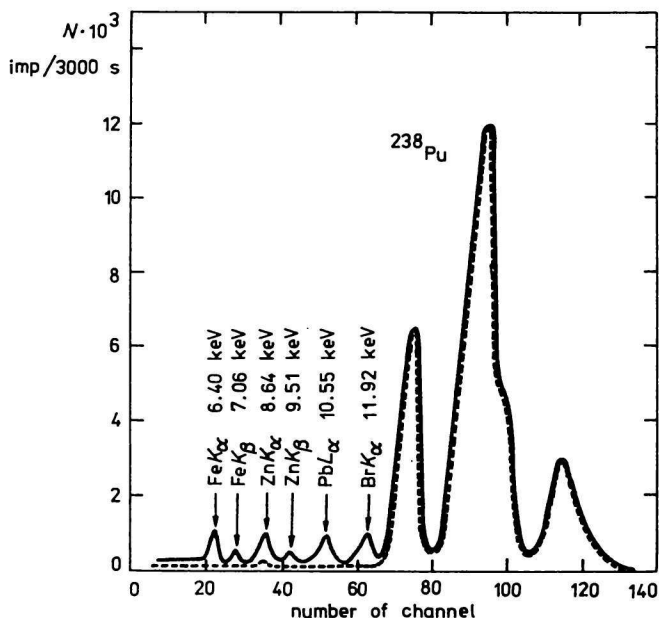


Fig. 1. Spectrum of a membrane filter Synpor 4 (---) and of a multielement standard sample (—) excited by a radionuclide source ^{238}Pu .

Prior to analysis, the calibration curves for the concentration ranges of 10^{-6} g/50 μ l of each element to be determined were constructed and their linearity was confirmed. Then the multielement standard sample 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 was prepared. For this purpose a calibrated 50 μ l pipette was used to dispense this standard solution onto a membrane filter. The area of standard sample was approximately equal to that of sample analyzed, i.e. 7.065 cm². The precision of standard sample analysis was estimated by standard deviation which for the count rate of characteristic PbL _{α} line was found to be 8659 ± 90 . The spectrum of a standard sample using a radionuclide source ²³⁹Pu and an Si/Li detector is in Fig. 1.

When applying the XRF method, the detected count rate of characteristic X-rays is proportional to the weight fraction of element in sample. The spectrum produced by a semiconductor Si/Li detector (Fig. 1) shows the positions of K lines of iron, zinc, and bromine and L line of lead excited in air samples. For multielement analysis fluorescence yield will be defined for each element once the energy region is selected thereby determining the lines to be used for measurements. On the basis of the above-mentioned spectrum for each element the measuring energy line (given in numbers of appropriate channels) was chosen to be: for FeK _{α} 16–26, for ZnK _{α} 33–43, for PbL _{α} 48–58, and for BrK _{α} 60–66. In this spectrum, there are also further lines originating from both simple and multiple Compton scattering of primary radiation of radionuclide source. Moreover, atmosphere samples contain not only elements of interest (in our case Fe, Zn, Pb, and Br) but many other elements at various concentration levels, which results in varying values of mass per unit area of sample deposits. Table 2 illustrates the amount of elements occurring in a representative air pollution sample (determined by activation analysis) [4].

Table 2

Concentration ranges of elements occurring in a representative air pollution sample (determined by activation analysis)

Element	Concentration ranges $\mu\text{g m}^{-3}$
Fe, K	100–10 000
Na, Zn, Br, Ni	100–1 000
Cr, As, Hg	10–100
Rb, Se, Sb, Co, Ce, La, Sc, Cs	1–10
Sm, Th	0.1–1
Eu, Au	0.01–0.1

Results and discussion

The spectrum accumulated in a multichannel analyzer must be evaluated and information contained in it converted into contents of chemical elements. Processing the spectra we have taken into account the fact that in case of constant values

of deposit mass per unit area the dependence between the concentration of determined element and the count rate value of its characteristic X-rays is linear. The count rate for characteristic X-rays is then given by different count rate being measured for real samples and blank carrier (Synpor 4). The count rate measured for characteristic X-rays of element to be determined was compared with that of standard sample containing the known amount of element of interest

$$W_{sp} = \frac{N_F - N_{F'}}{N_S - N_{F'}} W_S \quad (1)$$

where W_{sp} — amount of element to be determined in sample [μg], N_F — count rate value of characteristic X-rays of element to be determined [s^{-1}], $N_{F'}$ — background due to a carrier; count rate measured in the energy region selected for the element to be determined [s^{-1}], N_S — value of standard sample count rate [s^{-1}], W_S — amount of element to be determined in standard sample [μg].

The real samples measured by us had varying values of deposit mass per unit area as well as varying interfering matrix elements (e.g. elements not to be determined), which caused that the obtained information about content of determined element in the sample is not accurately true. Of the various techniques for the correction of matrix effects the method using the simple or multiple Compton scattered radiation was chosen. It should be noted that the Compton scattered radiation is independent of Z but varies as the number of electrons per atomic mass of sample traverses. The X-ray peaks of determined elements are overlapped with the Compton scatter peak due to the multiple scattering of primary radiation; its intensity is proportional to the amount of analyzed material. Thus, the result of the measurement with the use of multiple Compton scattering has been obtained by comparison with that of standard sample measurement

$$W_{sp} = \frac{N_F - N'_{F_{\text{real}}}}{N_S - N'_{S_{\text{real}}}} W_S \quad (2)$$

where $N'_{F_{\text{real}}} = \frac{a+b}{2}n$ — background count rate of real sample [s^{-1}], $N'_{S_{\text{real}}}$ — background count rate of standard sample [s^{-1}], n — number of channels selected for measurements, a — count rate value measured in the first of the selected channels, b — count rate value measured in the last of the selected channels.

Therefore, eqn (2) includes a correction for multiple Compton scattered radiation. The obtained contents of determined elements are lower (in comparison with contents calculated from eqn (1)) being in a good agreement with the values given by atomic absorption spectrometry. This fact confirms the assumption that matrix elements (not to be determined), especially those with low Z , influence the increase of Compton scatter intensity and thereby increase the magnitude of background regions of elements to be determined. Simple Compton scatter peak

observed on the high-energy side of the spectrum, occurs with high probability; this is resulting in the value of measured count rate and thus, the more accurate information about the mass changes of the total sample can be obtained. That is

Table 3

Determination of iron, zinc, lead, and bromine in air samples
Comparison of results obtained by XRF and atomic absorption spectrometry

Sample	Element to be determined	Results of measurements [$\mu\text{g m}^{-3}$]			
		XRF			AA
		Synpor 4	Correction using Compton scattered radiation		
			multiple	simple	
2B	Fe	5.26	3.20	3.12	3.15
	Zn	0.74	0.51	0.43	0.40
	Pb	1.72	1.48	1.43	1.35
	Br	0.84	0.57	0.55	—
4B	Fe	8.01	5.18	5.01	5.07
	Zn	0.63	0.38	0.32	0.33
	Pb	1.93	1.69	1.60	1.63
	Br	0.93	0.73	0.70	—
6B	Fe	5.22	3.07	2.82	3.11
	Zn	0.65	0.27	0.23	0.24
	Pb	1.16	0.83	0.78	0.80
	Br	0.42	0.30	0.27	—
8B	Fe	2.57	1.39	1.13	1.32
	Zn	0.53	0.23	0.20	0.21
	Pb	1.00	0.33	0.29	0.30
	Br	0.32	0.15	0.15	—
10B	Fe	2.18	1.03	0.91	1.00
	Zn	0.96	0.36	0.31	0.33
	Pb	0.52	0.10	0.09	0.12
	Br	0.23	0.08	0.05	—
11B	Fe	2.51	1.35	1.22	1.24
	Zn	0.47	0.30	0.27	0.30
	Pb	0.63	0.21	0.18	0.20
	Br	0.37	0.10	0.10	—

why the relationship (2) for the samples differing in values of mass per unit area by more than 20% must be modified to

$$W_{\text{Sp}} = \frac{N_{\text{F}} - N'_{\text{F,real}}}{N_{\text{S}} - N'_{\text{S,real}}} \frac{N_{\text{Cs}}}{N_{\text{C}}} W_{\text{S}} \quad (3)$$

where N_{C} — count rate of Compton scattered radiation for real sample [s^{-1}], N_{Cs} — count rate of Compton scattered radiation for standard sample [s^{-1}].

The results presented in Table 3 show quite a good agreement between the results obtained by different methods of matrix correction (using the simple or multiple Compton scattered radiation); furthermore, it should be noted that the values obtained by using correction methods are lower in comparison with those calculated from Synpor 4, and these lower values compare favourably with the results given by atomic absorption measurements. The latter were performed at the Research Institute of Hygiene in Bratislava following mineralization of samples in 5 ml of 0.2 M hydrochloric acid during 10 h.

The developed method of X-ray fluorescence determination of Fe, Zn, Pb, and Br content in air samples using Compton scattering for matrix compensation allows to obtain a required analytical information from only one measurement; moreover, the nondestructive nature of the technique has obvious attractions for environmental monitoring, in view of the need to preserve sample.

References

1. *Chemical Analysis of Ecological Material*. (Allen, S. E., Editor.) Blackwell Sci. Publ., Oxford, 1974.
2. Natush, D. F. S., Bauer, C. F., and Loh, A., in *Air Pollution Control, Part III*. (Strauss, W., Editor.) P. 221. J. Wiley, New York, 1978.
3. Havránek, E., Bumbálová, A., and Dejmková, E., *Chem. Zvesti* 34, 373 (1980).
4. Harangozó, M., private communication.

Translated by E. Dejmková