

# Nondestructive determination of airborne lead particulates by the radionuclide X-ray fluorescence analysis

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In this work, airborne lead particulates collected on membrane filter were determined by the nondestructive X-ray fluorescence method. A gamma/X radionuclide source  $^{241}\text{Am}/\text{Ag}$  for the excitation, and a scintillation detector with a NaI/Tl crystal for the detection of *L* X-rays of Pb were used. We can say, with the reference to the obtained results, that the sensitivity and accuracy of the measurement are more than adequate for monitoring of Pb level in air.

В статье описано определение свинца в воздухе методом рентгенорадиометрического анализа. Источником излучения служил низкоэнергетический излучатель типа  $\gamma/\text{X}$   $^{241}\text{Am}/\text{Ag}$  кольцевой формы и для детекции был использован сцинтилляционный счетчик с кристаллом NaI/Tl. Содержание свинца в воздухе было определено по  $\text{PbL}_{\alpha_1}$ -линии. В качестве материала для фильтровки воздуха был применен мембранный фильтр Супрог-4. Наши эксперименты показали, что рентгенорадиометрический анализ является удобным методом для непрерывного контроля загрязнения воздуха свинцом.

Methods for applying the various X-ray techniques to air particulate samples have been under development over the past several years at a number of laboratories. The first papers have been published about the year 1970 [1—5]. Investigations have shown that the thin-film X-ray fluorescence, using an energy dispersive system, is ideally applicable to the elemental analysis of environmental samples. This method is rapid, nondestructive, entails no pre-analysis treatment of the sample, and it requires only small amounts of sample. Its principal requisite is that the sample be thin (of the order of 10  $\mu\text{m}$ ) relative to the depth of penetration of the characteristic X-rays of the elements of interest, causing the intensity of the measured X-rays to be solely a function of the mass of each element present in the sample. In the usual X-ray fluorescence analysis (XRF) of pelletized samples,

which are "infinitely" thick, the measured X-ray intensity is a function both of the concentration of a given element and of matrix effects related to the bulk composition of the sample itself.

We have investigated the multielement analysis of thin specimens by X-ray fluorescence method [6, 7]; the obtained experience we have applied to the determination of airborne lead collected on membrane filters. According to the WHO (World Health Organization) Air Quality Standards the concentration of lead in air should be no more than  $2 \mu\text{g m}^{-3}$ . In 1967, the Czechoslovak Standard [8] limited the content of atmospheric lead to a maximum of  $0.7 \mu\text{g m}^{-3}$  per 24 h. The short-term concentration of lead in air has not been limited up till now.

Excepting industry the principal source of lead in the atmosphere is the combustion of gasoline containing lead antiknock additives and coal. Because of increasing traffic density, mainly in the industrial countries with widely developed individual motorism and heavy traffic, it is urgently necessary to control the environmental lead level and to study its danger to man's health.

In CSSR several research projects into the air pollution problems are underway. In both our capitals — Prague and Bratislava — an intensive research concerned with the health effects of lead in the ambient air has been made, too. For this purpose we have developed the X-ray fluorescence method for monitoring the concentration level of particulate lead in air deposited on nitrocellulose membrane filters — Synpor 4. Samples of airborne dust were collected at several stations selected in Prague and Bratislava cities by drawing with a pump through a membrane filter in a determined time. The pump was located about 150 cm above street level. In our work an attempt was made to develop a rapid and sufficiently accurate method for the determination of airborne lead using a simple equipment system suitable for field measurements, *e.g.* allowing its mounting directly into the portable field laboratory set. Taking all these aspects into account, we have employed XRF system consisting of a single channel analyzer, a scintillation detector with NaI/Tl crystal, and an annular radionuclide source.

In our previous work [9] a literature survey on the application of nuclear and isotope technique for the determination of airborne lead particulates is given. As evident from this survey, the use of high resolution semiconductor Ge/Li or Si/Li detector is preferred [10—14] (only new references), while the proportional counters [2, 4] and scintillation detectors [15] are used less frequently.

Urban atmosphere samples contain many elements at various concentration levels and consist of particles having a relatively broad size distribution. Therefore, the quantitative measurement of airborne lead particulates by X-ray fluorescence can be complicated by the presence of other surrounding atoms on the filter paper, *e.g.* by interelement interferences, absorption and enhancement effects. As a result the negative influence on the analytical information about the lead content in sample is observed.

## Experimental

The determination of airborne lead was carried out by measuring the  $L$  X-rays of Pb ( $L_{\alpha 1} = 10.549$  keV,  $L_{\beta 1} = 12.611$  keV,  $L_{\gamma 1} = 14.762$  keV) induced by an annular  $^{241}\text{Am}/\text{Ag}$  source-target with the energy of 22.2 keV. The detector employed was a  $25 \times 2$  mm NaI/Tl scintillation crystal with beryllium window; pulses were linearly amplified and then fed into a single channel analyzer. Only in order to establish possible interferences in the measured energy range the semiconductor Si/Li detector linked to a multichannel X-ray analyzer 8 100 Canberra was used; its resolving power was  $\sim 300$  eV for an energy about 13 keV.

An X-ray spectrum of real air sample obtained by a Si/Li semiconductor detector and a radionuclide  $^{241}\text{Am}/\text{Ag}$  source is shown in Fig. 1. Each of energy lines present in the spectrum was identified by using standards. Energy values calculated from the spectrum were in good agreement with the tabulated data.

As evident from the spectrum, in the energy range investigated the spectral interferences between  $K$  X-rays of bromine and  $L$  X-rays of lead occur (bromine is always associated with lead from automobile exhaust because the former is added into gasoline in form of ethylene bromide). Using a scintillation detector which has insufficient energy resolution to separate the above-mentioned neighbouring X-rays, the bromine fluorescence overlaps a portion of the lead fluorescence and thus, the information about lead content in the sample is not accurately true.

One possible way to compensate for this negative bromine effect is to use a Ge filter. Germanium, having the absorption edge at 11.103 keV, is capable to absorb all the

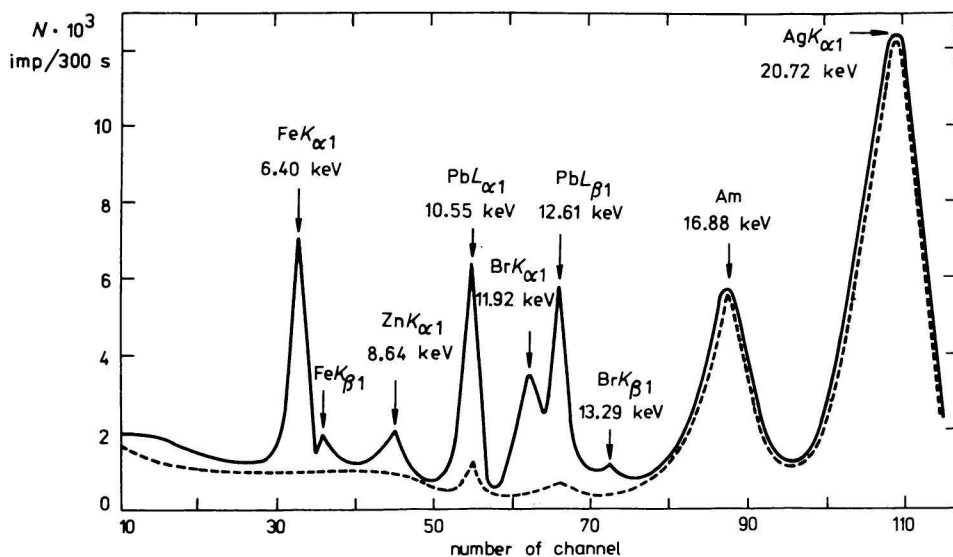


Fig. 1. Spectrum obtained by a radionuclide  $^{241}\text{Am}/\text{Ag}$  from a real air sample (—); from a membrane filter — Synpor 4 (---).

fluorescence due to bromine ( $\text{BrK}_{\alpha 1}$  line = 11.923 keV) and moreover, all the energy lines occurring in the spectrum both fore and beyond the range of  $\text{PbL}_{\alpha 1}$  line, too.

For this purpose we have prepared a series of Ge filters with arising values of mass per unit area using  $\text{GeO}_2$ . In our preliminary measurements the most suitable Ge filter was found to have the value of mass per unit area  $6 \text{ mg/cm}^2$ ; spectra measured both with and without this filter using a semiconductor Si/Li detector are shown in Fig. 2.

All our preliminary experiments were made with a 24 h air sample; a parallelly collected air sample was analyzed for lead by atomic absorption spectrometry after the chemical sample pre-treatment by 0.2 M hydrochloric acid solution (5 ml). The Pb content in sample found by this method was  $9.5 \times 10^{-5} \text{ g}$ .

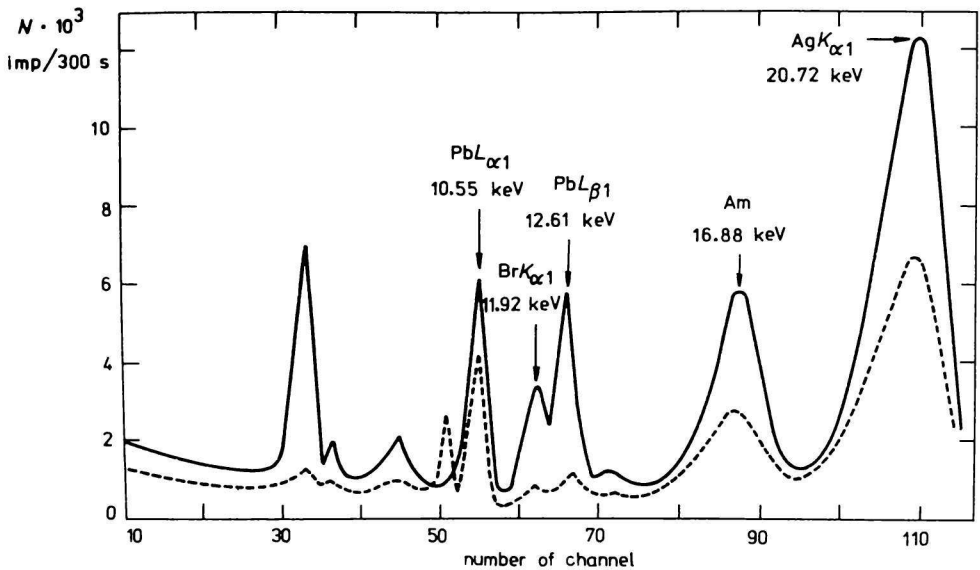


Fig. 2. Spectra obtained using a semiconductor Si/Li detector both with (---) and without (—) a Ge filter.

## Results and discussion

For proper measurements we have used the XRF system consisting of a NaI/Tl scintillation crystal, an annular radionuclide  $^{241}\text{Am}/\text{Ag}$  source, and a single channel analyzer. In order to eliminate spectral interferences due to the presence of bromine in the sample we have employed a Ge filter (as described above).

Since the calibration curve in the concentration range of  $10^{-5}$ – $10^{-6} \text{ g Pb}$  in air sample was linear only one standard was needed. Using a standard containing  $5.3 \times 10^{-5} \text{ g Pb}$  we have performed analyses for lead in a great number of air samples collected in different selected areas and different day- or night-time. The

results from these measurements are summarized in Table 1, where are the data about volume of sampled air, number of cars that passed in a reasonable time, measured total amounts of lead in the sample and those calculated per unit volume of the sampled air, respectively.

The samples No. 1—13 were taken during day-time (7 a.m.—19 p.m.), while the samples No. 14—25 during night-time (19 p.m.—7 a.m.). It should be noted, with reference to Table 1, that the amounts of lead found in day-time samples are in comparison larger. We believe it is the result of high intensive traffic density both at morning and early afternoon time, which has been included in day-time samples. On the contrary, Pb contents found in night-time samples were in comparison lower: one may suggest that the most part of this lead was originating from the beginning of early morning high traffic. This indicates direct dependence between

Table 1  
Pb content in air samples obtained by the XRF method

Sample No.	Sampled air m <sup>3</sup>	Number of passed cars	Pb content in sample g · 10 <sup>-6</sup>	
			total	per m <sup>-3</sup>
1	7.538	805	21.2	2.8
2	7.308	767	12.0	1.6
3	7.716	812	9.9	1.3
4	7.637	385	12.9	1.7
5	7.995	813	12.5	1.6
6	6.726	875	21.7	3.2
7	6.064	1198	26.9	4.4
8	6.322	1126	15.9	2.5
9	6.283	1199	23.7	3.8
10	5.912	1155	17.4	2.9
11	10.327	1092	33.0	3.2
12	5.879	1193	17.1	2.9
13	7.274	249	15.6	2.1
14	9.432	358	14.6	1.5
15	7.290	191	7.3	1.0
16	8.865	246	8.7	1.0
17	6.252	177	7.1	1.1
18	5.498	146	12.7	2.3
19	6.482	533	12.1	1.9
20	6.172	381	10.4	1.7
21	6.884	341	18.7	2.7
22	6.293	387	10.8	1.7
23	6.455	214	14.2	2.2
24	6.738	465	26.3	3.9
25	11.599	415	15.3	1.3

the Pb content in air and the number of passed cars. However, there are some deviations from this dependence due to the fact that the total number of passed cars includes not only the cars with gasoline engines.

Our experiments have shown that the developed radionuclide X-ray fluorescence method is a suitable practical technique for routine airborne Pb monitoring. Its main advantages are:

1. no specimen preparation is required (the material is analyzed directly on the filter);
2. it is nondestructive (enabling specimens to be reanalyzed in case of argument);
3. it is sensitive enough to perform quantitative trace elements analysis on milligram amounts of materials;
4. it is simple and rapid (it is fast enough to determine element at the rate of about 1 min).

There are some conventional analytical techniques used in this kind of applications which provide the required sensitivity for detection of airborne lead, too, but they are time-consuming and expensive, e.g. the original sample must be dissolved and cannot be preserved for repeated analyses. Also, the necessary wet chemical sample preparation is a source of error. Moreover, measurements of a long-term (24 h and more) sample as required by the conventional analytical techniques, provide information about only average daily concentration of atmospheric lead; they do not allow to study the direct relationship between a various traffic density and the changes of Pb level in air during a day. When applying the XRF method, a short-term (1 h and less) sample can be analyzed and thus required rapid and adequately accurate atmospheric Pb monitoring can be made.

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