

X-RAY FLUORESCENCE METHOD FOR MULTIELEMENTAL ANALYSIS OF AEROSOL COMPOSITION USING THE SYNCHROTRON RADIATION

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Feasibility of application of the X-ray fluorescence analysis of the atmospheric aerosol is discussed and sources of errors in determining the concentration of chemical elements are given. Examples of analysis of atmospheric aerosol samples taken in the Novosibirsk region are given.

Chemical aerosol composition is an important characteristic of this disperse system. Peculiarities that make an analysis of the atmospheric aerosols (AAs) difficult are the multielemental composition with a wide range of variation of concentrations of individual components and low mass concentrations of substances to be analyzed. Therefore, at present very modern high-sensitive analytic methods are used for measuring the AA composition. Among them, special position is occupied by different modifications of nuclear-physics methods and in particular, X-ray fluorescence method. High sensitivity of determining the multielemental composition leads to widespread use of this method for studying the characteristics of the atmospheric aerosols.

The use of the synchrotron polychromatic X-ray radiation for the fluorescence excitation in the X-ray fluorescence elemental analysis (SRXRFA) yields much better results in comparison with electron, proton, and ion beams used with the same purpose. This is connected with the fact that for the roentgen radiation, the ionization cross sections of the inner K and L atomic shells of intermediate and heavy elements are by 1–3 orders of magnitude higher than those of the particles and the bremsstrahlung-produced background radiation of electrons in a specimen is by 1–3 orders of magnitude lower. SRXRFA is more promising in comparison with the classical X-ray fluorescence method, because excitation of characteristic radiation with the help of synchrotron radiation permits one to increase the sensitivity of this method by 2–3 orders of magnitude.¹

Efficiency of one or another analytic method depends largely on the accuracy of determining a measurable quantity. Therefore, in the present article we first consider the main sources of errors in measuring the concentrations of chemical elements of the atmospheric aerosol in multielemental SRXRFA and present some results obtained with the help of the

above-described technique that show possibilities of the method by the example of the Siberian aerosols. The results given below solve the problems of analytical part of the integrated project "Siberian Aerosols."² Sources of errors are considered for specific stages of obtaining the concentrations of chemical elements.

The first stage is measuring the X-ray spectrum of aerosol samples. Procedure for measuring the X-ray spectrum with the help of synchrotron radiation is described in Ref. 3. A detector used by us was capable of investigating the spectra of elements from potassium to uranium. For elements from K to Sn, we used the lines at the $L2-K$ and $L3-K$ transitions to determine the concentration, that is, the $K\alpha_1$ and $K\alpha_2$ doublet lines considered as one line because of the small difference in energies. The sum of $L2-K$ and $L3-K$ transition probabilities, considered together, varies from 0.8870 to 0.8212, that is, by no more than 8%, which nevertheless should be considered in quantitative measurements of concentration. For the elements from Sb to U, we used the spectral lines at the $M5-L3$ and $M4-L3$ transitions, which were also considered together. Relative probabilities of the sum of these lines in the $L3$ line group vary from 0.8423 to 0.7429, that is, by 13%. This also should be considered further.

Most measurements were performed with the beam energy of the order of 25 keV. This energy of excitation did not allow us to measure the concentration of element group from Ru to Sn because of difficulties associated with separation of spectral lines of these elements and the Compton radiation.

In Fig. 1, the dependence of the minimum energy of beam excitation $E(N)$ is shown which permits the lines of corresponding elements (N is the serial number of element in the Mendeleev Table) to be stably recorded.

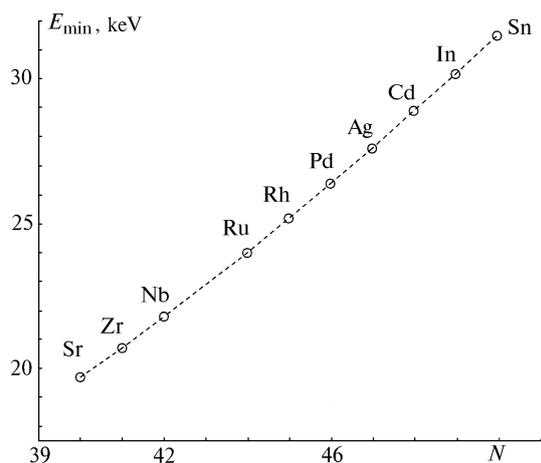


FIG. 1. Dependence of the minimum energy of the beam excitation permits the lines of the corresponding elements to be stably recorded.

The main sources of errors in measuring the spectrum are connected with detector type, variation of the beam intensity (and hence the intensity of roentgen radiation) during the experiment, and nonuniformity of the chemical element distribution on the surface of the specimen.

To determine reproducibility of experimental data, the results of two-year 44 measurements of the standard specimen, containing the equal amounts ($10 \mu\text{g}/\text{cm}^2$) of Ca, Cr, Fe, Cu, and Sr elements, were considered. When analyzing the results, the amplitude of peaks of the spectral lines, corresponding to each element, were considered. A comparison of the results shows that sensitivity of the detector to a given line depended on the energy of beam excitation. We speak about the relative sensitivity $a = S_i/S_{\text{Fe}}$, where S_i is the line peak height of the i th element and S_{Fe} is the peak height of the ferrum line. The results of this run are tabulated in Table I, where E is the excitation energy, a is the mean sensitivity of the channel to Ca with respect to Fe, da is the mean error, and n is the number of analyzed specimens. Measurements 1, 3, and 4 were performed with one detector, measurements 2 – after the detector was changed. As seen from the table, the spread does not exceed 2.4%. The spread was due to the nonuniformity of distribution of chemical elements on the surface of the standard specimen.

The spectrum in the tabular form (the number of pulses in each of 1000 energy channels of the detector) was processed numerically to obtain the relative intensities of the spectral lines. This was the second stage of the procedure for measuring the chemical element concentration.

The relative intensities of lines are determined by the area bounded by the line profile and the background curve. The relative intensities were

calculated with the help of the standard technique⁴: the spectrum (bounded by the line profiles and the background curve) was approximated by a polynomial. The background curve was represented in the form of a certain function with the unknown parameters and the line profiles – in the form of the Gauss curve, also with the unknown parameters. Parameters determining the spectral line profile were calculated from the minimization condition for the standard deviation of the measured line profile from the calculated one.

TABLE I. Reproducibility of the results.

Serial number of experimental run	e , keV	a	da , %	n
1	25	0.142	2.4	21
2	25	0.168	1.2	8
3	23	0.114	2.2	7
4	20	0.0957	2.2	8

The main source of errors at this stage was the calculation for the model inadequate to the measured spectrum. (The model comprised the assignment of the profile of the background curve and list of the elements considered in the calculation.)

In Table II, the results of calculation of the relative line intensities for two models of the background curve are presented. Model 1 is the exponent of the third order (exponent of the polynomial of the third order) and model 2 is the exponent of the sixth order (exponent of the polynomial of the sixth order).

As seen from Table II, when measuring the small concentrations, the chosen profile of the background curve may cause large errors. An analysis of the large number of specimens with the given number of elements shows that the smallest error due to the choice of the form of the background curve is introduced for the exponent of the third order.

The main error of mathematical analysis of the spectrum by the standard technique is due to neglect of really existing lines in the model. The matter is that neglect of these lines leads to overestimation of the standard deviation between the measured and calculated spectra. According to the minimization procedure, this leads to the increase of the background contribution and thereby to the decrease of the intensities of lines considered in the model and lying close to the neglected line (on the energy scale). The error is significant for measuring the intensities of weak lines, because due to this error, the threshold of determining the concentration is increased. For example, Table III tabulates the results for the same standard specimens for two models, comprising different numbers of elements.

TABLE II. Relative intensities of lines of the chemical elements for two models of the background curve (standard specimen).

Model	Element									
	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sr	Zr
1	677	320	0	14142	0	0	29952	1128	93912	473
2	543	458	216	14594	280	296	30463	1468	93490	543

TABLE III. Dependence of the results from the choice of the model.

Element	<i>e</i> line, keV	Relative concentration	
		First model	Second model
Ca	3.691	1112	1230
I	3.937	—	73
Sc	4.089	—	137
Ba	4.464	—	89
La	4.651	—	134
Ce	4.838	—	57
V	4.950	—	30
Nd	5.228	—	28
Cr	5.412	5765	6096
Sm	5.633	—	203
Fe	6.399	18591	19144
Er	6.945	—	344
Cu	8.041	39840	40163
Zn	8.631	203	453

The data in Table III were chosen from the calculations for models with 20 (the first model) and 35 elements (the second model). For AAs, which have in their composition the large number of elements, their maximum number should be considered in model construction. An example of this calculation is given in Table IV.

As seen from Table IV, in addition to Sc, Cs, Pr, and U, each of the elements enumerated in column 1 was identified at least in one of the analyzed spectra. Thus, we see SRXRFA is capable of measuring simultaneously up to 40 elements in aerosol samples.

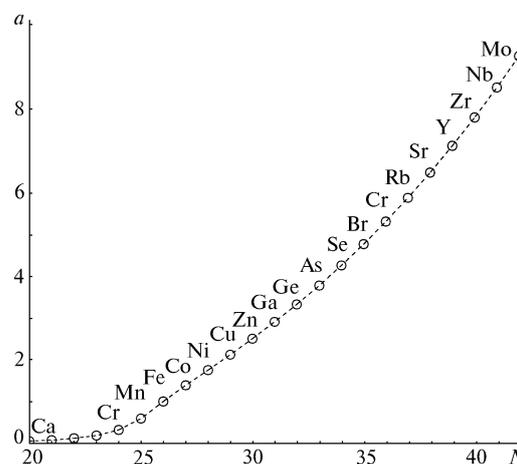
The third stage is the determination of the absolute concentrations of the chemical elements. For this end in each run, in addition to the analyzed samples, the standard specimen was measured (the reference specimen with well-known surface density of the elements). The accuracy of calculated surface density of the analyzed specimens was determined by the accuracy of assigning the parameters of the standard specimen.

For multielemental analysis of AAs, the following standards were used:

1. Standard specimen comprising the elements Ca, Cr, Fe, Cu, and Sr in amounts of $10 \mu\text{g}/\text{cm}^2$.
2. Standard specimen with the same elements, but in amounts of $13.6 \mu\text{g}/\text{cm}^2$.
3. Standard specimen with the elements Ca, Zn, Sr, and Pb, in amounts of $13.6 \mu\text{g}/\text{cm}^2$.

The sensitivity of the detector calculated with the help of standard specimens for each element was subsequently normalized by the sensitivity to ferrum.

The sensitivity to other elements was obtained with the help of interpolation. In Fig. 2, for example, the calibration curve is shown for the elements with numbers from $N = 20$ to $N = 42$. The spread of data for the calibration curve is within 5%.

FIG. 2. Calibration curve for the chemical elements with numbers from N a 20 to N a 42 (excitation energy is 25 keV).

The last stage of analysis of the specimens is the calculation of concentrations of the chemical elements in aerosol particles. The accuracy of this calculation is determined by the specifications of the hardware used for the intake of atmospheric samples. Discussion of this problem is beyond the scope of this article.

TABLE IV. Results of analysis of aerosol specimens sampled at the Background Monitoring Station in Novosibirsk (Station Ogurtsovo).

Density of chemical elements on the specimens, $\mu\text{g}/\text{cm}^2$					
Element	Specimen number				
	1	2	3	4	5
K	2.0820	0.0000	3.3115	0.0000	8.4918
Ca	3.4459	6.4189	25.5676	17.7027	15.7027
Sc	0.0000	0.0000	0.0000	0.0000	0.0000
Ti	0.0000	0.7512	2.4732	3.4293	2.6732
V	0.0000	0.0000	0.0000	0.2779	0.0000
Cr	0.0467	0.0844	0.0000	0.0700	0.0000
Mn	0.0583	0.0937	0.1692	0.4120	0.0000
Fe	2.6426	2.7977	11.0108	10.5080	9.9983
Co	0.0140	0.0251	0.0538	0.0308	0.0563
Ni	0.0169	0.0075	0.0000	0.0140	0.0179
Cu	0.0712	0.0456	0.0615	0.0422	0.0545
Zn	0.1436	0.0643	0.1588	0.1265	0.1090
Ga	0.0049	0.0061	0.0057	0.0111	0.0043
As	0.0362	0.0272	0.0678	0.0965	0.0393
Se	0.0080	0.0031	0.0033	0.0027	0.0045
Br	0.6499	0.5528	0.5606	0.5615	0.5936
Kr	0.0257	0.0197	0.0454	0.0573	0.0218
Rb	0.0116	0.0101	0.0453	0.0214	0.0299
Sr	0.0174	0.0097	0.0640	0.0542	0.0563
Y	0.0000	0.0000	0.0112	0.0012	0.0043
Zr	0.0060	0.0079	0.0359	0.0751	0.0396
Mo	0.0016	0.0000	0.0000	0.0000	0.0015
Sb	0.6477	0.0000	0.0000	0.0000	0.0000
Te	1.7156	0.0000	0.0000	3.6239	0.0000
I	0.0000	0.0000	0.0000	0.0000	1.6667
Cs	0.0000	0.0000	0.0000	0.0000	0.0000
Ba	0.6701	0.0000	0.0000	0.0000	0.0000
La	0.2727	0.1780	0.3485	0.0000	0.7008
Ce	0.0000	0.0000	0.0000	0.0000	0.8294
Pr	0.0000	0.0000	0.0000	0.0000	0.0000
Nd	0.1137	0.0000	0.0000	0.0000	0.0000
Sm	0.0000	0.0000	0.0000	0.0000	0.0882
Eu	0.0000	0.0000	0.1686	0.0000	0.3487
Gd	0.0539	0.0000	0.0464	0.0000	0.2162
Tb	0.0000	0.0000	0.1827	0.0959	0.0861
Dy	0.0733	0.0000	0.0000	0.0000	0.0000
Er	0.0181	0.0000	0.0000	0.0000	0.0000
Lu	0.0109	0.0059	0.0000	0.0000	0.0000
Hf	0.0000	0.0098	0.0000	0.0025	0.0000
W	0.0061	0.0110	0.0000	0.0000	0.0000
Hg	0.0047	0.0080	0.0000	0.0029	0.0071
Tl	0.0039	0.0000	0.0041	0.0000	0.0000
Pb	0.0531	0.0000	0.0633	0.0000	0.0000
Bi	0.0000	0.0000	0.0086	0.0041	0.0000
Ra	0.0000	0.0000	0.0000	0.0065	0.0000
U	0.0000	0.0000	0.0000	0.0000	0.0000

TABLE V. Analysis of multielemental composition of aerosols of different sizes.

Serial number of station	d 50, μm	Element	First factor									Second factor					Third factor		
			K	Ca	Ga	Rb	Pb	-	-	-	-Cl	Ti	Mn	Fe	-	Br	-	-	
1	>6.6	<i>EF</i>	1.05	8.0	7.5	1.54	34	-	-	-	580	3.3	0.8	1	-	68	-	-	
		<i>SQ</i>	1.71	1.5	4.5	2.6	2.0	-	-	-	3,5	1.5	1.4	1	-	3.6	-	-	
		Static load	0.42									0.34					0.14		
2	6.6- 3.8	<i>EF</i>	1.5	6.0	2.7	6.6	25	58	1.4	40	270	1.1	6.2	-	-	1	1.6	-	
		<i>SQ</i>	1.4	1.4	1.8	2.5	1.8	2,6	1.7	2.0	1.7	1.7	1.9	-	-	1	1.2	-	
		Static load	0.41									0.20					0.26		
3	3.8-1	<i>EF</i>	590	150	2.6	2.2	1.4	-	-	-	4.3	6.8	510	2.2	160	1.3	4.1	1	
		<i>SQ</i>	1.8	1.8	1.3	2.1	1.4	-	-	-	3.2	1.8	5.2	1.8	2.0	1.9	1.3	1	
		Static load	0.30									0.29					0.30		

Note: Here *EF* is the enrichment factor and *SQ* is the standard deviation.

The results of an analysis of multielemental composition of the aerosols, sampled with a multicascade virtual impactor at the Geophysical Station of the JIGHM of the SB RAS, located at a distance of 12 km from Novosibirsk Akademgorodok, are presented above. In this experiment, diurnal samples were taken with a four-cascade impactor during 9 days in spring 1993. Because on the last cascade of the impactor ($d < 1 \mu\text{m}$) the deposit was insignificant during the first day, so the aerosols were sampled on this cascade during the rest of time. Therefore, in Table V the results of statistical processing are given only for the coarsely dispersed aerosol fraction ($d > 1 \mu\text{m}$). In Table V, the results of the factor analysis of multielemental composition of the aerosol particles of three different fractions are presented ($d > 6.6$, $6.6 > d > 3.8$, and $3.8 > d > 1 \mu\text{m}$). In each of the three rows corresponding to the individual cascade of the impactor the elemental composition of the examined factor, the enrichment factor with respect to ferrum for each from the above-indicated elements, its average geometrical deviation, and statistical weight of individual factor (static load) are indicated.

Though up to 30 elements of multielemental composition of individual fraction of aerosol particle size were measured by the SRXRFA in a number of samples, the concentrations of some elements were lower than the minimum detectable level. Therefore, we could use only 13 elements for statistical processing. As seen from Table V, up to three factors (types of particles) can be distinguished by the method of factor analysis. The elements with the enrichment factor no larger than 10 can be referred to the particles produced by erosion of mountain rocks. However, for a number of elements the enrichment factor (*EF*) is much greater than 10 and exceeds a hundred. Usually, this is true for aerosols of anthropogenic type. However, our previous

investigations have shown that the region of settlement Klyuchi belongs to the category of background territories.⁵ In addition, here we recorded high enrichment factors for the coarsely dispersed aerosol fraction ($d > 1 \mu\text{m}$). Therefore, as indicated earlier,⁶ it would be wrong to assign these particles to sources of anthropogenic pollution. It also should be noted that other elements entering into the composition of the examined factor may have *EF* close to unity. On the basis of this, we are inclined to the thought that in this case we are dealing with soil particles eroded from the upper soil layer formed primarily by the residue of the plant fall. For plants and living organisms, large accumulation coefficients of one or another element may be observed. In particular, K is one of the macroelements characteristic of plants. As seen from Table V, it is inevitably presented in one of the three factors of any fraction of particle sizes. Moreover, statistical weight of the factor comprising K, is rather high (0.3–0.42). These results agree qualitatively with conclusions about significant contribution of the particles of biogenic origin, drawn in Refs. 6–9 from an analysis of multielemental composition of the aerosol particles. Another important conclusion drawn from these investigations is that the accuracy of measuring different sources and their relative contribution may change as functions of qualitative and quantitative multielemental composition of the aerosol particles. This result, in particular, follows from Table V and the results of determination of only 20 elements.¹⁰ Analogous conclusion was drawn when the data in Table III were discussed.

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