

The threshold of detecting trace elements in samples of atmospheric aerosols by use of the X-ray fluorescence method

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Received November 29, 2000

We have used an X-ray fluorescence method stimulated by synchrotron radiation (XFA SR) to study the detection limit of element analysis for all elements in the samples of atmospheric aerosols. The dependence of the detection limit on the method of sampling has been revealed. We have experimentally verified the distribution of the background fluctuations to be normal.

Introduction

Atmospheric aerosols (AA) are complex systems from the standpoint of both their chemical and disperse composition.¹ The element composition is very informative characteristic of AA. It is not an overestimation to say that AA contain the major part of the elements of the periodic system, but the content of some of them is negligible. The elements of small content (trace elements) also are of great significance for solving the problem of determination of the source of AA. So it is important to know the metrological characteristics of analysis, and especially the detection threshold (DT). The requirements to metrological characteristics of analysis are significantly caused by the specific features of such a complex object as the AA, taking into account their multielement composition, unpredictable character of the ratio of the elements (the scatter of several orders of magnitude), great number of trace elements, and so on.

One of the nuclear-physics methods of element analysis of AA is the X-ray fluorescence method using the synchrotron radiation (XFA SR).^{2,3} Element analysis using the X-ray radiation provides for the possibility of simultaneously detecting tens of elements independently of the fact, in which chemical compound each element is present in the sample under study. In connection with the relatively high energy of the characteristic quanta accompanying the transition of electrons at the levels close to the nucleus, the method is characterized by high resolution (discreteness of the characteristic signals).⁴ In connection with the use of synchrotron monochromatic X-ray radiation for excitation of fluorescence, the XFA SR method, in comparison with the classic X-ray fluorescence method, has the lower background radiation and 2–3 orders of magnitude higher sensitivity. One of principal advantages of XFA SR is that it is nondestructive, that makes it possible to repeat analysis, if necessary. However there is a disadvantage of the method, compared to other nuclear-physics methods. It is the indirect character of measurements, requiring

simultaneous measurements using a standard, blank sample (to take into account the background), and the sample to be studied.

As a result, at the final stage of the analysis, we have a multicomponent analytical signal that is functionally related to the content of elements to be determined. The process of measurements based on counting the photons emitted at the characteristic lines has the statistical character. Revealing the peculiarities of the metrological characteristics of the specific method of analysis (XFA SR in our case), common for all samples of the same type is of great significance. It is important to know the DT for each element contained in the samples of AA. First consider the specific instrumentation needed for analysis (for example, the station for element analysis in INPh SB RAS, the VEPP-3 accumulator), the metrological characteristics of measurement of the element composition of AA for the samples of the same type are inherently dependent on the performance characteristics of the instrumentation and the characteristics of the sample (type of the substrate, the amount of the collected matter, etc.).

This paper is devoted to experimental determination of the DT in measuring the element composition of AA by the XFA SR method using the specific instrumentation and to the study of the effect of individual peculiarities of samples on the metrological characteristics, i.e., the effect of the way for the sampling technology. Two methods of sampling are considered, which are most frequently used to collect samples of AA, – collection to the AFA-HA filters (acetylation pulp) and to the Wattman-41 filters. This paper is an attempt to show the possibility of improving such an important characteristic of analysis as the DT by choosing the proper technique of sampling.

Detection threshold

Determination of the low contents (traces) of chemical elements by use of the X-ray spectroscopy is

limited by the loss of visual image of the analytical line in the spectrum of the characteristic radiation. The complex structure of the spectrum caused by the matrix effects restricts the possibility of isolating analytical signal and compensating for the background. The least-square method is traditionally used for improving the observation in quantitative interpretation of the characteristic spectrum. The data on DT are presented in Refs. 5 and 6 for several lines of the standard sample at isolation of the background component by means of the least-square method. The possibility of direct statistical interpretation of the data of X-ray spectroscopy is considered in this paper as well.

In relation to AA samples, the DT is the minimum quantity of the given element, which can be detected within a preset confidence probability. First, the detection sensitivity corresponds to the qualitative analysis and is characterized by the concentration level of an element, at which the analytical line sufficiently exceeds the background and can be detected quite reliably. Second, the threshold of the quantitative detection is the least concentration, starting from which the coefficient of variation does not exceed a preset value. As the measured concentration of the element decreases, one can observe gradual transformation of quantitative analysis to qualitative one, which is caused by the growth of the statistical error.

The AA samples are thin,⁷ i.e., the thickness of the radiator is so small that one can ignore absorption of primary and secondary radiation in it. In this case the direct-proportionality dependence of the line intensity on the content of the element in the sample takes place. Therefore, the notion of DT of the concentration of the i th element for the samples AA is also applicable to the analytical signal, with which the concentration is connected by a linear dependence. As the concentration is always determined against the background of the blank sample signal, then the DT, in terms of measured analytical signal is the minimum signal $S_{i\min}$, which can reliably be distinguished from the blank sample signal (background) S_f . There are relationships connecting the DT of the analytical signal $S_{i\min}$ and the DT of the concentration $C_{i\min}$, which are written in terms of the corresponding coefficients of the instrumental sensitivity k_i and depend on the element number and the parameters of the detector used for measurements:

$$S_i = k_i C_i.$$

Statistical consideration of the problem of detection of the element traces was presented in Refs. 9 and 10, where the problem was stated on the examination of the statistical hypothesis H_0 – the absence of the analytical signal (error of the first type) versus the alternative H_1 of its presence. The graphical interpretation of the detection threshold¹⁰ is shown in Fig. 1, where Y -axis is the analytical signal value (Y_f and Y_s are the mean values of the background and analytical signals, respectively).

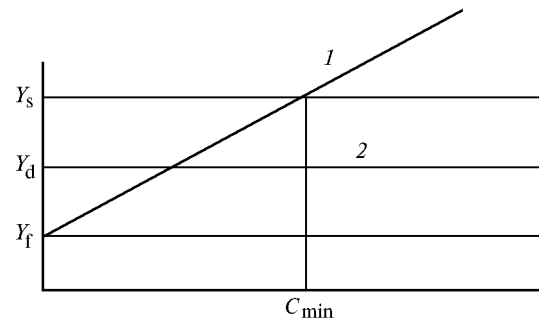


Fig. 1. Graphical interpretation of the detection threshold: calibration curve (1), rejection level (2).

The so-called rejection (or discrimination) level Y_d was placed between the values of the background and analytical signals. It divides all signals into two parts: $Y < Y_d$ is the background, and $Y > Y_d$ is the analytical signal of the element to be detected. The position of the rejection level was selected so that the probabilities of the first (missing of the analytical signal) and second (detection of the signal in the absence of the element in the sample) types were equal. It was supposed that the background and analytical signals in the close proximity of the background are distributed following the same law.

Experimental determination of the detection threshold

Determination of the background was carried out from 15 parallel measurements of blank filters AFA-HA and Wattman-41 in connection with the idea of direct statistical interpretation. The energy of primary radiation was 25 keV, the analytical signal was recorded to 2000 energy channels. Since the analytical signal is an integral value, i.e., it is the area under the analytical line; also the integral signal of the background sample was measured. Summing was performed over 14 channels (energy of the order of 170 eV) that corresponded to the value of the energy resolution (the characteristic spectrum line width) for the detector used. The background was measured in the ranges of the principal analytical lines – energy from 3.5 to 15 keV, that is 70 regions of the spectrum. Some of the results measured within 11 spectral ranges are presented in Table 1 (as was said above, 15 parallel measurements and summing over 14 channels were carried out in each range).

Examination was carried out over 20 and 25 parallel measurements in some spectral ranges. There were no noticeable differences in the results of statistical processing in comparison with the case of 15 parallel measurements.

The problem of confidence probability or reliability of the estimate of the DT is resolved by selecting the distribution law. To solve this problem, examination of the distribution law of the background

fluctuations was carried out using a standard technique.¹⁰ The Gaussian character of the distribution of background fluctuations was confirmed in all measurement ranges both for the AFA-HA and Wattman-41 filters. Based on this fact, the confidence interval of 3σ was selected in calculating the DT.¹¹ Calculation of the DT value for concentration of the given element was carried out taking into account the instrumental sensitivity (based on the calibration data) and data on the sample measured, for a comparison, under the same conditions using the technique developed for the quantitative interpretation of the measured characteristic spectrum at the element analysis of AA.¹² The calculated results on the DT of different chemical elements for two regimes of the sample collection are presented in Table 2.

Table 1. AFA-HA filter

Energy, keV	\bar{S}_y , pulses	Standard deviation σ , pulses	Coefficient of variation, %
4	86	9.0	10.6
5	79	6.1	7.7
6	140	12	8.6
7	90	9.2	10.2
8	100	12	11.8
9	68	18	26.5
10	52	8.0	15.3
11	50	12	24.0
12	54	8.0	14.8
13	54	7.4	13.8
14	53	8.2	15.5

Table 2. Detection threshold for the AFA-HA and Wattman-41 filters

Element	$C_{\min 1}$	$C_{\min 2}$	Element	$C_{\min 1}$	$C_{\min 2}$
	AFA-HA, ng/cm ²	Wattman, ng/cm ²		AFA-HA, ng/cm ²	Wattman, ng/cm ²
Ca	350	980	Zn	6.8	20
Sc	110	490	Ga	5.1	17
Ti	65	330	Ge	4.0	15
V	65	200	As	6.1	13
Cr	21	120	Se	5.0	11
Mn	25	83	Br	3.8	10
Fe	27	49	Rb	2.0	8.0
Co	11	35	Sr	2.1	7.5
Ni	9	28	Y	1.8	6.9
Cu	7.8	23	Zr	2.3	6.3

As is seen from Table 2, the DT for the samples collected on Wattman-41 filters is several times higher than that for samples collected on the AFA-HA filter, what is explained by higher density of the Wattman filter (the density of AFA-HA is 2.9 mg/cm², and that of Wattman is 8.3 mg/cm²). Measurements carried out at different intensity of the incident radiation (loading of the detector 0.3 and 0.9 kHz) gave practically the same results.

Measurements of the reproducibility (15 parallel measurements) of different samples have shown that the statistical error in measuring the element concentration depends on the ratio of the measured signal to DT of this element and on the type of the filter used in

sampling. Reproducibility of analysis data is shown in Fig. 2 as a function of the ratio of measured concentration of the i th element to its DT. The coincidence of this dependence for the samples on AFA-HA and Wattman-41 filters is well seen from this figure regardless of the large difference in the DT values.

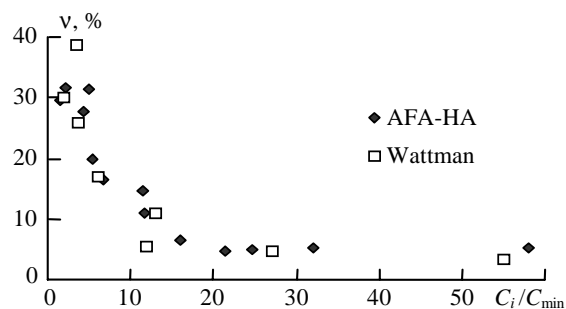


Fig. 2. Reproducibility of the analysis, v , as function of the ratio of the measured concentration of the i th element to its detection threshold.

Measurements were carried out of the reproducibility of the same sample of AA in the case of standard wrapping samples by two layers of the mylar film and without the film. The results are presented in Table 3.

Table 3

Element	Mean concentration, $\mu\text{g}/\text{cm}^2$	Reproducibility, standard wrapping, %	Reproducibility without wrapping film, %
Ca	106	4.2	3.7
Cr	0.15	45	35
Zn	0.33	5.2	2.9
Se	0.003	47	31
Sr	0.069	7.9	8
Zr	0.029	17	17
Mo	0.002	64	53

Assuming that the reproducibility correlates with the ratio of the element concentration to its DT, one can see from the data of Table 3 that the DT for the given element decreases in the absence of wrapping film. The exceptions are strontium and zirconium. This can be explained by the fact that the film at the energy of 13–15 keV does not contribute to the background as was examined by the change of the background of a blank filter with and without the film.

Conclusions

1. The DT for samples of AA changes depending on the parameters of the substrate on which the aerosols have been collected.

2. The DT for the given substrate is different for different elements (decreases as the atom number increases) what is determined by the instrumental sensitivity of the measurement method.

3. The statistical error (reproducibility) is not the parameter of the method, but depends on the ratio of the measured signal to the detection threshold. As the concentration of the element under study decreases (close to the detection threshold), the increase of statistical errors leads to transformation of quantitative analysis to the qualitative one.

4. The background fluctuations obey normal (Gaussian) distribution law.

Acknowledgments

The work was supported in part by the Russian Foundation for Basic Research (Grant No. 98-03-32467).

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