

Use of the X-ray spectrometry for analysis of atmospheric aerosols

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We present some results on the content of metals determined in atmospheric aerosols sampled on a filter. The quality of the domestic (AFA-KhA and FPP) and foreign (Whatman-41) filters is compared and the recommendations for sampling atmospheric aerosols for their subsequent analysis by the X-ray spectrometry are given. The techniques of X-ray spectrometric determination of V, Mn, Fe, Ni, Zn, and Pb in urban and industrial aerosols are developed and studied from the standpoint of metrology.

The X-ray spectrometry (XS) can be efficiently used for determination of the element composition of atmospheric aerosols. Advantages of this method are the possibility of direct multielement analysis of filters loaded with aerosol and, consequently, high rate and productivity.^{1,2} In our practice the XS is rarely used for monitoring of atmospheric air. In this paper, we consider the sources of errors and describe the technique of X-ray spectrometric analysis of atmospheric aerosols.

Estimating the errors of sampling

Sampling is a very important stage in monitoring of the atmospheric air. The quality of work done at this stage depends on a number of factors: the amount of sampled material and particle size, physical and chemical properties of aspiration filters and the type of a sampler, the rate of air blowing through a filter, atmospheric conditions, etc. Therefore, first we have evaluated the quality of aspiration filters. The comparative studies were conducted for the Russian domestic AFA-KhA and FPP filters and foreign Whatman-41 filter. For this purpose, we have determined pollution of these filters with elements, whose X-ray spectra lie in the 0.08–0.26 nm spectral interval.

A criterion for evaluation of the filter quality was the stability of the $I_{\text{on}}/I_{\text{off}}$ ratio, where I_{on} and I_{off} are the intensities of X-ray radiation recorded at an analytical spectral line of an element and nearby this line. This parameter was chosen because variations of I_{on} for different filters may be connected with variations of both the element content in them and their surface density (P_S). The value of I_{off} also depends on P_S , therefore variations of the $I_{\text{on}}/I_{\text{off}}$ ratio are largely determined by variations of element contents in filters.

The experiment on evaluation of the filter quality was planned by the scheme of two-factor dispersion

analysis.³ For this purpose, several filters were selected from different lots of filters of each type studied. The values of I_{on} and I_{off} from each of them were measured twice with the VRA-30 spectrometer (X-ray tube with Rh anode, voltage of 35 kV, current of 40 mA). The total experimental error $S_{r\Sigma}$ was separated into the constituents:

$$S_{r\Sigma}^2 = S_{rd}^2 + S_{rs}^2 + S_{rdif}^2,$$

where S_{rd} is the relative standard deviation (RSD), characterizing the reproducibility of the $I_{\text{on}}/I_{\text{off}}$ ratio measurements for one filter; S_{rs} and S_{rdif} are RSD's determining the differences in the $I_{\text{on}}/I_{\text{off}}$ values measured for filters from the same and different lots, respectively.

The results of dispersion analysis showed that S_{rd} varied from 0.007 to 0.054, increasing, as a rule, with the increasing radiation wavelength. Against the background of reproducibility of analytical parameters, only for Fe in FPP filters the value of S_{rs} equal to 0.038 turned out to be significant. The errors S_{rdif} were found for Fe in filters of all types (FPP, AFA-KhA and Whatman-41) with the values, respectively, of 0.16, 0.036, and 0.022; for Br in FPP filters $S_{rdif} = 0.046$ and for Mn in AFA-KhA filters $S_{rdif} = 0.036$. Thus, FPP filters were found to be the least suitable for X-ray analysis, while AFA-KhA and Whatman-41 filters showed roughly the same quality.

Based on the obtained results, we can give the following recommendations for aerosol sampling onto filters for the following X-ray analysis:

- aerosol should be sampled onto AFA-KhA and Whatman-41 filters when available, otherwise FPP filters can be used, but the sample mass should be increased;
- to account for unstable surface density of filters, the standard-background method should be used;
- at X-ray analysis of aerosols, clear filters used as background samples should be taken from the same lot as the filters used for sampling.

To estimate the sampling error (S_{ro}), two experiments were planned and then conducted by the scheme of dispersion analysis at two posts of the Irkutsk Hydrology & Meteorology Center. At the first post, single-factor experiment was conducted in order to determine only S_{ro} . For this purpose, two aerosol samples were collected quasi-simultaneously (air was blown through one filter for 25–30 min, then the filter was replaced with another one, and air was blown through the second filter as well), and each sample was independently analyzed twice by the XSM. At the second post, a two-factor experiment was conducted: besides S_{ro} , the parameter S_{rir} characterizing irregularity of material distribution over filter was analyzed. In this case, two samples were collected quasi-simultaneously, each sample was divided into two parts, and each part was independently analyzed twice. Aerosol samples were collected onto AFA-KhA filters. At the first post the air volume blown through the filter was measured automatically, while at the second post it was measured manually. The air volume blown through the filter varied from 10 to 30 m³. The variability ranges of element contents on a filter, detection limits and errors of measurements are given in Table 1.

As can be seen from Table 1, the smallest values of S_{rd} and S_{ro} were obtained for Fe, whose mean content in aerosols collected on filters is an order of magnitude higher than the mean content of other elements. Sampling errors at the second post turned out to be twice as high as that at the first one. The causes for this were not found.

Calibration of the XS instrument

It is rather difficult to calibrate the X-ray spectrometers in analysis of loaded aspiration filters and to check the correctness of their results because of the absence of domestic standards adequate to actual aerosol samples. Synthetic standard samples (SS) modeling aerosols collected on a filter are usually used for this purpose. We tested three approaches to manufacture such SS. The first approach consists in coating of “blue strip” cellulose filters with standard solution of components to be determined. These filters are chosen, because the solution distributes uniformly over the filter

and the surface quality keeps after desiccation.⁴ It was found experimentally that with the use of a paper disk of 50 mm in diameter, the optimal volume of the solution is 0.1 ml. A significant disadvantage of such SS is inadequacy to actual aerosol samples, in which solid aerosol particles usually contain metal compounds.

The main sources of atmospheric pollution are soil dust and industrial emissions therefore it was proposed to use the material of state standard samples (StS) of soil and coal flue ash as a powder carrier of aerosol particles. Metal compounds were added to the StS material to make its composition similar to that of atmospheric aerosols in cities and industrial zones.

These powder mixtures were used for preparation of two SS's in the form of sediment on a filter (second approach) and polymer films (third approach). A powder of mass ≤ 5 mg was deposited onto a disk (diameter of 36 mm) of “blue strip” filter paper with a specially designed filter unit. To prevent powder crumbling off the filter, a wet powder layer was covered by a thin layer of water-soluble glue. To produce SS based on a polymer film, we have developed an original technology that allowed production of samples with aerosol particulate load from 20 to 500 $\mu\text{g}/\text{cm}^2$.

To estimate the SS quality (S_{rdif}), we conducted an experiment by a single-stage scheme of dispersion analysis. Thus, we tested two methods of analysis: direct external standard (DES, I_{on}) and the standard-background method (SB, I_{on}/I_{off}). As can be seen from Table 2, S_{rdif} characterizing the instability of preparation of different SS types does not exceed 0.09. When using the SB method, the error of production of film SS was mostly insignificant against the background of the error (S_{rd}) of reproducibility of analytical parameter measurement. For SS in the form of sediment on a filter, the use of the SB method is less efficient.

Based on the results obtained, it was recommended to use the SS prepared following the first or third approaches for calibration of the X-ray spectrometer for analysis of aerosols. To account for uncertain conditions of preparation of individual SS specimens, as well as different physical and chemical characteristics of loaded aspiration filters and SS, the standard-background method should be used.

Table 1. Estimated error of aerosol sampling

Plan	Element	Content on filter, $\mu\text{g}/\text{cm}^2$	Detection limit, $\mu\text{g}/\text{cm}^2$	Estimated error			
				S_{rd}	S_{rir}	S_{ro}	$S_{r\Sigma}$
Post 1	Pb	0.10–0.44	0.09	0.17	–	0.28	0.33
	Zn	0.10–0.35	0.03	0.14	–	0.19	0.24
	Fe	0.9–4.5	0.06	0.037	–	0.09	0.10
	Mn	0.02–0.49	0.03	0.26	–	0.33	0.42
Post 2	Pb	0.09–0.25	0.09	0.43	n/s	n/s	0.43
	Zn	0.09–0.31	0.03	0.14	n/s	0.49	0.51
	Fe	0.5–8.2	0.06	0.025	0.063	0.19	0.20
	Mn	0.12–0.37	0.03	0.079	0.21	n/s	0.22

Note. n/s means that error is not significant.

Table 2. Estimated error of SS preparation ($S_{r\Sigma}^2 = S_{rd}^2 + S_{rdif}^2$)

Approach of SS preparation	Method of analysis	Error components	RSD			
			Pb	Zn	Fe	Mn
1	DES	S_{rd}	0.068	0.069	0.095	0.037
		S_{rdif}	n/s	0.081	n/s	0.043
		$S_{r\Sigma}$	0.068	0.106	0.095	0.056
2	DES	S_{rd}	0.032	0.037	0.034	0.024
		S_{rdif}	0.083	0.085	0.053	0.082
		$S_{r\Sigma}$	0.089	0.093	0.064	0.085
	SB	S_{rd}	0.042	0.067	0.028	0.025
		S_{rdif}	0.057	0.069	0.033	0.079
		$S_{r\Sigma}$	0.071	0.094	0.043	0.083
3	DES	S_{rd}	0.024	0.008	0.020	0.033
		S_{rdif}	0.043	0.047	0.026	0.056
		$S_{r\Sigma}$	0.049	0.049	0.032	0.065
	SB	S_{rd}	0.039	0.016	0.034	0.036
		S_{rdif}	n/s	0.027	n/s	n/s
		$S_{r\Sigma}$	0.039	0.031	0.034	0.036

Metrological study of analysis techniques

Keeping in mind the above recommendations, we have developed two techniques for X-ray spectrometric determination of V, Mn, Fe, Ni, Cu, Zn, and Pb in aerosols. One of these techniques was used for analysis of atmospheric aerosols in Irkutsk Region. Aerosol samples were collected in accordance with the Program of Observations over the Content of Benzapilene, Metals, and Dust in Air developed by the A.I. Voeikov Main Geophysical Observatory (St. Petersburg). The calibration functions were drawn with SS prepared following the first approach. Some results of this analysis are given in Table 3.

Table 3. Comparison of the results of analysis of urban aerosols

Method of analysis	Element content, $\mu\text{g}/\text{m}^3$				
	Mn	Fe	Ni	Zn	Pb
XS	0.17	3.73	0.023	0.26	0.26
AESA	0.17	3.8	0.037	0.14	0.13
XS	0.18	4.39	0.032	0.25	0.21
AESA	0.18	4.3	0.024	0.12	0.094
XS	0.11	2.05	0.015	0.27	0.28
AESA	0.043	1.8	n/f	0.10	0.052
XS reproducibility, S_{rd}	0.13	0.02	0.20	0.05	0.24

Another technique was used for analysis of aerosols in industrial zones of different nonferrous metallurgy plants. Aerosol was sampled onto AFA-VP-20 filters near stationary sources (Table 4). This technique was calibrated against film SS (third approach). The StS

mixture of coal flue ash (ZUA-1) and compound of nonferrous metals was used as a powder-carrier of aerosol particles.

Metrological study of the developed X-ray spectrometry techniques was conducted. The reproducibility of the results is characterized by the relative standard deviation from 0.02 to 0.5 depending on the element content on the exposed filter. To check the correctness of the techniques developed, the results of X-ray analysis of 3-month samples of urban aerosols were compared with the data of atomic emission spectral analysis (AESA) made in the Scientific-Production Association "Taifun" (Obninsk) (Table 3). A satisfactory agreement between the data was observed. Samples of industrial dust were analyzed using the technique of atomic absorption analysis (AAA).⁵

In Table 4 we can see a significant difference between the XS and AAA results for Pb, Cu, and Fe. This difference may be caused by incomplete decomposition of aerosol samples in the AAA method. The silicic acid sediment remaining after ash dissolution keeps a significant amount of these components. To confirm this assumption, we studied qualitatively sediments on a filter by the XS and found that they contained Pb, Cu, and Fe. This fact agrees with the information from Ref. 6.

The data of AAA, AESA, and XSM differ most widely for Pb, therefore the correctness of the XSM data was estimated by the method of addition (Table 5). For this purpose, the loaded AFA-KhA filters were decomposed by the AAA technique.⁵ The solution and sediment were placed in powder cellulose, and after desiccation the mixture was thoroughly mixed. The standard sample was also prepared based on powder cellulose with some components introduced in the form of solution. As can be seen from Table 5, the systematic error of XS results is insignificant.

Table 4. Estimated reproducibility and correctness of XS results

Characteristic	Method of analysis	Element content, $\mu\text{g}/\text{cm}^2$				
		Pb	Cu	Ni	Fe	
Correctness	XSM	0.71±0.17	2.65±0.10	1.80±0.10	5.2±0.3	
	AAA	0.26±0.04	0.89±0.13	2.04±0.31	4.0±0.6	
	XSM	0.72±0.17	3.27±0.13	2.20±0.12	6.1±0.3	
	AAA	0.26±0.04	1.22±0.18	1.68±0.25	5.0±0.8	
	XSM	0.71±0.17	2.43±0.10	1.60±0.09	4.5±0.3	
	AAA	0.52±0.08	0.82±0.12	1.43±0.21	3.9±0.6	
	XSM	0.70±0.17	5.50±0.22	1.10±0.06	2.5±0.1	
	AAA	0.35±0.05	3.44±0.52	1.27±0.19	1.7±0.3	
	XSM	0.72±0.17	1.58±0.06	0.30±0.02	2.3±0.1	
	AAA	0.20±0.03	0.64±0.10	0.41±0.06	1.1±0.2	
	XSM	0.72±0.17	3.21±0.13	1.22±0.07	2.9±0.2	
	AAA	0.23±0.03	1.61±0.24	1.27±0.19	1.6±0.2	
	Reproducibility, S_{rd}	XSM	0.17	0.028	0.038	0.040
		AAA ⁵	0.075	0.075	0.075	0.075

Table 5. Estimated correctness of X-ray determination of Pb

Sampling site	Addition, μg	
	introduced	found
Listvyanka	62.5	51 ± 12
Shelekhov	62.5	63 ± 15
Irkutsk	62.5	57 ± 14
Irkutsk	62.5	67 ± 16

Conclusions

It was found that the aerosol sampling error S_{ro} depends on the element studied and its content in the air. Under conditions of our experiment, S_{ro} varied from 0.09 to 0.49. At automatic measurement of the volume of air blown through a filter, the value S_{ro} is almost twice as small as that at manual measurements. It was shown that the error S_{rir} due to irregular distribution of elements over the filter surface could achieve 0.2.

The techniques for X-ray spectrometric determination of metals in atmospheric aerosols sampled onto a filter were developed and metrologically studied. It was shown that the technique of atomic absorption analysis recommended for analysis of atmospheric

aerosol has systematic errors due to incomplete decomposition of the sample material.

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