

Chemical and atomic–emission spectral analysis of atmospheric and industrial aerosols for the presence of base metals

V.I. Otmakhov, E.V. Petrova, Z.I. Otmakhova, and T.V. Lapova

Tomsk State University
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Aerosol filters of different types, which are used for air sampling, have been studied experimentally. Matrices of various filter materials have been analyzed for the amounts of admixtures extracted from them. BaF₂ is recommended to be used as a carrier, which allows one to eliminate the influence of a filter matrix on the results of the atomic–emission analysis. A mechanism of optimizing effect introduced by BaF₂ is studied. A chemical and atomic–emission method for analysis of atmospheric air, air in an industrial zone, and industrial emissions has been developed and metrologically approved.

At present about 10% of the total aerosol content on the global scale comes to the atmosphere due to human activity. By year 2000 it will be as high as 15%. However, in the urban environments natural aerosols make up, on the average, only several per cent of all particles present in the urban atmosphere.¹ Base metals are present in the atmospheric air mostly as solid aerosols, which consist of sublimated particles of 0.2 to 5 μm in diameter. Such aerosols fall in the category of fine disperse aerosols and are harmful for human beings.² When monitoring the level of aerosol pollution with base metals, it is recommended to perform sampling by the aspiration method onto Petryanov aerosol filters.³ Different analytical methods can be applied, but the atomic–emission method is most informative; it allows simultaneous detection of up to 30 to 40 metals in an analyzed sample.

This work was aimed at development and metrological attestation of the method for quantitative chemical analysis of air samples from the atmosphere, industrial zones, and industrial emissions on the presence of base metals by the method of atomic–emission spectroscopy.

Experiment

Sampling onto aerosol filters was performed according to the Standard RD 52.04.186–89 for the atmospheric air, State Standard No. 12.1.005–88 for the air of an industrial zone, and State Standards No. 17.2.4.05–83 and No. 17.2.3.01–77 for industrial emissions.

The atomic–emission analysis was used as an analytical method. The dc arc supplied by the UGE–4 generator served as an excitation source. Spectra were recorded with an ISP–30 quartz medium-disperse power spectrograph with a raster-condenser illumination system. The SP–2 photographic plates with 20-unit sensitivity were used. The exposure time was 25 s with the slit width of 0.008 mm. OSCh–7–4

graphite bars with the crater depth and diameter of 4 mm were used as the dc arc electrodes. The degree of blackening of an analytic signal was measured with an MF–2 microphotometer. Numerical estimation was done against calibration characteristics constructed based on standards SOG–21 (GSO No. 4519–89–4523–89) and SOG–28 (GSO No. 4166–87–4171–87).

Results and discussion

Preparation of samples is one of the most demanding stages of the analysis and, at the same time, the stage introducing the largest number of errors. The literature describes different approaches to extract elements depending on a type of aerosol filters and an analytical control method used.^{4,5} The approach employing mineralization of filter materials based on the graphite collector holds promise for the atomic–emission analysis because it combines sample preparation and obtaining of the analytical concentrate in the same cycle, as well as excludes the stage of solution evaporation. Thermal ashing at the temperature of 400 to 500°C is used for complete decomposition of the filter's organic component.⁶ This method is recommended for the AFA–KhP, AFA–VP, and AFA–KhS filters, which form a fragile frame when ashed. However, not all filters can be ashed in such a way. For example, AFA–KhA filters made from acetylcellulose pass the melt stage in the process of thermal destruction, what hampers separation of an analytical concentrate from the cell walls.

The method of acid decomposition of the matrix can be recommended only for AFA–KhA filters. These filters, being completely soluble, transfer aerosol particles into a solution. The AFA–KhP and AFA–VP filters are stable to acid, therefore admixtures are extracted from them without filter decomposition. Acid extraction of monitored components with or without decomposition of the filter material involves an undesired stage of sample preparation – evaporation of sample solution.

To reduce the number of intermediate stages in the process of aerosol filter transformation into an easy-to-analyze form, to decrease the errors, and to shorten the time of analysis, we propose a different method for sample preparation. This method is acceptable for filters of any type (Table 1). It consists in a preliminary carbonization of the filter materials with 0.1 cm³ of concentrated sulfuric acid H₂SO₄ at the temperature of 150°C during 5 minutes followed

by ashing of the mineral remainder in a quartz furnace for 15 minutes at a temperature of 450 to 500°C in the presence of 50 mg of graphite powder. The mineralized sample obtained is used as a base for the following analysis by the atomic-emission method. Table 2 presents the data on admixture extraction by making use of the method proposed. One can see from Table 2 that all admixtures are collected almost completely onto the graphite collector.

Table 1. Characteristic of the analytical aerosol filters (AFAs)

Type of the filter material	Function: determination of	Material of ultrathin fibers*	Working area, cm ²	Efficiency, %	Chemical stability
AFA-VP-10	weight concentration of aerosols	perchlorvinyl	10	99	Stable to acid and alkali
AFA-VP-18			18		
AFA-KhA-18	chemical nature of aerosols	acetylcellulose	18	97	Soluble in acid, acetone, dichlorethane
AFA-KhP-18			18		
AFA-KhS-19	radioactive aerosols	polystyrene	19	99	Stable to acid and alkali
AFA-RS-3			3		
AFA-RS-10	aerosols	perchlorvinyl	0	99	The same
AFA-RS-20			20		

*All the materials are hydrophobic.

Table 2. The degree of admixture extraction from the filter material by using the combined method ($n = 3$, $P = 0.95$, $C_{lim} = 5 \cdot 10^{-3}$ % of mass, $S_r = 0.10-0.25$)

Element	AFA-KhA		AFA-KhP		AFA-VP	
	Detected, mg/filter	Extracted, %	Detected, mg/filter	Extracted, %	Detected, mg/filter	Extracted, %
Ba	4.77	95	5.00	100	5.00	100
Be	4.66	93	5.00	100	5.00	100
Co	4.85	97	5.00	100	5.05	100
B	5.00	100	4.27	85	5.02	100
Mn	5.00	100	5.03	100	5.03	100
Mg	5.00	100	5.10	100	4.55	91
Pb	5.00	100	5.00	100	5.00	100
Cr	4.47	89	4.41	88	4.59	92
Sn	4.46	89	4.31	86	4.16	83
Ti	4.34	87	4.26	85	4.32	86
Ni	4.30	86	4.82	96	4.13	83
Mo	4.05	81	4.35	87	4.05	81
V	4.00	80	4.18	84	4.05	81
Cd	5.00	100	5.00	100	5.00	100
Fe	4.92	98	4.71	94	4.62	92
Ag	4.79	96	4.56	91	4.16	83
Cu	4.71	94	4.71	94	4.50	90

Note. We have introduced 5 mg of every element onto a clean filter.

A salient feature of the atmospheric and industrial aerosols is their multicomponent and variable composition, which includes both natural (Si, Ca, Al, Mg) and technogenic (Pb, Ni, Mn, Cd, Cr, and others) elements in various forms and combinations. Anion composition of air may be different too. All this factors influence significantly the intensity of spectral lines of monitored elements both when a substance comes into the discharge zone and as atoms in plasma are excited.

Carriers are used in the atomic-emission analysis to exclude matrix effects caused by large concentrations of some dominant components in a sample, to stabilize the arc lighting conditions, and to decrease the minimum detectable concentrations of monitored admixtures. As a rule, salts of alkali metals are used as carriers.⁷ The stabilizing effect of such carriers is due to their low ionization potentials, which favor regulation of plasma parameters.

Some carriers, such as BiF₃, BaF₂, and NaF with metal concentration from 1 to 10% of mass, were tested in order to optimize the atomic-emission analysis. The choice of these carriers is caused by possible fluorination reactions running in the crater of the carbon electrodes, as well as different ionization potentials and atomic masses of the carrier cations.

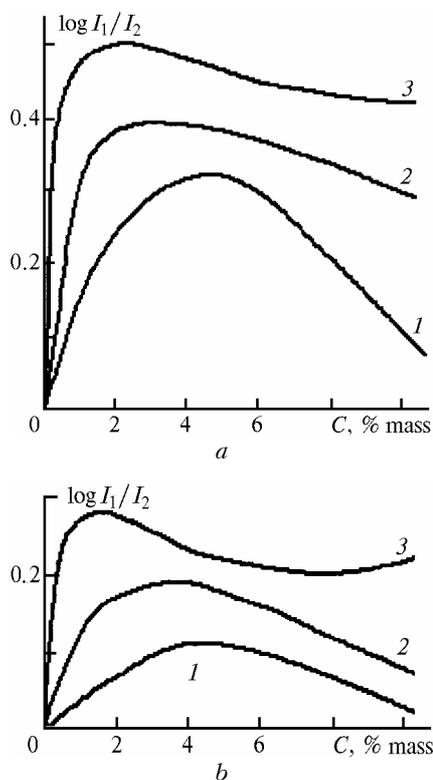


Fig. 1. Relative change of the spectral line intensity (Sn, Mn, Mg, Fe, Al (a); Ti, Ni, Pb, Cd, V (b)) vs. the carrier content in a sample: NaF (curve 1), BaF₂ (curve 2), BiF₃ (curve 3).

Figure 1 shows logarithms of the intensity ratio of admixture spectral lines with and without carriers (I_1

and I_2 , respectively). As seen, the spectral line intensity of most elements under study increases in the presence of NaF. As the carrier concentration grows, the intensity passes through a maximum and then drops. Such a behavior agrees well with the results obtained by other authors⁸ and can be explained by a decrease in the arc plasma temperature. Introduction of Ba and Bi fluorides into a sample results in a further (as compared to NaF) intensification of spectral lines of all elements without any exception. The increase in intensity is maximum when their content ranges from 2 to 4% of mass. At a further increase of BiF₃ and BaF₂ concentration, the tendency to a decrease in the line intensity retains.

To explain the mechanism of carrier influence, we have calculated the effective temperature of plasma, electronic concentration, and the degree of ionization of elements to be detected in the discharge zone. The calculated parameters are tabulated in Table 3. The algorithm described in Ref. 9 have been used for calculation. It follows from Table 3 that in the series BiF₃ > BaF₂ > NaF the arc plasma temperature decreases because of the carrier ionization. This fact agrees well with the change of the degree of ionization of the elements to be detected. As the arc discharge temperature increases in the presence of Bi, the degree of ionization increases. The latter must result in a decreased intensity of atomic spectral lines of the elements to be detected. However, the experimentally observed phenomenon is just the opposite (see Fig. 1). Apparently, an arc gap is predominantly filled with the carriers, whose concentration far exceeds that of the elements to be detected. Therefore, the carriers not only regulates arc parameters, but also are responsible for diffusion processes running in the discharge zone. Since barium and especially bismuth have large atomic masses, they prevent convective removal and hold atoms, ions, and electrons in the hot discharge zone due to the screening effect. This, in turn, leads to an increase in the spectral line intensity of the elements to be detected.

Table 3. Effective temperature of arc plasma, electron concentration, and degree of ionization of admixture elements depending on the carrier introduced ($C_{\text{carrier}} = 3\%$ of mass, $n = 5$, $P = 0.95$)

Carrier	T, K	$n_e \cdot 10^{-15}, \text{cm}^{-3}$	Degree of ionization, \bar{x}						
			Be	Co	Sn	Ti	Mo	V	Mn
—	6370	0.4	0.16	0.59	0.73	0.58	0.89	0.94	0.96
NaF	5350	0.9	0.01	0.07	0.13	0.06	0.21	0.46	0.61
BaF ₂	5730	1.3	0.01	0.13	0.22	0.13	0.35	0.60	0.73
BiF ₃	5910	0.7	0.05	0.34	0.51	0.33	0.65	0.83	0.90

Note. The confidence interval is $\pm 200 K$ for T and $\pm 0.2 \cdot 10^{-15} \text{cm}^{-3}$ for n_e .

Thermodynamic calculations show that the fluorination can run in a chosen set of carriers. However, for this reaction to run, special chamber electrodes with extra heating are needed. In our case,

as may be judged from the element inflow kinetics in the discharge zone, these reactions do not occur.

We recommend BiF₃ and BaF₂ to be used as a carrier stabilizing the excitation conditions.

Table 4. Results of metrological attestation of the method.

Component to be detected	Random error $\sigma(\Delta)$, %	Total error Δ , %	The standard of prompt control of accuracy and reproducibility, $C = 0.005 \text{ mg/m}^3$,	
			K , mg/m^3	D , mg/m^3
Ba	19	37	0.0019	0.0010
Co	20	39.2	0.0020	0.0010
B	20	39.2	0.0020	0.0010
Mn	22.5	44.1	0.0023	0.0011
Mg	16	31.4	0.0016	0.0008
Fe	22.5	44.1	0.0023	0.0011
Pb	22.5	44.1	0.0023	0.0011
Cr	21	41.2	0.0021	0.0011
Sn	10	19.6	0.0010	0.0005
Ni	22.5	44.1	0.0023	0.0011
Al	14	27.4	0.0014	0.0007
Ti	22.5	44.1	0.0023	0.0011
Cd	16	31.4	0.0016	0.0008
V	14	27.4	0.0014	0.0007
Ag	12	23.5	0.0012	0.0006

Note. The concentrations varied from $5 \cdot 10^{-3}$ to $5 \cdot 10^{-2} \text{ mg/m}^3$; $K = 0.84\Delta$ is the standard of the prompt control of accuracy; $D = 2.77\sigma(\Delta)$ is the standard of the prompt control of reproducibility.

Based on the studies conducted, we have developed a technique of chemical–spectral analysis of samples of the atmospheric air, air of an industrial zone, and industrial emissions. The technique has been metrologically tested by the MI 2336–95 algorithms (Table 4) and approved; some statistics on this technique has been collected.

Conclusions

The optimal method for sample preparation has been proposed to be used with aerosol filters of any type.

The conditions of atomic–emission spectral analysis of atmospheric and industrial aerosols have been optimized; the metrological attestation of the method against the RF State Standard requirements has been conducted.

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