

CHARACTERIZATION OF THE CHEMICAL COMPOSITION OF ATMOSPHERIC AEROSOL AS PART OF AN INTERLABORATORY EXPERIMENT

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In this paper we present an intercomparison made among the results from chemical analysis of atmospheric winter aerosol obtained using four independent techniques at the background station in Novosibirsk region. Systematic errors are shown to appear in some cases due to specific features of the methods used. The results of statistical processing of the data obtained, after their reduction to normal distribution, are presented.

INTRODUCTION

Impacts of aerosol upon the quality of air, atmospheric processes, and regional and global climate are determined by the particle size distribution, concentration, chemical composition, and particle morphology.¹ Individual atmospheric species vary in concentration from $n \cdot 10^{-9}$ to $n \cdot 10\%$ mass, what makes a serious problem in analytical support of the studies targeting atmospheric aerosol.

Chemical analysis of aerosol species widely uses modern, high-sensitivity, instrumented techniques: neutron-activation analysis (INAA) and X-ray fluorescent analysis (XFA), atomic-emission spectroscopy (AES) with different sources of spectrum excitation (inductively bonded plasma, direct current arc, etc.). The atomic-absorption spectrometry (AAS) is a single-species and, hence, much rarely used method, both in flaming and electrothermal versions. Each analytic technique has advantages and limitations and, consequently, specific sources of systematic errors (bias) that may translate into erroneous results. Most suitable methods for analysis of atmospheric aerosol, sampled by blowing air through filters made of the different materials (such as Whatman-41), are INAA and XFA using synchrotron radiation (XFA SR); they are capable of detecting simultaneously up to 40 species at an $0.1n$ to $n \cdot 10^{-5} \mu\text{g}/\text{m}^3$ level without presampling. However, certain care is necessary when using results of determining low-concentration species obtained using only one technique, particularly in the absence of reference samples of chemical composition.² Interlaboratory analysis improves reliability and

substantially lowers the possibility of obtaining erroneous data due to the bias in analytical techniques.

The present paper reports some results of interlaboratory analysis of atmospheric winter aerosol sampled in the southern Novosibirsk region.

EXPERIMENT

Sampling. Air samples were collected at a station near Karasuk village between February 5 and March 3, 1992, by blowing air through Whatman 41 filter at a constant pressure without size separation. Filter size is 500 cm², and the total volume of air blown is 700 m³. We analyzed separate parts of one and the same filter. In the control experiment we estimated reference values using pure filter. Concentration of aerosol species was calculated by the formula

$$C_i = 500 \left(\frac{M_i}{S_i} - \frac{M_f}{S_f} \right) / V,$$

where C_i is the concentration of the i th species in the atmospheric aerosol in $\mu\text{g}/\text{m}^3$, V is the volume of air blown, M_i and M_f are the contents of the i th species in the sample and filter, correspondingly, and S_i and S_f are the areas of the sample and pure filter.

Presampling. Filters with aerosol were dissolved in a closed volume* using strong hydrofluoric and nitric acids mixed in proportion 1:10 by volume; the

* In the experiment, we used polytetrafluoroalcoxyethylene by VitLab company (Germany).

treatment was for 3 h at a temperature of 100°C under infrared illumination. After filtering out of a white-colored deposit, the obtained solution was used for AES and AAS analyses. The same procedure was used for pure filter in the control run.

We employed the following analysis techniques.

NEUTRON-ACTIVATION ANALYSIS (INAA)

This is the direct analysis of filters which are pressed into tablets of 10 mm diameter after exposition to the thermal neutron flux of 22×10^{13} n/(cm²·s). Exposition time is 1 min for short-lived isotopes and 48 h for long-lived isotopes. Reference samples are STA-FFA-1, STA-AS-1 (Poland), SOIL (MAGATE), GM (Germany), SBMT-02 (Russia).³ Measurements of the induced radioactivity were made using a gamma-spectrometer LP-4900 Nokia and a Ge-Li detector GT-80B. Relative error of the analysis is 0.15–0.20.

The results presented are obtained at two independent laboratories, INAA₁ and INAA₂.

X-RAY FLUORESCENT ANALYSIS WITH THE USE OF SYNCHROTRON RADIATION (XFA SR)

This is the direct analysis of a filter in a special cell. Synchrotron radiation beam of 25–20 keV energy and diameter 1.4 mm is used to excite fluorescence. For light species (Ca–Na), the excitation energy is 10–16 KeV. As a reference, we took Whatman-41 filters coated with Ca, Fe, Cu, Zn, and Sr salts for calibration of the K-band of X-ray fluorescence, and then extrapolated these results to other elements.⁴

ATOMIC-EMISSION SPECTROSCOPY WITH SPECTRUM EXCITATION BY ARC (AES)

This is the direct analysis of graphite concentrate of impurities that is obtained by evaporating the solution after ashing the filter. A quartz spectrograph ISP-28 with a two-lens system was used to illuminate 10 μm wide slit for 8 s. As a reference sample we used

graphite powder with coatings of species salts. Relative standard deviation is 0.30–0.50.

ATOMIC-ABSORPTION SPECTROPHOTOMETRY (AAS)

This is the analysis of a solution after filter ashing. A Perkin-Elmer 303 version was employed in the analysis. Standard aqueous solutions of salts were used for calibration. The relative standard deviation was 0.05–0.08 for the flaming variant (Ca, Mg, Fe, and Zn) and 0.15–0.20 for the electrothermal variant (Pb, Mn, Cr, Sb, etc.).

RESULTS AND DISCUSSION

Statistical processing was performed of the results obtained by four or more techniques. Figure shows curves of the frequency distributions for Cr, Mn, Fe, Zn, Cu, Ca, Na, Al, and V in logarithmic coordinates. Many peaks in the distributions for Al, V, and Ca demonstrate their complicated character due to nonuniformity of the data obtained. The reason is high random error in determining Ca and Al due to high variance of the control run. For V concentrations about $n \cdot 10^{-3}$ μg/m³, i.e. near the sensitivity limit of the analytical technique, not only the random error is high, but also there appears a bias.

Skewness of the lognormal distribution for Cu toward positive values is due to the presence of biases of the same sign. This may be caused by different factors, but the most probable one seems to be the absence of correspondence between the reference samples and analyzed ones when the direct analysis techniques (INAA, XFA SR) are used.

Averaged results of the chemical analysis for each of the methods (geometrical means) and their rms errors, calculated as in Ref. 5, are presented in the Table I.

As seen from the table, in general different analytical methods of determining chemical composition of atmospheric aerosol reasonably agree within 50% uncertainty.

TABLE I. Chemical analysis of aerosol (Karasuk village, 1992): *C* is the geometrical mean concentration in μg/m³, *S*_{logC} is the rms deviation of log*C*, *n* is the number of measurements.

Element	Method														
	INAA ₁			INAA ₂			XFA SR			AAS			AES		
	<i>C</i>	<i>S</i> _{logC}	<i>n</i>	<i>C</i>	<i>S</i> _{logC}	<i>n</i>	<i>C</i>	<i>S</i> _{logC}	<i>n</i>	<i>C</i>	<i>S</i> _{logC}	<i>n</i>	<i>C</i>	<i>S</i> _{logC}	<i>n</i>
Mn	0.021	1.76	30	0.026	1.76	30	0.029	2.76	24	0.019	2.25	13	0.015	2.44	25
Cr	0.019	3.14	30	0.023	2.79	30	0.067	2.93	17	–	–	–	0.034	4.94	30
Fe	0.315	1.78	30	0.674	1.48	30	0.819	1.49	28	0.567	1.69	30	0.584	3.13	30
Al	0.94	1.73	30	1.38	1.79	29	–	–	–	1.14	3.39	22	1.06	4.72	29
Zn	0.048	1.88	30	0.123	1.72	30	0.078	1.67	28	0.047	2.34	28	–	–	–
Ca	0.52	1.75	27	0.004	3.93	12	2.46	1.38	28	0.49	2.17	26	0.91	2.6	13
Na	0.23	1.97	29	0.31	1.97	27	–	–	–	0.24	1.75	30	–	–	–
Cu	2.9	4.1	30	3.8	4.18	30	5.3	3.69	28	3	5.06	30	2.8	3.94	30
V	0.007	1.78	30	0.009	1.92	28	0.24	3.29	28	0.003	2.79	27	–	–	–

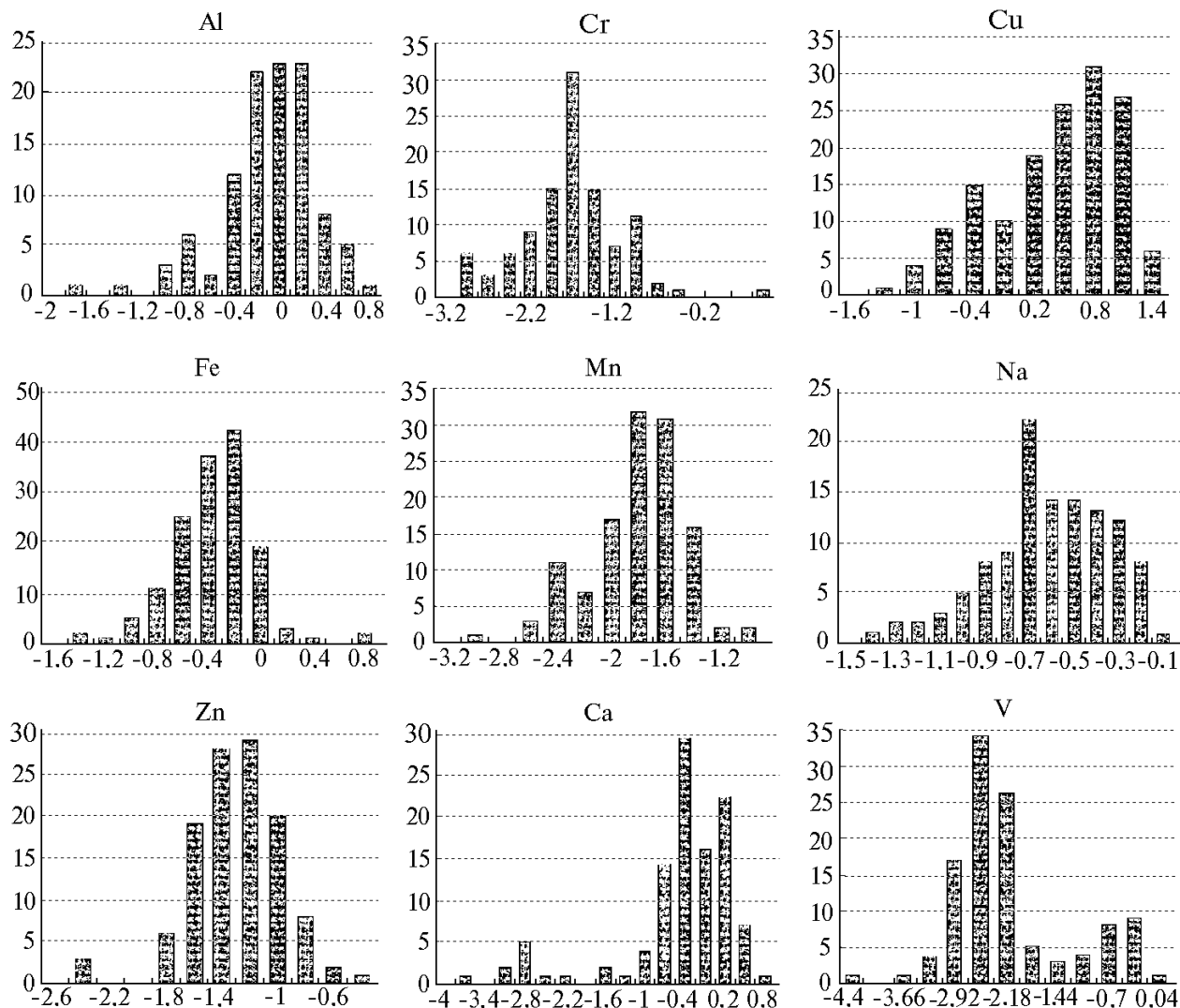


FIG. 1. Lognormal distributions of the results of determining chemical composition of winter aerosol (Karasuk village, 1992).

Substantial discrepancies occur in some cases, due to the biases of the methods employed (Ca – INAA₂ and XFA SR, V – XFA SR). It should be noted that deviations from the universal geometrical means are most significant in XFA SR results for the majority species because of specific features of the method (instability of the synchrotron radiation beam), as well as due to the lack of correspondence between the reference samples and actual objects analyzed.

CONCLUSION

The results of interlaboratory comparison experiment on characterization of the chemical composition of atmospheric aerosols presented clearly illustrate the importance of having reliable data on aerosol composition and the difficulty of their acquisition. At the same time, only “trueB data can serve as a basis in modeling atmospheric phenomena on local, regional, and global

scales. Choice of an analysis technique environmental monitoring must scrutinize all the alternatives, especially if no reference samples are available.

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