

Determination of the Phase Composition of Atmospheric Aerosol Using the Reference-Free Method of Differentiating Dissolution

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Abstract

Reference-free method of differential dissolution (DD) is used to obtain the data on stoichiometric composition and content of solid phases, including those of variable composition, in the samples of multi-element multiphase atmospheric aerosols. In aerosol sample collected in one of the regions of Novosibirsk, the content of water-soluble fractions (presumably hydrosulphites) of a series of metals was determined, as well as the content of individual calcium phase (presumably carbonate), calcium sulphate phase, and two aluminosilicate phases. In these phases, formed by the major elements comprising aerosol (Si, S, Al, Fe, Mg, Ca, K, Na), the content of a series of admixture elements was determined. For the alkaline-earth elements as example (Mg, Ca, Sr, and Ba), the ratios of these elements was determined in the phases formed by the major elements Mg and Ca, and by microelements Sr and Ba. It is concluded that the possibility to obtain detailed quantitative data on the phase composition of aerosols is essentially important in investigating various aspects linked both with the mechanisms of formation and evolution of atmospheric aerosols and with their effect on the status of environment.

INTRODUCTION

Chemical composition of solid atmospheric aerosols is usually characterized by total content of elements comprising aerosol. For many reasons, it is rather difficult to determine the phase composition of aerosols; so, the corresponding data are scarce. At present, structural methods are prevailing in the area of phase analysis: XPA, as well as IR spectroscopy, Raman spectroscopy, NMR, NGR and some others. However, it is well known that for the analysis of multi-element multiphase substances, of which atmospheric aerosols are an example, the efficiency of structural methods decreases sharply, first of all because of their insufficient selectivity and sensitivity. In such a situation, one should separate complicated matter into simpler mixtures or individual phases. However, non-destructive physical methods

are not indented for such a purpose. The most important item is that all the methods of phase analysis are based on the use of reference samples of individual phases. Complicated samples may contain unknown phases for which it is impossible to prepare reference samples. For this reason, quantitative phase analysis is very seldom; only X-ray diffraction patterns are published, as well as various spectra, which mainly provide only qualitative characterization of the phase composition of substances to be analyzed.

Many of the listed limitations can be overcome with the help of relatively new chemical method of phase analysis, *i. e.*, differentiating dissolution (DD) [1, 2]. The possibilities of this method are unique, because it allows simultaneous determination of both the stoichiometric formulas of complicated substances and quantitative content of solid phases in them

without using the corresponding reference samples.

Principles of the DD method and numerous examples of its use for the phase analysis of complicated samples have been reported many times. To explain in brief, the essence of this method is dynamic regime of dissolution of a mixture of phases with temporal changes in the composition, concentration and temperature of solvents, and with simultaneous determination of the stoichiometry of elemental composition of the substance flux. An increase in concentration and temperature of solvents is accompanied by an increase in their chemical potential μ . As a consequence, different solid phases pass into solution sequentially as soon as the corresponding μ value is achieved. However, solid phases are destroyed by dissolution, and one can only record the rate of dissolution of elements comprising these phases. The dissolution in dynamic regime, *i. e.* with programmable temporal change in composition and concentrations of components of solvents, is conducted from the initial soft conditions to the final rigid ones, providing complete dissolution of the sample to be analyzed. The composition of solvents and specific characteristics of the dynamic dissolution regime are strongly dependent on the characteristics of real structure of the solid phases: their disperse state and defects of lattice. For specific objects of analysis, these parameters can be determined only empirically.

The kinetic dependence of dissolution of elements is further transformed into stoichiograms, which are a dependence of molar ratio of elements on time. The total number of stoichiograms is equal to the number of combinations two by two of all the elements comprising the sample to be analyzed. If the single phase is dissolved, stoichiograms of the corresponding elements are constant during all period of time; they are equal to stoichiometric coefficients connecting these elements in the simplest formula of this solid phase. If two or more phases are dissolved simultaneously, stoichiograms will be variable during such a period. So, DD allows determining phases by their prime characteristic, *i. e.* stoichiometry of elemental composition. It is important that the objects for DD can be phases of constant and

of variable composition, both crystalline and amorphous ones. High sensitivity of DD method allows one to perform microanalysis and to determine microphases in macro objects. At present, a special instrument called stoichiograph [3] has been developed for the DD analysis, together with a special procedure of stoichiographic titration with the help of which one can rapidly analyze samples of unknown phase composition [4].

The basic limitations of DD method depend, on the one hand, on chemical nature and real structure of solids (when their dissolution goes on too rapidly or too slowly), as well as on some effects of the interaction between solids and solvents (formation of precipitates, gaseous products, *etc.*). On the other hand, limitations are explained by the ability of analyzing detector of the stoichiograph to determine the elemental composition of solutions in full. Unfortunately, at present there are no adequate methods of determination of a series of elements, first of all hydrogen and oxygen. In this case, the corresponding formulas of phases turn out to be fragmentary since they depict the stoichiometry only with respect to elements under determination. It has been agreed [5] that index 1 in a fragmental formula of a simple or complex compound will be used to distinguish these formulas from traditional ones. For example, a fragmentary formula of magnesium chromite MgCr_2O_4 is Mg_1Cr_2 .

The DD method was already used in the phase analysis of various solids: catalysts, high-temperature superconductors, luminophors, inorganic pigments, *etc.* [6–8], including aerosol [9]. In the present paper we report on new results related to the determination of phase composition of atmospheric aerosols which were obtained in the investigations within the integration programme of SB RAS “Aerosol of Siberia”.

EXPERIMENTAL

Stoichiograph and procedures for DD analysis

In the scheme of stoichiograph (Fig. 1), 1 and 2 are reservoirs with components of a solvent, for example, the first one containing

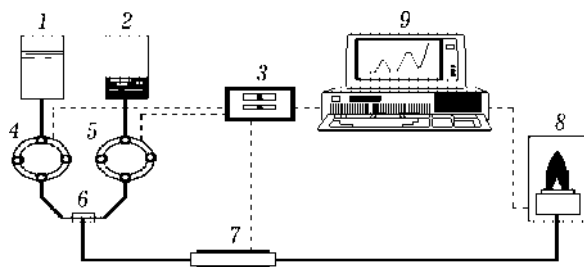


Fig. 1. A scheme of stoichiograph (for explanations, see text).

water and the second one containing concentrated HCl solution. With the help of peristaltic pumps 4 and 5, the components of the solvent are admitted through capillaries into mixer 6 at variable rates. The electronic device 3 governs the rates of these flows according to a prescribed programme so that a united flow is admitted from the mixer 6 into reactor 7 at a constant flow rate (~ 2 ml/min) and continuously increasing concentration of the solvent containing HCl. The dissolution of a weighed portion of the substance to be analyzed is placed in reactor 7; the resulting solution enters directly into the analyzing detector 8, which is atomic emission spectrometer with inductively

coupled plasma (AES ICP) operating with polychromator (38 analytical channels). The operation of the entire system is controlled by computer. Stoichiograph allows one to perform phase analysis in flow or stationary reactors using macro or micro weighed portions of the substance to be analyzed.

Some possibilities of the stoichiograph can be characterized by the following data: up to 38 elements of the Periodic Table in a required combination can be determined in the solution formed by means of the differential dissolution; the sensitivity is about $n \cdot 10^{-3}$ mg/ml, error is 1–5 %, periodicity of measurement is 1 s and more. This allows one to carry out almost continuous recording of the kinetic curves of dissolution and to observe fine effects during the process. The software package for the computer of stoichiograph allows one to perform all the necessary calculations. As a rule, for the AES ICP working in combination with polychromator, the error of determining element concentrations does not exceed 5 %. As a consequence, error of determining stoichiometric coefficients in empirical formulas and quantitative content of phases does not exceed 10 %.

TABLE 1

Elemental composition of the aerosol, determined by means of atomic emission spectroscopy with inductively coupled plasma, % of the sum of masses of all the elements under determination

Element	Weighed portion No.			XPA SR*
	1	2	3	
Al	27.3	25.2	22.9	no data
Fe	18.4	20.2	18.8	13.8
Cu	0.13	0.036	0.008	1.24
Ni	0.23	0.29	0.025	0.057
Mn	0.61	0.28	0.11	0.10
Cd	0.33	0.19	0.31	no data
Zn	1.38	2.16	4.14	0.21
Cr	0.32	0.036	0.00	0.00
Co	0.51	0.16	0.081	0.00
Mg	6.63	7.09	6.88	no data
Ca	28.5	33.9	39.1	35.4
Na	6.05	4.43	4.06	no data
Sr	0.044	0.051	0.081	0.001
Ba	0.23	0.18	0.15	0.00
K	9.32	5.76	3.37	8.50

*The data of X-ray fluorescent analysis using synchrotron radiation.

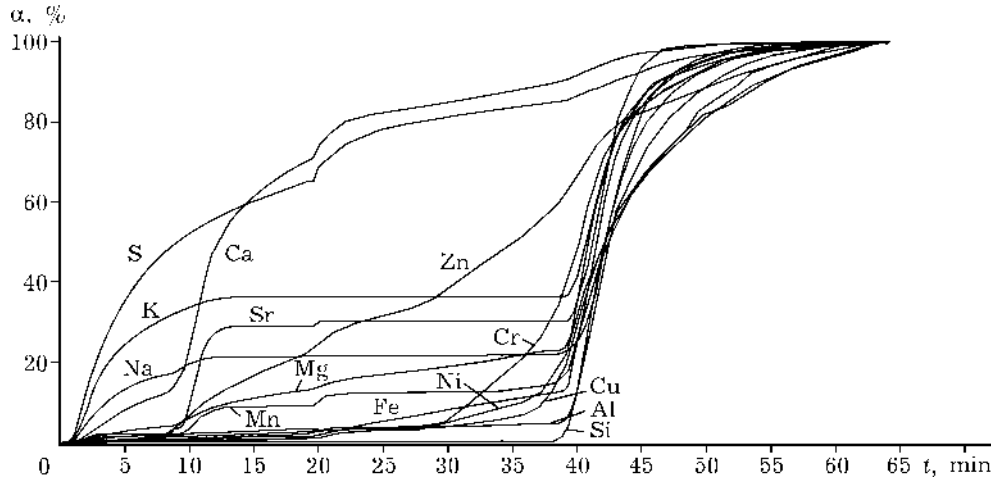


Fig. 2. Kinetic curves of dissolution of elements incorporated in aerosol.

Phase analysis of aerosol samples was performed in the flow dynamic regime of dissolution, in the regime of stoichiographic titration, changing the composition of the solvent sequentially from H₂O to HCl (pH 2), further to HCl solution (1 : 10) and then to HF solution (1 : 5). In doing this, solvent temperature increased from 0 or 20 to 50 °C.

An analyzed aerosol sample was a strip of a filter (1 × 7 cm²) which was placed into a flow reactor of the stoichiograph.

The procedures for the AES ICP determination of elemental composition of solutions formed during differentiating dissolution of aerosol samples were developed preliminarily; 15 elements were determined: Na, K, Mg, Cu, Ca, Sr, Ba, Zn, Cd, Al, Si, S, Fe, Co and Ni. The effects of mutual influence of the elements under determination were taken into account, as well as the effects linked with the

changes in composition and temperature of solutions.

Objects under investigation

The objects of phase analysis were atmospheric aerosol samples collected on filters in one of the regions of Novosibirsk. Sampling was carried out by researchers from the Institute of Chemical Kinetics and Combustion, SB RAS, according to the programme of works on the integration project of the SB RAS "Aerosol of Siberia".

RESULTS AND DISCUSSION

The amount of information on chemical composition of aerosol which can be obtained by means of the DD technique is many times

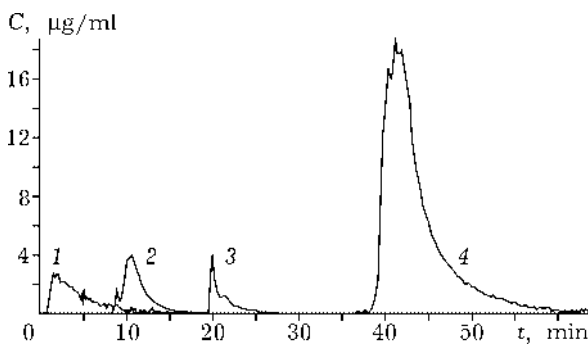


Fig. 3. Kinetic curves of phases dissolution (fragmentary formulas): 1 - Me_{0.95}S₁, 2 - Me₁, 3 - Me₁S₁, 4 - silicates.

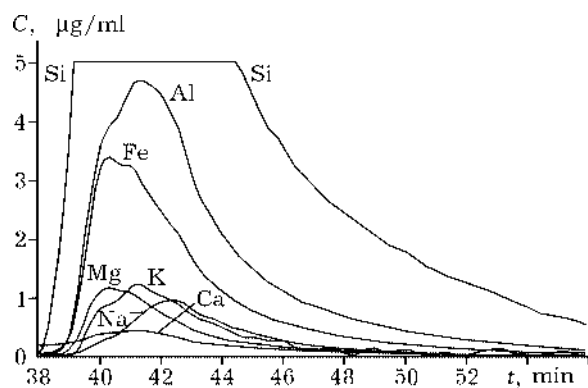


Fig. 4. Kinetic curves of elements dissolution in the silicate region.

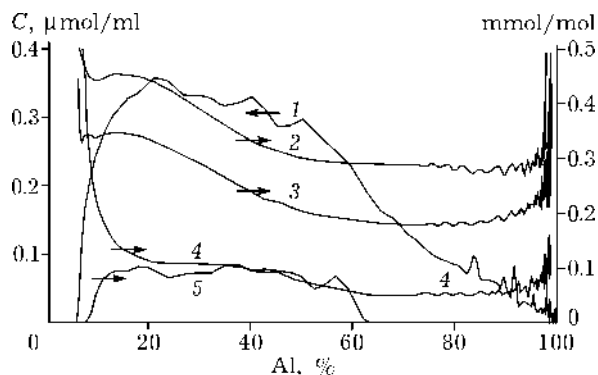


Fig. 5. Kinetic curve of the dissolution of silicon (1) and stoichiograms of Fe : Al (2), Mg : Al (3), Ca : Al (4), K : Al (5).

more than that obtained by usual elemental analysis. A detailed description of the results of DD requires too much space, so, below we will list only the basic and, in our opinion, most interesting data concerning composition and content of the main and admixture phases, as well as the distribution of admixture elements over these phases. For the same reason, only a part of the kinetic curves of dissolution of elements (in differential or integral forms) and a part of the corresponding stoichiograms are shown in the Figures. It is almost impossible to show the kinetic curves of dissolution of all the 15 elements and all the possible 105 stoichiograms in one figure and in one and the same scale. However, all these dependencies were taken into account when performing computer calculations.

The results of phase analysis of the atmospheric aerosol sample No. 19 are shown below.

The data characterizing elemental composition of the aerosol are shown in Table 1. These

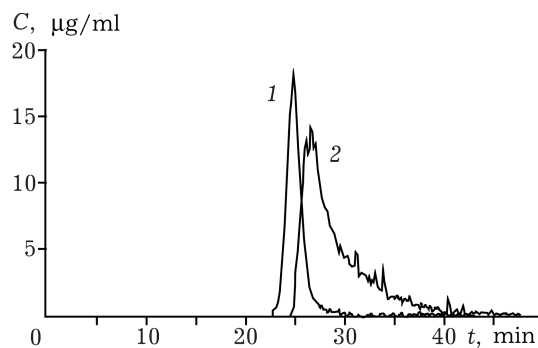


Fig. 6. Kinetic curves of dissolution of silicate phases (fragmentary formulas): 1 - $\text{Fe}_{0.45}\text{Mg}_{0.34}\text{Ca}_{0.11}\text{K}_{0.09}\text{Al}_{1.00}\text{Si}_x$, 2 - $\text{Fe}_{0.28}\text{Mg}_{0.18}\text{Ca}_{0.53}\text{Al}_{1.00}\text{Si}_x$.

data relate to the dissolved part of aerosol (the data on oxygen and carbon content are absent; data on silicon and sulphur content are not taken into account). Aerosol sample was analyzed three times but the corresponding data were not averaged since the reason of differences in the analysis results may be non-uniformity of the aerosol composition. Attention should be paid to the fact that the mass of aerosol weighed portions for analysis was only about 1 mg. The results of elemental analysis of this aerosol sample by means of X-ray fluorescent analysis using synchrotron radiation (XPA SR) are listed in the same Table. These results have been obtained at the Institute of Chemical Kinetics and Combustion within the Programme of inter-calibration investigations of the Aerosol of Siberia Project. The absence of sufficient statistical data does not allow us to draw strict conclusions concerning the metrological characteristics of these two techniques of analysis of aerosol. However,

TABLE 2

Results of phase analysis of the aerosol by means of DD

The region of dynamic dissolution regime	Fragmentary formulas of the phases; Content, % mass	The most probable chemical nature of the phases
H_2O	1) $\text{Me}_{0.95}\text{S}_1^*$ (Me = K, Na, Ca); 10.3	1) Potassium, sodium and calcium hydrosulphites
$\text{H}_2\text{O} \rightarrow \text{HCl}; \text{HCl}$	1) Ca_1 ; 10.4 2) Ca_1S_1 ; 22.0	1) Calcium hydroxide or carbonate 2) Calcium sulphate
$\text{HCl} \rightarrow \text{HF}; \text{HF}$	1) $\text{Fe}_{0.45}\text{Mg}_{0.34}\text{Ca}_{0.11}\text{K}_{0.09}\text{Al}_{1.00}\text{Si}_x$; 37.8 2) $\text{Fe}_{0.28}\text{Mg}_{0.18}\text{Ca}_{0.53}\text{Al}_{1.00}\text{Si}_x$; 19.5	Both phases (1, 2) are complex silicates of variable composition

*When calculating the stoichiometric coefficient of the formula $\text{Me}_{0.95}\text{S}_1$, the difference in the changes of ions $(\text{K}, \text{Na})^{+1}$ and Ca^{+2} was taken into account; the coefficient 0.95 corresponds to Me^{+1} .

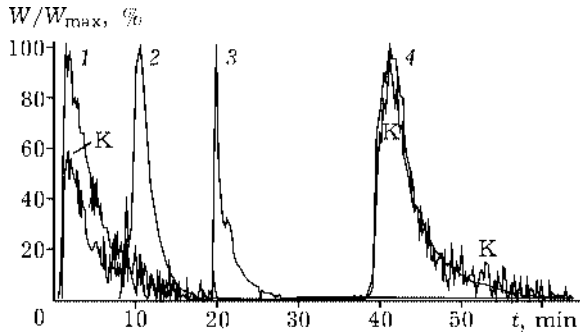


Fig. 7. Kinetic curves of the dissolution of water-soluble phase (1), calcium carbonate (2), calcium sulphate (3), silicates (4), and potassium.

taking into account non-uniformity of the elemental composition of the sample under analysis, we can stress moderate convergence of the results obtained in different laboratories by different analysis procedures (AES ICP and XPA SR).

The initial kinetic curves of dissolution of the elements incorporated in the aerosol are

shown in Fig. 2 in the integral form; these curves characterize the extent of dissolution of each element *versus* time. This form allows us to represent the corresponding dependencies for all the elements in one scale, though the absolute content of these elements varies within 3–4 orders of magnitude.

The kinetic curves of dissolution of phases incorporated into aerosol are shown in Fig. 3 in the differential form. These dependencies were reconstructed with the help of stoichiographic calculations from the dependencies shown in Fig. 2. As an example, Fig. 4 shows the scaled-up kinetic curves of dissolution for the elements of the silicate part of aerosol; stoichiograms $Me : Al$, where Me are the basic elements comprising aerosol, are shown in Fig. 5. On the basis of these dependencies, the stoichiographic calculations were performed; they allowed us to determine the fragmentary formulas and quantitative content of the two silicate phases (Table 2) and reconstruct kinetic

TABLE 3

Elemental and phase composition of aerosol

Element	Mass, mg	Distribution between phases, %				
		$Me_{0.95}S_1$	Ca_1	Ca_1S_1	Silicates	Individual phases*
Al	91.5	1	1	3	95	–
Fe	61.6	–	2	10	88	–
Si	280.1	–	–	–	100	–
Cu	0.043	–	–	10	90	–
Ni	0.78	–	–	–	50	(50 ?)
Mn	2.04	–	10	5	85	–
Cd	1.11	–	5	5	40	50
Zn	4.63	2	10	5	40	43
Cr	1.07	–	–	–	70	30
Co	1.72	–	–	–	70	30
Mg	22.2	5	15	5	75	–
Ca	95.7	–	70	15	15	–
Na	20.3	20	2	–	78	–
Sr	0.14	2	25	3	70	–
Ba	0.77	–	20	7	73	–
S	81.2	67	–	15	18	–
K	31.2	36	–	–	64	–
Σ	696.8					

*Element forms its own microphase.

TABLE 4

Ratios of alkaline-earth elements content of the aerosol phases

Phase	Ca : Mg : Sr : Ba molar ratio
Water-soluble	1 : 0.11 : 0.00027 : 0.00032
Calcium carbonate	1 : 0.078 : 0.00078 : 0.0010
Calcium sulphate	1 : 0.063 : 0.00019 : 0.0013
Silicates	1 : 2.44 : 0.0027 : 0.0033

curves of the dissolution of these phases (Fig. 6). Table 2 also shows the fragmentary formulas of the other detected phases and the data on the quantitative content of these phases in the aerosol sample under analysis.

However, it turned out that the paper filter used for collecting aerosol sample was contaminated with silicon, its mass being about 40 % of the silicon mass contained in the weighed portion of aerosol under analysis. Because of this, the DD data on silicon transfer into solution were distorted, which did not allow us to determine accurately the corresponding stoichiometric coefficient for the fragmentary formulas of silicates.

It is natural that the fragmentary formulas cannot provide a complete characterization of the phase content. Along with this, comparison between the fragmentary composition and conditions of dissolution for the phases in DD analysis, on the one hand, and chemical properties of the corresponding elements on the other hand allows assuming the most probable chemical nature of these phases (see Table 2).

It is important to note that in the flow regime a possibility arises to dissolve micro-phases of both the basic and admixture elements in a minimal volume of solvent. In doing this, the whole solution enters the analyzing detector of the stoichiograph. This allows to diminish the element detection limit by 1–2 orders of magnitude, compared with the analysis of solutions containing fully dissolved weighed portion to be analyzed. The kinetic curves of dissolution of the detected phases, as well as of potassium, are shown in Fig. 7. The dependencies are shown in the differential form and normalized for the maximal rate of the dissolution of phases and elements, which allows

us to represent all the dependencies in one and the same scale. One can see that potassium is incorporated only into the water-soluble and silicate phases. Similar dependencies were used to calculate the data shown in Table 3. These data characterize quantitatively the distribution of all the elements over the major phases of aerosol.

The DD technique allows obtaining other non-ordinary kinds of information on the chemical composition of aerosol. For example in Table 4 there are the data characterizing relative content of four alkaline-earth elements in three phases with prevailing calcium content and in two silicate phases (as a sum) in which magnesium content is prevailing. One can see that the relative content of these elements in the phases is rather different. The data of this kind can be substantial, for example in identifying the origin of aerosol.

CONCLUSIONS

We can state on the basis of investigation results that the DD method allows obtaining detailed information on the chemical composition of atmospheric aerosol. The quantitative data on the phase composition of the aerosols may be undoubtedly important in investigating the formation mechanisms and evolution of atmospheric aerosols, as well as their impact on the environment.

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