Stoichiography: New Ways Determining Chemical Composition and Real Structure of Materials

V. V. Malakhov*

Boreskov Institute of Catalysis SB RAS, 5 Lavrentieva str., 630090 Novosibirsk, Russia

Abstract

The principles of stoichiography and novel reference-free methods of molecular and phase analysis for complex unknown mixtures are considered. The stoichiography can be inferred from stoichiometry of mass transfer of unsteady homo- and heterophase processes and joins both operations: separation of mixture by means of chromatography, electromigration, dissolution or others and determination of stoichiometry of a substance flow with time. The stoichiography allows a chemical compound to be determined by its primary property, namely, by stoichiometry of elemental composition. Stoichiograms provided a basis for such type of information. They are time variances of molar ratio for mass transfer rates of chemical elements from multielement substances. Invariancy to concentration and temperature of solvents, hydrodynamic regime is a fundamental property of the stoichiograms in the case of individual compounds. Therefore the stoichiograms are kept constant and are equal to formula stoichiometric coefficients of the individual compound. Theory and methodology of new stoichographic methods, differential dissolution and ion-chromato-stoichiography are presented. New equipment, stoichiograph, and a new procedure of differential dissolution, stoichiographic titration, are discussed here in details. Applications of differential dissolution to analyze multielement and polyphase crystalline and amorphous samples are given.

The author devotes this paper to memory of his teacher, Professor O. A. Songina, an outstanding scientist, who began to develop fundamental ideas concerning chemical and electrochemical methods of the phase analysis. The essence of this paper was reported on International Conference of Analytical Chemistry, which was organized on the occasion of the 100th Birthday of Professor O. A. Songina on May 22-25th, 2001, in Almaty, Kazakhstan.

Introduction

The general principles of stoichiography as a new idea concerning stoichiometry of mass transfer of unsteady homo-, and heterophase processes are considered here. Such processes are the basic part of all separation methods in chemistry. Stoichiography, as such, appeared as a result of prolonged search of effective ways to solve one of fundamental problems of chemistry how to determine molecular composition of unknown compounds in complex mixtures. The problem of similar nature is long ago not in elemental analysis since all stable elements are discovered, their total number is quite limited, and methods are known how to determine any element in the presence of other elements. In contrast, the number of chemical compounds in nature is infinite and most of them have yet to be discovered.

The stoichigraphy principles were formulated and firstly used by us during development of a novel chemical method of the phase analysis [1-4]. The phase analysis, a version of the molecular analysis, deals with inorganic solids of different origin: from natural minerals to materials of high technologies. Our attention to the phase analysis of inorganic solids was absolutely regular. This field of analytical chemistry is one of most stubborn and poorly known, and inorganic analysis differs principially from molecular organic analysis. For organic mixtures just compounds rather than elements are determined. This is nonsense to characterize an organic mixture consisting for example from alcohols and aldehydes, in terms of total amounts of carbon, hydrogen, and oxygen. For multielement, multiphase inorganic solids, in contrast, it is the typical situation to determine

---

*corresponding authors. E-mail: malakhov@catalysis.nsk.su

only their gross elemental composition. Methods of the elemental analysis are, to be sure, used to determine compositions of single-phase compounds. However, first we must isolate this individual compound from mixture that may be difficult if not impossible to realize. Difficulties increase if the phase composition of sample under study is unknown, that is indeed typical for inorganic solids.

Selective dissolution is believed to be the basic chemical method of the phase analysis. However, this method being applied to solution of many modern aims of the phase analysis was doomed to failure. Below we will comment actual reasons of the failure, but notice that discarding this method as useless, analytical chemistry has wholy rejected also chemical approach to the phase analysis. As a result, today almost no specialists are in this field and only short notices concerning the phase analysis may be found in analytical textbooks. In this situation the phase analysis has become the subject of structural, spectroscopic and x-ray diffraction studies. However, it is known that efficiency of these physical methods is depressed by their scarce selectivity to analyse multielement and multiphase samples. In this situation again the necessity occurs to separate multiphase mixtures into ordinary fractions or even into individual phases, but being nondestructive, these physical methods are not meant for the purposes. And the all-important factor in the phase analysis is that the physical methods are built upon the use of reference materials of individual phases. And what is left for researchers to do when novel phases are present in samples under study? Even for known phases, it is difficult, if at all possible, to prepare reference materials totally identical with analyzed phases because of imperative distinctions between their real structures depending strongly on preparation conditions. As a rule, for multiphase samples the quantitative phase analysis using physical methods is performed more rarely than the qualitative phase identification.

Stoichiography allows many difficulties and limitations typical to modern methods of molecular and phase analysis to get over. The capabilities of stoichiography are unique because their basic principles allow qualitative and quantitative molecular and phase analysis to be performed without the use of reference materials for individual phases. By this technique stoichiometric formulas and quantities may be determined not only for known but also for novel chemical compounds forming the mixture. The principles of stoichiography are considered here by the

example of two stoichiographic methods: differential dissolution (DD) and ion chromato-stoichiography (ICS). The first is a novel reference-free technique of the phase analysis of solids. The second resulted from transformation of the well-known separation technique into the reference-free technique determining ionic composition of solutions.

Differential dissolution

The basis of the DD method is two physical-chemical regularities that determine:
1) the course of successive dissolution processes of individual phases from multiphase mixtures under the dynamic regime produced specially;
2) the variation of the dissolution stoichiometry during these processes.

Dynamic regime of chemical reactions

Describing kinetics of a chemical reaction $A+R=P$ usually one assumes that initial concentrations of A and R decrease while the concentration of P increases. If R is taken in a large excess, its concentration is believed to be kept constant in the course of the reaction whereas concentration A and P decreases and increases, respectively.

The unsteady kinetics proposes infinitely many different regimes of the chemical reactions. From these regimes it should be set off the dynamic regime that opens new possibilities in solution of many problems of chemical analysis and synthesis. This regime differs from others in that a concentration of reagent R taken in excess should increase with time, for example linearly, though a some part of R is used for interaction with A [3]. With increasing concentration C_R, the solvent chemical potential μ increases as well since $\mu = \mu_0 + RT \cdot lnC_R$. By this way different solid phases should dissolve one by one as fast as the chemical potentials of each phase and the solvent are made identical in magnitudes. This is necessary to notice that in chemical literature no papers were found where dissolution of solids under the unsteady dynamic regime was examined under such viewpoint. There is the full analogy between the dissolution dynamic regime and stripping voltammetry, and kinetic curves of the phases dissolving have profiles similar with profiles of voltammograms, Figs. 1 and 2.

Unfortunately, during dissolution solids are broken up and thus only curves of elements dissolving, more rarely of fragments or complex ions, rather than curves of phases dissolving can be recorded. And the

problem arises how to reconstruct curves of elements dissolving into those for phases. This problem has been settled based on the stoichiography principles. These principles related to dissolution processes are formulated as regularities of the dissolution stoichiometry.
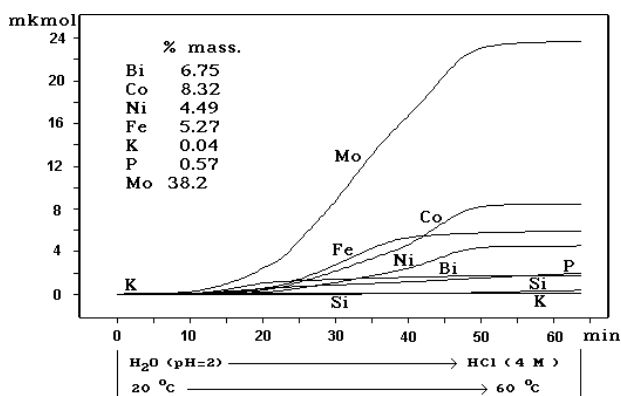

Fig. 1. Kinetic curves of elements dissolving and element contents for a multielement catalyst. Dissolving conditions are given in the bottom row.
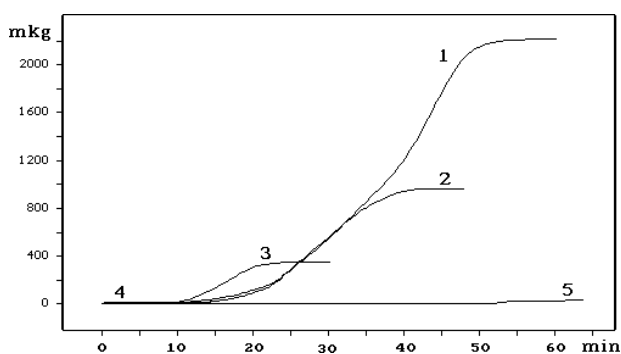

Fig. 2. Kinetic curves of phases dissolving and fragmental formulas for the same catalyst as in Fig.1: (1) $Ni_{0.313}Co_{0.567}Fe_{0.051}Bi_{0.022}P_{0.022}Mo_{1.0}$; (2) $Co_{0.026}Fe_{0.647}Bi_{0.043}P_{0.031}Mo_{1.0}$; (3) $Bi_{1.040}P_{0.44}Mo_{1.0}$; (4) K_2Mo_1; (5) Si.

Dissolution stoichiometry

The dissolution stoichiometry S is a set of molar ratios in wich elements passes from the solid into the solution at every moment of time, i.e. S is equal to the ratio of dissolving rates of the elements. The dissolution stoichiometry as a function of time, $S_i(t)$, is named as stoichiogram [1]. The number of the stoichiograms i for m chemical elements may be determined as the number of the paired combinations:

$$i_m^2 = \frac{m!}{2(m-2)!} \qquad (1)$$

The regularities determining the shape of the func-

tion $S_i(t)$ itself allow compositions (as empirical formulas) and amounts of individual phases of analyzed multiphase mixtures to be determined directly without the use of the phase reference materials and without special isolating individual phases from the mixture.

Invariancy of stoichiograms

Invariancy to dissolution conditions is the most important property of the stoichiograms of individual phases. The dissolution rate is known to depend on nature and real structure of phases. The term real structure is here used in reference to such parameters as shape, size porosity, and specific surface area of crystallites. On the other hand, the dissolution rate depends on the dissolution conditions such as chemical composition and concentration of solvents, temperature and hydrodynamic regime. Profile of stoichiograms in the case of individual phases are unaffected by all above parameters. For example, the stoichiogram of NaCl will always be $S_{Na:Cl}=1$, no matter what real structure had the sample, and what solvent and dissolution conditions were used. Fig. 3 shows dissolution of a high-temperature-superconducting $YBa_2Cu_3O_x$ single crystal under varying concentration and temperature of solvent. This process occurs with violent evolution of oxygen that has an important effect on the reacting area of the solid. As a result, strong oscillations appear on the kinetic curves of Cu and Ba dissolving whiles the stoichiogram Cu:Ba itself remains absolutely linear.
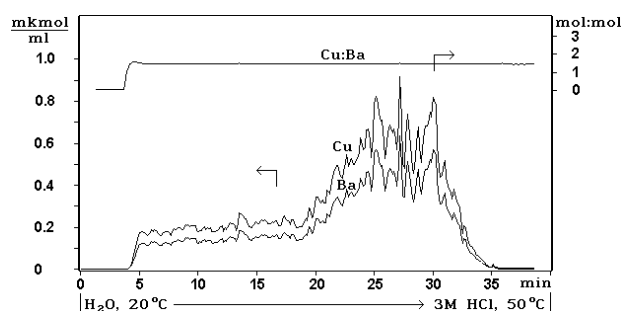

Fig. 3. Effect of oxygen evolution on profile of kinetic curves of Cu and Ba dissolving for a single crystal $YBa_2Cu_3O_x$. The stoichiogram Cu:Ba=1.5 remains linear during whole dissolving. Conditions are given in the bottom row.

It is apparent that the invariance principle is merely other formulation of a common statement that the chemical composition depends on neither amount nor conditions of existence of the compound. And there

appear new and unexpected applications of the principle. First, there is a possibility to change widely the dynamic regime parameters for reaching conditions of sequential dissolution of phases. Second, there is a possibility to determine realibility the separation degree of phases during their dissolution. To have a look at time-profiles of the stoichiograms will be large enough for this purpose.

The main regularities of dissolution stoichiometry

The time-profile of stoichiograms is determined by two main rules.

1) If any individual multielement phase dissolves, for all time molar ratios of its elements taken by pairs, S_i, retain constant and equal to stoichiometric coefficients c_i of the solid phase, i.e. $S_i(t) = c_i$.

2) In periods of simultaneous dissolution of two or more phases, molar ratios only of those elements held constant, which form one from these phases. It is the case shown in (1), when $S_i(t) = c_i$ =const. The remaining molar ratios S_j will be variable in time and $S_j(t) \neq$ const.

Let's to consider how the regularities show themselves if modeling mathematically the two-phase mixture $A_2B_3 + AB_3$ differential dissolution [5]. A classic model of reducing sphere was taken for the calculation, for which the integral form of the kinetic equation for the i-phase ($i=1, 2$) is:

$$\alpha = 1 - \left(1 - \frac{k}{r} \times \tau\right)^3 \qquad (2)$$

Here α is the degree of phase dissolution; τ is the time; r is the initial radius of spherical particle; k is the reaction rate constant; and $k = k^0 exp(-E/RT)c^n$, where k^0 is the constant of pre-exponential factor multiplied by the stoichiometric coefficient of the solid-solvent reaction; E is the activation energy; T is temperature; c is a solvent concentration, n is order of the reaction.

It was adopted that kinetic equations of two phases differ only by order of the reaction: $n_1 = 1$ and $n_2 = 2$. Figure 4 (A) shows the stoichiogram $S_{B:A}$ and differential kinetic curves of A and B dissolving from the mixture $A_2B_3 + AB_3$. It is seen that when the only phase A_2B_3 dissolves, the stoichiogram $S_{B:A}(t)$ over the (t_{01}- t_{02}) interval remains constant and equal to 1.5. When only the AB_3 phase dissolves, the stoichiogram $S_{B:A}(t)$ is also constant over the ($t_1 - t_2$) interval but it is equal to 3. For the simultaneous dissolution

of these phases over the ($t_{02} - t_1$) interval the stoichiogram is variable, $S_{B:A}(t) \neq$ const.
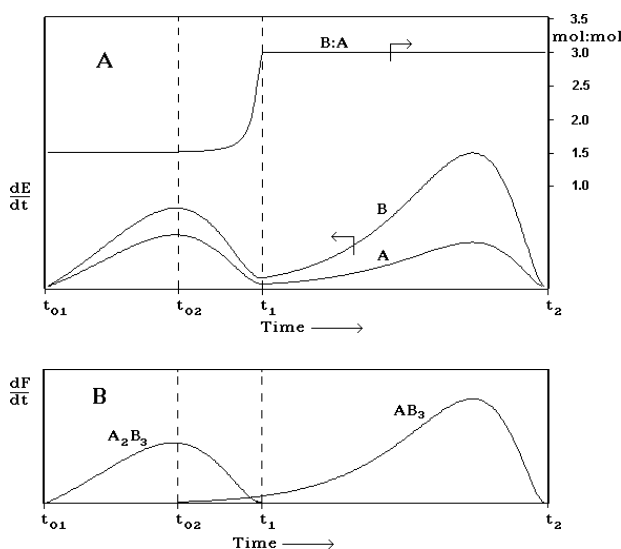

Fig. 4. (A) Kinetic curves of A and B elements dissolving and stoichiogram B:A for a model mixture $A_2B_3 + AB_3$. (B) Kinetic curves of phases dissolving for the same mixture as in (A).

In a general case at a period of simultaneous dissolution of two phases $AB_{C_1} + AB_{C_2}$ the molar ratio of A and B, i.e. $S_{B:A} = (dB/dt) : (dA/dt) = dB/dA$ at each moment of time t will be:

$$\frac{dB}{dA} = \frac{c_1\beta\xi + c_2}{\beta\xi + 1} \qquad (3)$$

where A and B refer to chemical elements; c_1 and c_2 are stoichiometric coefficients; $\beta = \mathbf{A_1}:\mathbf{A_2}$; $\mathbf{A_1}$ and $\mathbf{A_2}$ are moles of element A in AB_{C_1} and AB_{C_2}, respectively; $\xi = (d\alpha_1/dt) : (d\alpha_2/dt)$; α is the degree of dissolution; $d\alpha_1/dt$ and $d\alpha_2/dt$ are the dissolution rate of AB_{C_1} and AB_{C_2}, respectively [1].

There is no hope to describe prior dissolution kinetics of a real mixture of phases without knowing during the dissolution the order of reactions, the rate constants, activation energy of dissolution, reacting phase surfaces for each phase. Since these values are unknown, a shape of the function $\xi(t)$ from eq. (3) remains to be unpredictable. Along with this, the obligatory property of $\xi(t)$ is to be variable in time and for the model of the reducing sphere, for instance, the function $\xi(t)$ must be hyperbolic. Accordingly, the function $S_i(t)$ will be always variable if several phases dissolve simultaneously and rigorous proofs of this conclusion have already been considered in details in [2].

Selectivity of phase separation.

The selectivity of continuous processes is usually estimated by a ratio of parallel reactions rates. Therefore, the stoichiogram profile is direct characteristic of the differential dissolution selectivity. A marker of the selective dissolution is constant in time and linear sections on the stoichigrams and, then, to increase the selectivity, conditions should be varied such way to minimize all variable sections. The selectivity of DD may also be characterized by the degree of phase co-dissolution A_{21}, Fig. 5 [5]. Co-dissolution of two phases, $AB_{C_1} + AB_{C_2}$ or $F_1 + F_2$, (in the reducing sphere model) may be described as:

$$A_{21} = 1 - \left\{ 1 - \frac{r_1}{r_2} \times \frac{k_2^0}{k_1^0} \times \left[\exp \frac{E_1 - E_2}{RT(\tau_1)} \right] \times [C(\tau_1)]^{n_2 - n_1} \right\}^3 \quad (4)$$
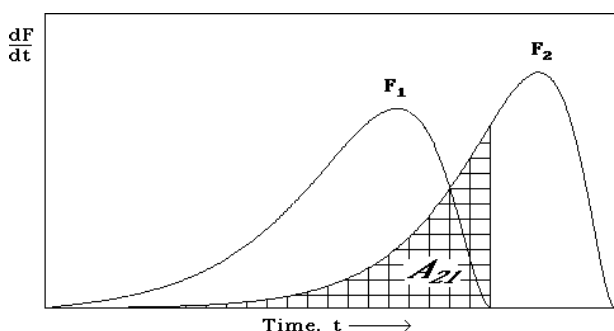

Fig. 5. Kinetic curves of F_1 and F_2 phases dissolving, co-dissolution region A_{21} is crosshatched.

For i phases ($i = 1, 2$) r_i is the initial radius of particle; k_i^0 is the pre-exponential factor; E_i is the activation energy; T is temperature; C is a solvent concentration; n_i is the order of reaction; $T(\tau)$ and $C(\tau)$ are the time-functions of temperature and concentration; τ_1 is time of the full dissolution of AB_{C1} phase.

Now we consider the most fascinating dependence of the co-dissolution degree of phases $AB_{C_1} + AB_{C_2}$ and shapes of the function $C_S(t)$ versus a change of the solvent concentration in time. The shape of $C_S(t)$ is determined by values of Z from eq. (5):

$$C(t) = k \times C^Z \quad (5)$$

Here k is the constant; $Z = (dC_\tau/dt)/(dC_o/dt)$, dC_o/dt and $dC\tau/dt$ is the change rate of the solvent concentration at initial moment C_0 and at moment of full dissolution of the mixture C_τ.

A set of the $C_S(t)$ functions *versus* Z are given in Fig. 6. For Z<1 the solvent concentration increases fast in initial period, and then slows down. For Z>1

the inverse dependence is observed. For Z=1 the solvent concentration increases linearly in time. The separation efficiency of the mixture $A_2B_3 + AB_3$ for Z equal to 0.001, 1.0, and 1000 is shown in Fig. 7. It was suggested that kinetic equations of individual phases dissolving differ from one another only by the order of the reaction, $n_1 = 1$, $n_2 = 2$, while other parameters were similar. Our modeling has verified of the fact that variations of the shape of $C_S(t)$ lead to variations of the selectivity for the phase separation: the selectivity increases essentially with increasing the parameter Z.

Stoichiographic calculations

The results of the stoichiographic calculations are empirical formulas and amounts of individual phases for mixtures. Both a set of kinetic curves of elements dissolving and a set of stoichiograms serve as the basis for the calculations. For two-phase mixture $AB_{C_1} + AB_{C_2}$ (or F_1 and F_2) the following parameters become known due to DD:

1) the number of moles, **A** and **B**, for A and B elements passed into the solution. The values of **A** and **B** may be determined at each moment of time from the kinetic curves of these elements dissolving;

2) the formular stoichiometric coefficients of phases, c_1 and c_2, based on linear sections of the stoichiogram $S_{B:A}$, for example, sections over the t_{01}- t_{02} and t_1- t_2 intervals in Fig. 4 (A).

The kinetic curves of the elements dissolving may be recorded in integral form as functions $A(t)$ and $B(t)$ given in Fig. 8 and in this case amounts of elements are expressed in moles. To determine c_1 and c_2 the functions of $A(t)$ and $B(t)$ are transformed to a parametric function $B(A)$ where time serves as the
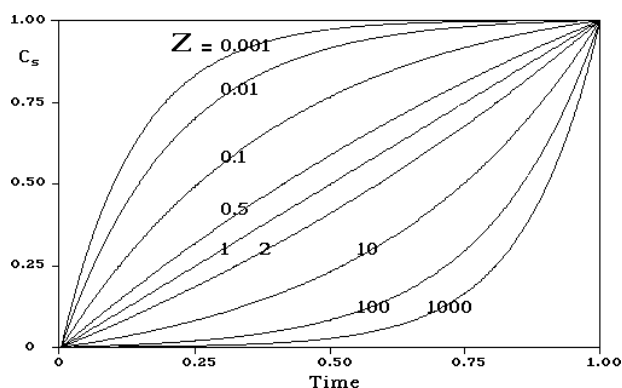

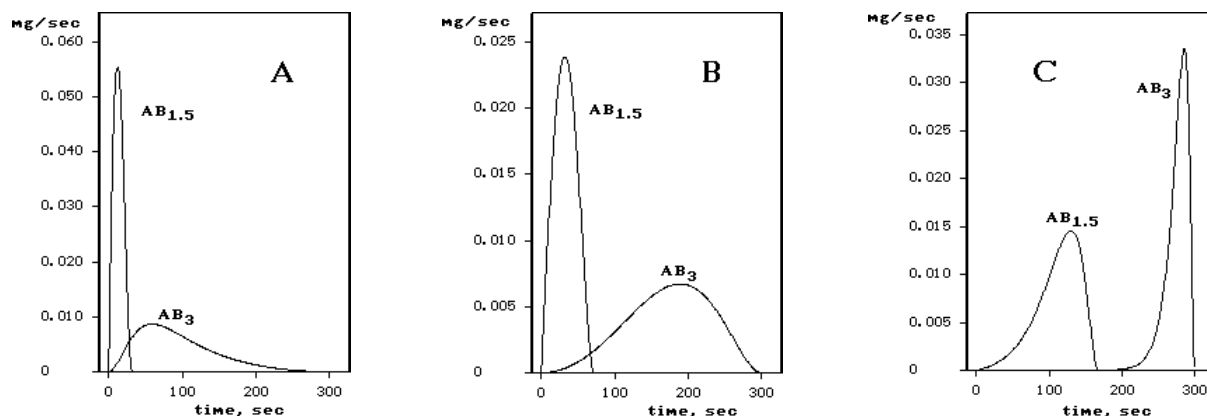Fig. 6. Solvent concentration C_S varied in time versus Z from eq. 5.

Fig. 7. Selectivity of separation of the same mixture as in Fig.4 as a function of Z. (A) Z=0.001; (B) Z=1; (C) Z=1000.

parameter, Fig. 9. The linear sections 1 and 3 of the function $B(A)$ reflect dissolution of individual phases and values of c_l and c_2 are found from $\Delta B_l{:}\Delta A_l$ and $\Delta B_3{:}\Delta A_3$, respectively, to be $c_l=1.5$ and $c_2=3$. The section 2 shows simultaneous dissolution of the phases as shown for the interval $t_{02} - t_1$ in Fig. 4.
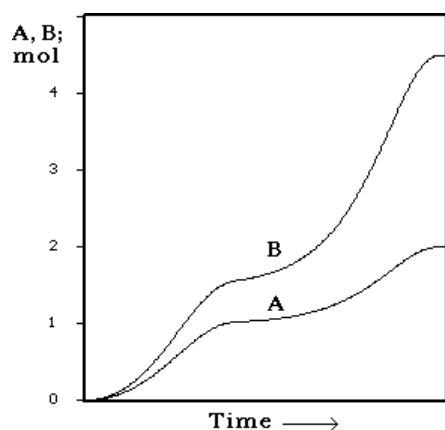

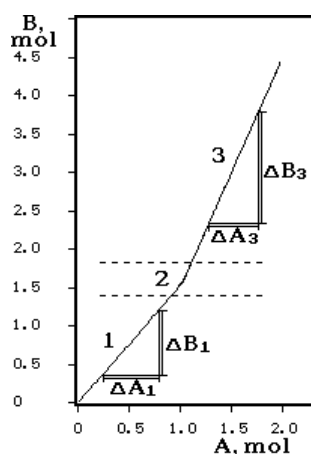Fig. 8. Integral shape of kinetic curves of A and B dissolving for the same mixture as in Fig. 4.

Fig. 9. Parametric function B(A) for the same kinetic curves as in Fig. 8.

If phases were completely separated it is easily to perform the stoichiographic calculations matching up for one time base both the stoichiograms and the kinetic curves. Linear sections of the stoichiograms then lead to stoichiometric formulas of the phases. The appropriate sections of the kinetic curves give amounts of the phases, after summarizing quantities of all elements forming these phases as shown in Fig. 4. If the phase separation was not full (Fig. 4, interval t_{02} - t_1), it is necessary in order magnitudes of $\mathbf{A}_{F_1}$, $\mathbf{B}_{F_1}$, and $\mathbf{A}_{F_2}$, $\mathbf{B}_{F_2}$ were found, i.e. the number of moles for elements A and B in each from two phases AB_{C_1} and AB_{C_2}. Considering that $\mathbf{A}$, $\mathbf{B}$, c_1, c_2 are known and $\mathbf{B}_{F_1} = c_l\mathbf{A}_{F_1}$, $\mathbf{B}_{F_2} = c_2\mathbf{A}_{F_2}$ a set of two equations with two unknown terms $\mathbf{A}_{F_1}$ and $\mathbf{A}_{F_2}$ are solved for each moment of time:

$$\mathbf{A} = \mathbf{A}_{F_1} + \mathbf{A}_{F_2}$$

$$\mathbf{B} = c_l\mathbf{A}_{F_1} + c_2\mathbf{A}_{F_2} \qquad (6)$$

Accordingly, the number of moles for each from two phases F_1 and F_2 are $F_1 = A_{\mathbf{F}_1}$ and $F_2 = A_{\mathbf{F}_2}$. As a result, the kinetic curves of elements dissolving may be recalculated to those of phases dissolving and in this case areas under the kinetic curves correspond to amounts of the phases as seen in Fig. 4 (B).

Unfortunately, now there are no analytical methods adequate to DD determining such elements as oxygen, hydrogen, and nitrogen. And formulas of phases with these elements are only fragmental and reflect stoichiometry of determined elements. So, Mg_1Cr_2 is fragmental formula of $MgCr_2O_4$. The only formula Fe_1 will be suitable for Fe(II), Fe(III) oxides and elemental Fe^0 as well. So, index "1" in the fragmental formula of simple or complex compounds shows distinction of the DD formulas from those traditional [6]. However, when nature of samples analyzed is known (oxide or sulfide, for examples)

we can use the traditional arrangements of the DD formula. The limitations in determination of the above named anions are incidentel to the nature of DD, and they may behandled as soon as novel methods determining these elements will appear.

Dissolution kinetics of real processes

Solid phases may be identical in stoichiometric compositions what can hardly be said about their real structures. It is difficult to propose and control a variety of real structures therefore it is impossible to describe rigorously the dissolution kinetics of a real phase mixture prior since compositionally similar samples being treated variously show different types of the dissolution kinetic curves. Dissolution in HCl of a series of samples prepared from initial α-Fe_2O_3 ($S_{surf.}$ = 170 m^2/g) with identical granular compositions but dissimilar specific surface areas is shown in Fig. 10. The greater was a calcination temperature of the initial oxide, the smaller became the specific surface area and the greater time is required to dissolve wholly this sample. It is seen as in accordance with real structures of the samples the kinetic curves varied from the σ-shape to the s-shape with an induction period [3]. Fig. 11 shows the selectivity of separation in the case of the three-phase mixture, $ZnO + CuO + Al_2O_3$. As may be seen the kinetic curve of ZnO dissolving consists of three sections, 1, 2, and 3, that means dissolution of three fractions of ZnO with different real structures. Positions of these sections relative to the kinetic curve for CuO as well the degree of the ZnO and CuO separation change considerably. We can be assured that dissolution of two polymorphs, for instance, α-Al_2O_3 and γ-Al_2O_3 must come variously as in the case of two organic isomers in chromatography. Fig. 12 shows dissolution of a thin film ZnS doped with Mn deposited during the technological MOCVD process. Two peaks in this case indicate a spatially inhomogeneous distribution of Mn in the film: the Mn:Zn ratio is 0.136 and 0.02 for the thin surface layer and for the width of the film, respectively. Oscillations observed here on the kinetic curves are absent in profiles of chromatography and voltammetry curves since the oscillations reflect features of dissolution of solids, namely their real structure.

Let's now to compare capabilities of two chemical methods of the phase analysis: the selective dissolution (SD) and differential dissolution. Most, if not all processes of the selective dissolution involve systematic errors resulting from not full dissolution and/
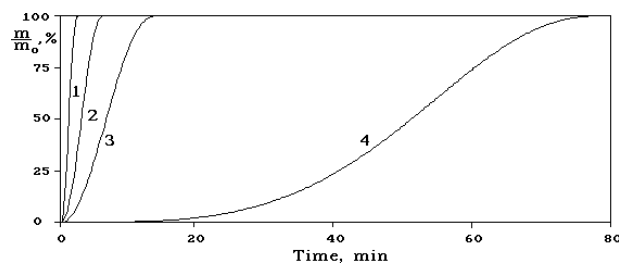

Fig. 10. Kinetic curves of α-Fe_2O_3 phases dissolving as a function of specific surface area (in m^2/g). (1) 170; (2) 62.3; (3) 39.0; (4) 17.0.
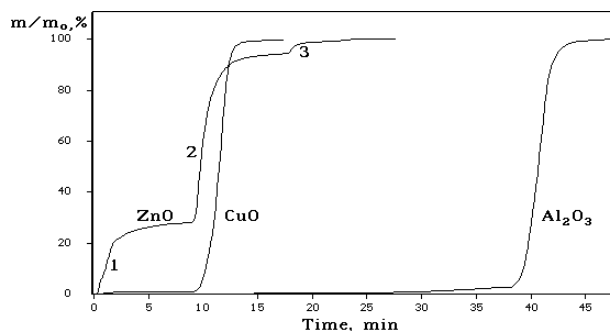

Fig. 11. Kinetic curves of ZnO, CuO, and Al_2O_3 dissolving. Dissolution conditions: dynamic regime, $HNO_3 \rightarrow H_2SO_4$.
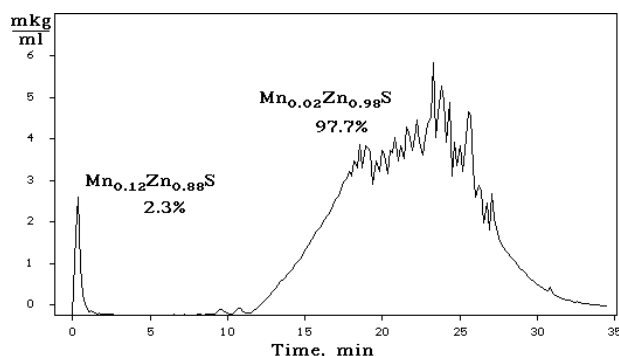

Fig. 12. Oscillation-type kinetic curves for a $Zn_{1-x}Mn_xS$ solid solution dissolving.

or co-dissolution of phases. To minimize these errors, dissolution conditions such as composition, concentration, and temperature of solvents, size of particles, stripping rates, gas atmosphere under solutions, dissolution time should be strongly specified. The SD conditions are empirically selected by preparing the proper reference materials for phases of the mixture to be determined. But a difference in real structures between the reference materials and the phases determined results to an unprovided change of their dissolution rates. The situation becomes more dramatic for samples with unknown before phases. As a result, some ambiguous estimations and incorrect interpre-

tations of the experimental data take place. Besides, being time consuming and "wet" procedure by its very nature, the selective dissolution can hardly be converted into an instrumental tool.

DD is a reference-free technique and, then, may be used for phase analysis, regardless of what known or novel phases are in mixtures. In this case dissolution of the phases under the dynamic regime goes in accordance with their real structure and, therefore, dissolution time even for phases of the identical stoichiometry may essentially vary. However the DD technique identified and determined quantitatively each phase by its primary and intrinsic property, the elemental composition stoichiometry, which as was shown above is independent of real structure and dissolution conditions. Contrary to the selective dissolution, instrumentation of DD is not only possible but of necessity.

Stoichiograph

Theory and methodology of DD have been already known in 1986, but DD analysis came into play as soon as special equipment was designed [1]. The high accurate and sensitive multielement analysis and rapid data processing were taken as the basis of the equipment. The latter procedure is of imperative since even for a 3–5 component sample the stoichiographic calculations take more than 10^6 operations.

Two types of equipment were worked out starting from a possibility to realize DD under steady state and flow regimes. The equipment of steady state type, Fig. 13 (A), is a capacity filled by a low-concentrated solvent taken in large excess with respect to a sample weight. To realize the dynamic regime, small portions of a high-concentrated solvent are gradually added using a burette. To control contents of all elements the solution flow is directed into a detector-analyzer, in other variant the solution may periodically be taken. By such way kinetic curves of elements dissolving are presented in the integral form. The flow-type reactor is shown in Fig. 13 (B). Here a solid reacts at every moment with a fresh portion of the solvent since all products formed are pumped out from the reactor to the detector-analyzer. In this case the kinetic curves are recorded in the differential form.

Each of the regimes has own advantages and disadvantages. The steady-state regime allows large weight of samples and very concentrated acids at temperatures up to 300°C to be used. The former factor is especially important for preparative chemistry when the DD procedure is used for collection or isolation
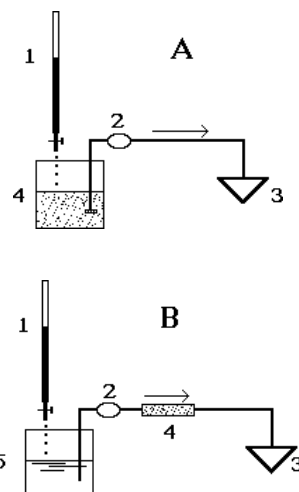

Fig. 13. Schematic diagram of the DD instrument for the steady state (A) and flow (B) variants: (1) burette; (2) pump; (3) analyzer ICP AES; (4) reactor; (5) mixture of solvent components.

of any individual phase from mixtures. But starting with a large initial volume, very diluted solutions are analyzed in the beginning. Besides, the solution volume itself could not be controlled accurately since two operations, sampling for analysis and adding new portions, are performed at the same time. All this reflects considerably on the total accuracy of the DD analysis in this variant. The use of the flow regime, on the other hand, allows us to determine elements with the high sensitivity and accuracy, to minimize the solvent flow rate, and to control carefully the dissolving dynamic conditions.

Stoichiograph as a new equipment for the phase analysis has been designed 10 years ago in Boreskov Institute of Catalysis [7]. Fig. 14 shows the system including vessels (1, 2) with solvent components, for example, H_2O and HCl acid concentrated, electron device (3), peristaltic pumps (4, 5), mixer (6), reactor (7), detector-analyzer, here AES ICP together with 38 channel polycromator (8), and computer (9). The solvent components at different flow rates enter the mixer through capillaries due to peristaltic pumps. Electronic device regulates the rates under the given program so that the one combined flow goes from mixer to reactor with every-increasing concentration at a rate of 2÷4 ml/min. A sample placed in reactor dissolves and the solution flow is directed toward detector-analyzer. All the operations controlled by computer are output on display. Using AES ICP analyzer it is possible to work with macro-, or micro amounts (as small as 10^{-5}g) and to determine up to 38 chemical elements in different combinations.

With metrological parameters of ICP AES such as the sensitivity at the level of n·10^{-3} μg/ml and the error of 1-5 %, errors in determination of stoichiometric coefficients and phase contents were found to be about 10 rel. %. Since the element registration goes in every 1-5 sec, the kinetic curves are recorded practically uninterruptedly. This allows fine features of dissolution process to be considered.
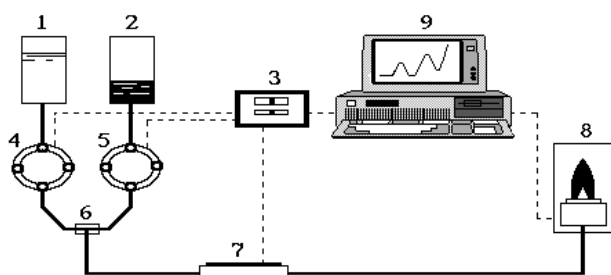

Fig. 14. Detailed schematic diagram of stoichiograph.

The package of computer programs has been developed to realize stoichiographic calculations. Intermediate information may be obtained as kinetic curves of elements dissolving in absolute or normalized type using integral and differential forms as well as stoichiograms. The ended information may be presented in tables and as well as the kinetic curves of individual phases dissolving.

To support idea on the similarity of DD and voltammetry we would like to compare schemes of the stoichiograph and the Geirovskii polarograph, Fig. 15. Vessels with solvents in DD act as a power supply in polarography, electronic device regulating the solvent composition is operated as a slide-wire, the reactor works as the electrolytic cell, and AES ICP performs the function of a galvanometer. However, the polarograph records the only voltammetric curve, the stoichiograph records already "current" of all the elements determined by the AES ICP spectrometer.
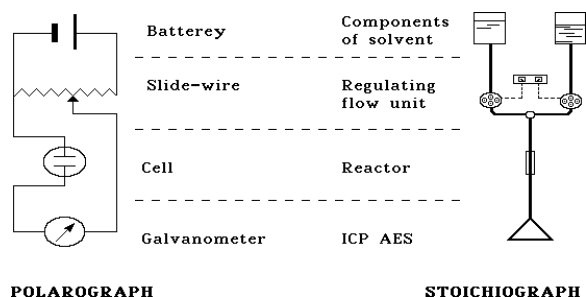

Fig. 15. Schematic diagrams of stoiciograph and polarograph.

Methodology of DD

When phase comosition is unknown, all parameters determining dissolution rate of each phase from the mixture remain also unknown. However with DD there is no need to know these parameters. They may be easily and rapid experimentally found from profile of the stoichiograms. However, to search of the DD conditions, you should know all arsenal of dissolution procedures used in common chemical analysis of solids with different origin. Composition of solvents, concentration boundaries of their components and temperatures are usually specified based on chemical properties of elements of the analyzed sample. After the first response of the system analyzed on the taken conditions, the primary conditions are varied by such way that extent of linear sections of stoichigrams was so far as possible. It is essentially that the dynamic regime is realized and no loss was in mass as insoluble or volatile compounds. But this must not be doing at the cost of a severe sacrifice in metrological analytical parameters.

Information on solvents and temperatures going from "soft to severe" conditions of the dynamic regimes are shown in Table 1. Beginning with water or low-acid solutions (*pH*=2) preventing undesirable effects (hydrolysis, sorption or ionic exchange) the acidity then is increased. An isothermal or temperature-programmed regime may be taken that is dictated by the nature of solids under study. Compositions and temperatures of solvents may vary linearly or by other ways, for example, by stoichiographic titration [8]. The last procedure is especially good to analyze substances with unknown phase composition.

Stoichiographic titration (ST)

Titration is traditionally used in chemical analysis to determine amounts of a well-known substance. ST serves for quantitative determination of both known and unknown phases of complex solids. The procedure consists in correlation between the rates changing parameters of dynamic regime and the observed dissolving rates of elements from the analyzed solid. In the case of ST instead of to observe how an indicator varies its color, an operator observes directly the dissolving procedure reproduced on display in the form of kinetic curves. The necessary correlation is made directly on the course of the dissolution based on two mains rules:

1) to add a solvent more frequently or to increase its concentration or/and temperature, if dissolution

Table 1
Dissolution Conditions for Samples of Different Nature

Samples	Solvents	Temperature, °C
Difficult-soluble spinels	$H_2SO_4 + H_3PO_4 + HClO_4$	~ 300
Silicates		
Alumosilicates	$H_2SO_4 + HF$	60 - 75 (Water-solutions)
Zeolites		
Difficult-soluble oxides		
Sulfides	$HCl + HF$	
Metals		
Oxides	$HCl + HNO_3$	
Hydroxides	NH_4OH	
Nonsoluble salts	HCl H_3SO_4 HNO_3	
Water-soluble salts	H_2O	0 ÷ 20

goes slowly or stopped.

2) to leave the solvent concentration and temperature unchanged if dissolution of only one element goes with a considerable velocity.

In contrary to the classic titration, ST does not require to know the flow of reactant, ratios in which the solvent reacts with the solid phase, and to use reactions only with a high velocity. It is in nature of ST itself: i) to determine quantitatively those products, which are formed between a titrant and a titrated matter, i.e. elements passing into solution, and ii) to give stoichiographic formulas and amounts of individual phases of mixtures after appropriate calculations. Using ST, rapid finding optimal dissolution conditions is possible, often even in the only experiment. Under these conditions dissolution goes consecutively and phases determine quantitatively even if no elemental composition and stoichiometry, no the number and content, no real structure, no dissolution velocities of the phases in mixtures were known prior. As analogous to the stoichiometric titration the following methods may be considered: the gradient elution and temperature-programming chromatography, the Q-regime in thermography, electrolysis at a constant potential in quantitative element analysis.

DD analysis of a varying composition compounds (VCC's)

These compounds occur in nature more often then those of a constant composition, but analytical chemistry does not discuss how to determine quantitatively VCC's in multielement and multiphase mixtures. We do also not consider this problem in details, but would like to notice that DD with its stoichiography principles is able to identify well both of constant and varying composition phases. Fig. 16 shows the ended results of the differential dissolution of a vanadium-bearing oxide metallurgical slag involving VCC's as well. The information obtained by DD on stoichiometry of individual VCC's may be hardly extracted by other methods of the phase analysis. The x-ray diffraction results for this slag are quite row since the observed angle diffraction data could not be related to the expected individual phases. However, to determine composition of any VCC, concentration profiles of all its elements must be spatially uniform over the whole region analyzed. Unfortunately, spatial uniformity of VCC is not always achieved for complex natural and synthetic materials for which equilibrium state, as a rule, establishes too long. In terms of the DD stoichiograms of spatially nonuniform phases are also variable as in the cases of imperfectly separated phases. Therefore an effective criteria, the principle of affinity for stoichiograms, was suggested which allows us to distinguish the variable stoichiograms of co-dissolving phases from those of spatially nonuniform phases [9]. Only the stoichiograms of spatially non-uniform phases will be unresponsive to any changes of the phase dissolving velocities.

The subjects of DD

Stoichiograph and the stoichiographic titration are converted DD into a simple, precise, and express tool of the phase analysis, which has been applied to different materials taken as powders, ceramics, small and large crystals, thin films. We are dealing with catalysts [6,10-17], high-temperature superconductors [18,19], luminophors [20,21], optical materials [22], inorganic pigments [23], natural minerals [3], atmospheric aerosols [24-25], metallurgical slags, archaeological findings, products of mechanical-chemical reactions [26,27], hetero-poly-compounds [12], and others. Analysis was performed for more than 60 elements of the Periodic Table, which have been involved in these materials. Now there are about 100 papers and reports with the DD results. They
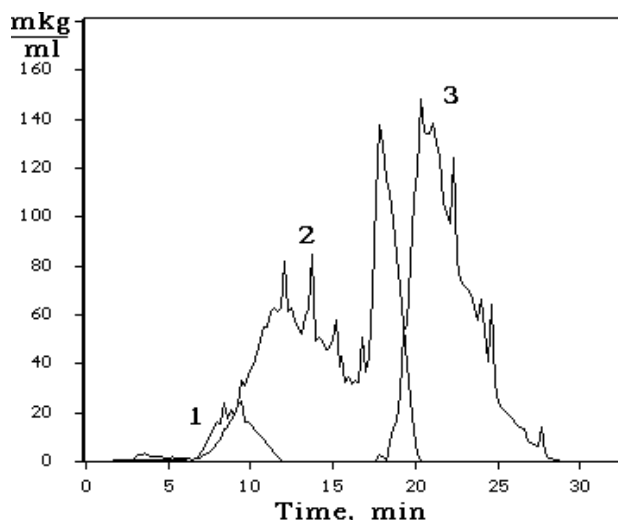
Fig. 16. Kinetic curves of phases dissolving for an oxide vanadium-bearing slag. Formulas of phases: (1) $Ca_2Si_1O_x$; (2) $Ca_1V_{0.18}Si_{0.21}O_x$; (3) $Fe_1 Mg_{0.43}Ti_1O_x$.

were used to a better understanding of origin of the materials as well to improve conditions and to prepare high-quality products. We represent two unconventional examples when phase identification was done for a very thin superconducting film and for an aerosol mineral fraction, collected on filter in one of Siberian regions. The first example shows that informative and accurate data may be obtained by DD even for weight as small as $10^{-5}g$, Fig. 17. Aerosols as multielement and multiphase natural matters are of the most difficult subject for any techniques except of DD. Due to DD, for aerosols unique quantitative results were obtained for the first time. The fraction was dissolved under the dynamic regime, at temperature 20 - 50 ºC using a linear law of the solvent concentration variation runging from water to dilute HCl (pH=2), then to HCl (1:10) and at last to HF (1:5). The kinetic curves of elements dissolving in the integral form are presented in Fig. 18. They show the dissolution degree of each element and allow the kinetic curves of all elements to be plotted in one scale in spite of the element contents are distinguished by several orders in magnitudes. The differential kinetic curves of phases dissolving recalculated from those curves for elements are shown in Fig. 19. Composition and content of the phases are easily determined from this Figure to be water-soluble sulfates - 10.3%, an individual phase of Ca, most probably, carbonate - 10.4 %, the Ca sulfate - 22.0 %, and silicate phases dissolving together (clay minerals) - 57.3%. The content of silica was not determined because of its incomplete dissolution as follows from Fig. 19. By the

following operation the dissolving kinetic curves of the above named phases were combined with the dissolving curves of metallic elements. Figs. 20 and 21 show it for K and Mg elements, respectively, although the similar pictures were also considered with the rest elements. In these pictures the curves are given in the differential form and as the normalized to maximum dissolving rates of the elements and the phases, V/V_m. This consideration leads to results given in Table 2 concerning absolute content of the elements, nature of the phases, and distribution of elements among the phases. We believe none among well-known analytical methods was able to provide results of such type for multielement and multiphase aerosols.

Concluding this section, agreement of results obtained by DD and by other methods for the common matter is achieved since DD was often performed in parallel with the x-ray diffraction, IR and Raman spectroscopy, NMR, EPR methods [10-27]. Doing so, in no case conflicting or incompatible information has been obtained. And every time the need to use DD as the only reference-free technique has been specially underlined. The unique possibilities of DD manifest
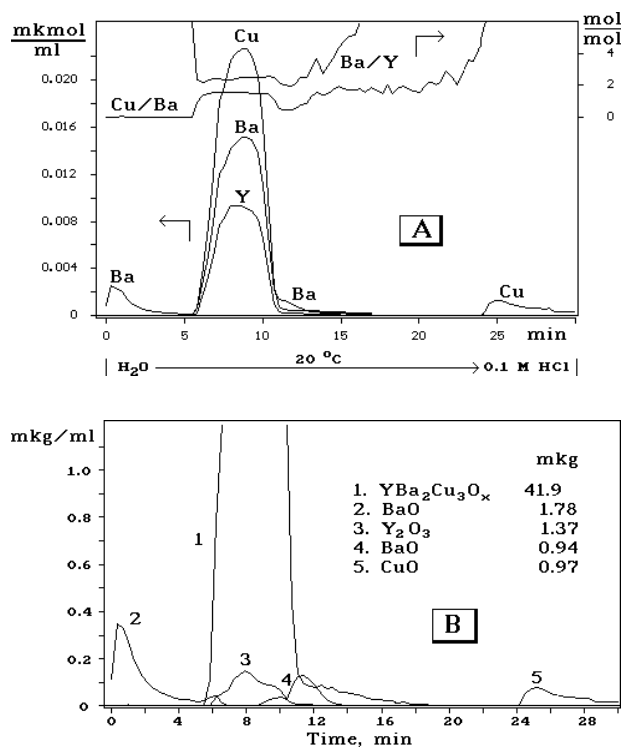

Fig. 17. (A) Kinetic curves of Y, Ba, and Cu dissolving and the stoichiograms Cu/Ba and Ba/Y for a film $YBa_2Cu_3O_x$ with thickness of about 600 Å. (B) Kinetic curves of phases dissolving and their contents recalculated from the same curves as in (A). BaO phase is distributed outside (2) and inside (4) of the $YBa_2Cu_3O_x$ phase.

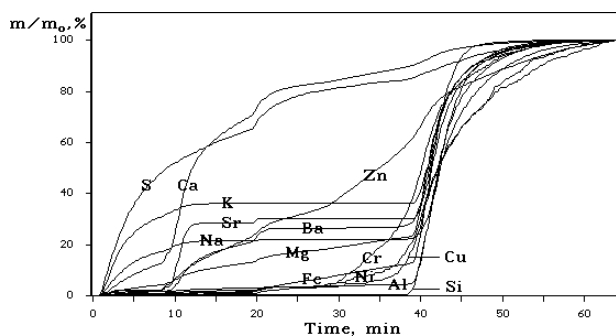Fig. 18. Kinetic curves of 14 elements dissolving for an aerosol. Dissolution conditions are given in the text.

Fig. 20. Dissolving kinetic curves of the same phases as in Fig. 19 normalized to the maximum dissolving rate (1-5) and kinetic curves of potassium dissolving (K).
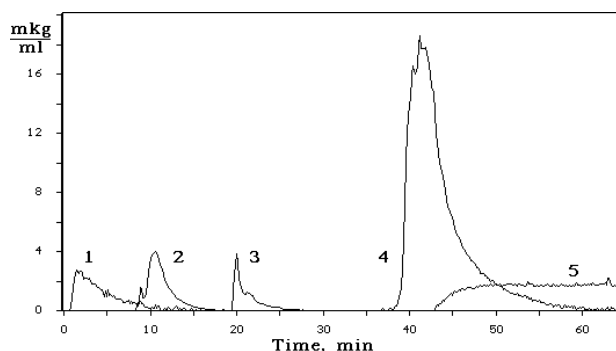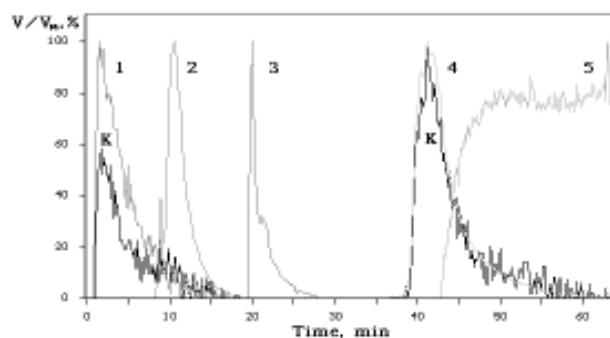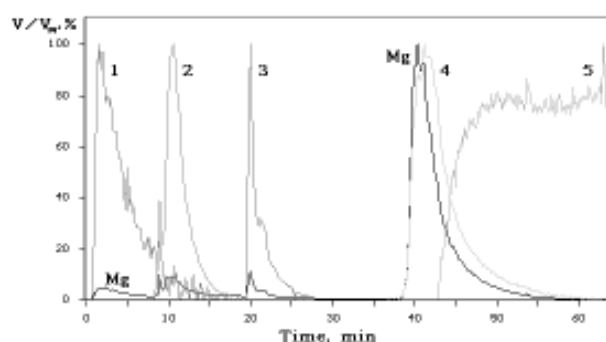

Fig. 19. Kinetic curves of phases dissolving recalculated from the same curves as in Fig. 18: (1) water-soluble sulfates; (2) calcium carbonate; (3) calcium sulfate; (4) silicates (clay); (5) silica.

Fig. 21. The same as in Fig. 20 curves (1-5) and kinetic curves of magnesium dissolving (Mg).

Table 2

Elemental and Phase Composition of Aerosol.

Amounts of elements, μg		Element distribution over phases in rel. %					Individual phases
		Sulfates	CaCO₃	CaSO₄	Silicates	Silica	
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	-	-

Table 2

Continued

Amounts of elements, μg		Element distribution over phases in rel. %					Individual phases
		Sulfates	$CaCO_3$	$CaSO_4$	Silicates	Silica	
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						

themselves especially for mixtures involving unknown phases, amorphous phases, phases with very low amounts, as well phases of a varying composition. Besides, the preparative variant of DD intended to a fine correction of phase composition of multiphase mixtures was also of value. This procedure allows physical properties of matters to be measured and related to an individual phase rather than to any mixture, and allows also the phase interpretation for overlapping signals obtained by structural, spectroscopic, and microscopy methods to be performed correctly [16,17].

Ion-chromato-stoichiography

Separation methods and stoichiography

The stoichiographic approach to the chemical analysis could not been limited only by dissolution processes. Other separation procedures may be also modified to reference-free methods in order to determine molecular or ionic composition of complex substances, Table 3, [10]. With this aim the principles of the dissolution stoichiometry should be over-formulate to the general principles of stoichiography.

1) If a matter flow is an individual compound, molar ratios of each paired elements are kept constant in time and equal to stoichiometric coefficients of the compound.

2) If a matter flow is a mixture of compounds, the molar ratios will be kept constant in time and equal to stoichiometric coefficients only for those elements, which enter into one of the compounds of the mixture. The remaining molar ratios will be variable in time.

Shape of common analytical relationships describing the separation processes may not always be of an indicator of separation completeness and several

Table 3

Separation Methods Promising to be Stoichograpic

Separation	Methods	Types of process
Atomic or molecular level	Chromatography	Heterophase
	Ionic exchange	
	Electrolysis	
	Dissolution	
	Distillation	
	Extraction	
	Diffusion	Homophase
	Electromigration	
	Magnetic mass-separations	
Macrolevel	Gravitational field	Without phase transitions
	Magnetic field	
	Electrical field	

compounds may be hidden in one chromatographic peak. However if the chromatograph is endowed with properties of the stoichograph, the degree of separation of the mixture phases as well as conditions of the full separation will result directly from time-profile of the stoichiograms.

Chromato-stoichiograph

The first variant of such equipment provided with a packet of programs for stoichiometric calculations was designed recently in our Institute. For this purpose the chromatograph "ZVET" and multielement detector-analyzer ICP AES "BAIRD" were combined together [28]. Fig. 22 (A) shows the chromatogram of a Na_2SO_3 and Na_2SeSO_3 aqueous solution recorded

by ion-chromatograph with the electrical-conduction detector. It is difficult to identify correctly the phases based on the overlapping peaks. Two chromatograms of a solution with S and Se elements were recorded then with ion-chromato-stoichiograph, Fig. 22 (B). It is seen two linear parts on the Se:S stoichiogram with molar ratios Se:S equal to 0 and 1, that determines two types of anions in the mixture: anions only with S and with fragment formula S_1, and anions with both

S and Se elements in the ratio of 1:1 with fragment formula S_1Se_1. The performed stoichiographic calculations led to individual chromatograms for S_1 and S_1Se_1 and their contents in the solution were determined to be 2.96 and 0.55 mg/ml, respectively, Fig. 22 (C). Doing so, we need not to record chromatograms for the SO_3^{2-} and for $SeSO_3^{2-}$ reference solutions and use only the common calibration standard with S and Se elements.
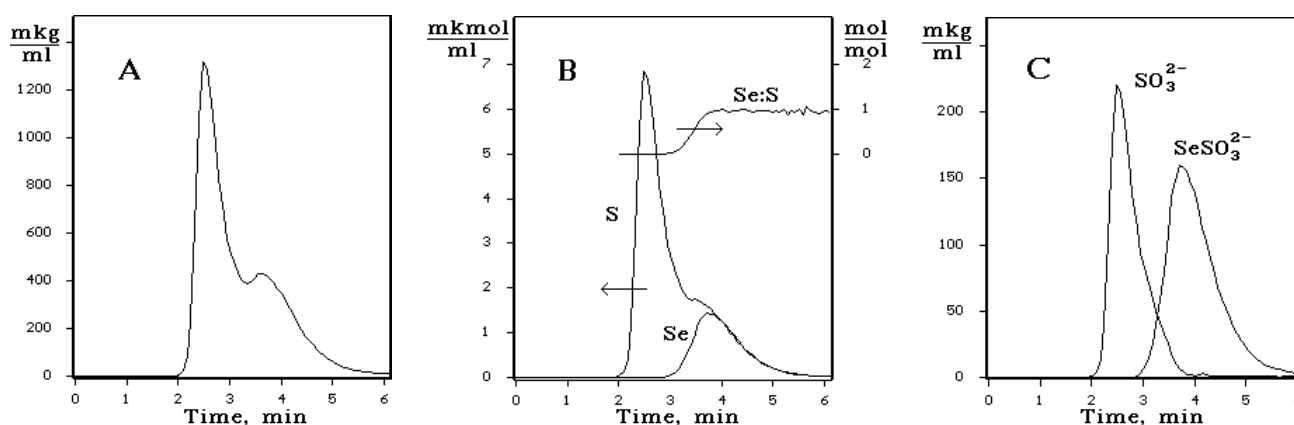

Fig. 22. Chromatograms of a $Na_2SO_3 + Na_2SeSO_3$ aqueous solution recorded with ion chromatograph; (A) an electric-conduction detector; (B) ICP AES detector: the chromatograms for S and Se elements and stoichiogram Se:S; (C) chromatograms SO_3^{2-} and $SeSO_3^{2-}$ recalculated from the same curves as in (B).

Today there is a real possibility to design a chromato-stoichiograph for gaseous and high-effective liquid chromatography and a stoichiograph for capillary electrophoresis. For these techniques multielement atom-emission or mass-spectral spectrometers were used as detectors [29-31]. A one action remains to be done is to endow these techniques with functions of the stoichiograph. The similar systems are known and for ion-chromatography. Therefore the ion-chromato-stochiography may be of considerable promise being applied to analysis of complex solutions, say, hetero-poly-compounds (P-Mo, As-W) or sulfo-phtalo-cyanins with metals Co, Ni, Cu and others.

Conclusion

Theory, methodology and principles of instrumental design of stoichiometric methods of molecular and phase analysis are presented in this paper. Novel devices of molecular analysis, stoichographs, proposed by us are demonstrated. Some principles of the DD technique, recommendations how may change the solvent composition during dissolution of complex solids are given. A set of computer programs to treat and interpret of experimental results obtained by the DD technique and chromatographic analysis and to estimate metrologically the analytical data are developed. Possibilities of a new procedure, stoichiographic titration, for effective separation are shown.

To-date many hundreds of very varied subjects have already been analyzed by these means. Generally, compositions of these subjects included almost 60 elements of the Periodic Table. Many examples of effective application of the DD technique to identify the phase composition of complex solids (crystalline and amorphous phases of constant or variable composition) are demonstrated. Reliability of the results, if possible, is supported by other modern chemical and structural methods. As regards materials, they were heterogeneous catalysts, high-temperature superconductors, luminescent films, inorganic pigments, minerals, natural aerosols, archaeological finds. In addition to phase analysis, DD technique may be applied to determination of composition surfaces, to perform various physical-chemical investigations and procedures of preparative chemistry.

Acknowledgments

References

1. Malakhov V. V. Dokl. Akad. Nauk SSSR, 1986, 290, 1152-1156.
2. Malakhov V. V. Zh. Analit. Khim., 1989, 44, 1177-1190
3. Malakhov V. V. Zavod. Lab., 1990, 56 (9), 1-10.
4. Malakhov V. V. Zh. Analit. Khim., 1994, 49, 349-360.
5. Vlasov A. A.; Malakhov V. V. Proc. International congress on analytical chemistry, Moscow, Russia, June 15 - 21, 1997.
6. Malakhov V. V.; Vlasov A. A. Kinetika i Katalis, 1995, 36, 503-514.
7. Patent RU, 2075338.
8. Patent RU, 2056635.
9. Malakhov V. V.; Vlasov A. A.; Boldyreva N. N.; Dovlitova L. S. Proc. 6th Conference "Analytica of Siberia and Far East". Novosibirsk, Russia, November 21-24, 2000.
10. Malakhov V. V. J. Molec. Cat. A., 2000, 158, 143-148.
11. Malakhov V. V.; Vlasov A. A.; Boldireva N. N.; Dovlitova L. S.; Plyasova L. M.; Andrushkevich T. V.; Kuznetsova T. G. Kinetika i Katalis. 1996, 37, 457-464.
12. Detusheva L. G.; Fedotov M. A.; Kuznetsova L. I.; Vlasov A. A.; Likholobov V. A. React. Kinet. Catal. Lett. 1996, 59, 367-374.
13. Bondareva V. M.; Andrushkevich T. V.; Chumachenko N. N.; Maksimovskaj R. I.; Plyasova L. M.; Malakhov V. V.; Dovlitova L. S. Kinetika i Katalis. 2000, 41, 245-254.
14. Isupova L. A.; Jakovleva I. S.; Tsybulya S.V.; Kryukova G. N.; Vlasov A. A.; Boldyreva N. N.; Sadikov V. A. Kinetika i Katalis. 2000, 41, 315-320.
15. Plyasova L. M.; Yurieva T. M.; Molina I. Yu.; Kriger T. A.; Malakhov V. V.; Dovlitova L. S. Kinetika i Katalis. 2000, 41, 472-480.
16. Zenkovets G. A.; Kryukova G. N.; Tsybulya S.V.; Andrushkevich T. V.; Lapina O. B.; Burgina E. B.; Dovlitova L. S.; Malakhov V. V. Kinetika i Katalis. 2000, 41, 628-640.
17. Bondareva V. M.; Andrushkevich T. V.; Lapina O. B.; Malakhov V. V.; Dovlitova L. S.; Vlasov A. A. Kinetika i Katalis. 2000, 41, 736-744.
18. Vasilyeva I. G.; Malakhov V. V.; Vlasov A. A.; Predtechensky M. R. Thin Solid Films, 1997, 292, 85-90.
19. Vasilyeva I. G.; Malakhov V. V.; Dovlitova L. S.; Bach H. Mater. Res. Bull., 1999, 34, 81-92.
20. Bessergenev V. G.; Ivanova E. N.; Kovalevskaya Yu. A.; Gromilov S. A.; Kirichenko V. N.; Zemskova S. M.; Vasilyeva I. G. Mat. Res. Bull., 1995, 30, 1393-1400.
21. Bessergenev V. G.; Ivanova E. N.; Kovalevskaya Yu. A.; Vasilieva I. G.; Varand V. L.; Zemskova S. M.; Larionov S. V.; Kolesov B. A.; Ayupov B. M.; Logvinenko V. A. Mat. Res. Bull. 1997, 32, 1403-1410.
22. Isaenko L.; Vasilyeva I.; Yelisseyev A.; Lobanov S.; Malakhov V.; Dovlitova L. J. Cryst. Growth, 2000, 218, 313-321.
23. Vasilyeva I. G.; Ayupov B. M.; Vlasov A. A.; Malakhov V. V.; Macaudiere P.; Maestro P. J. Alloys and Compounds, 1998, 268, 72-77.
24. Malakhov V. V.; Vlasov A. A.; Boldireva N. N.; Dovlitova L. S.; Pushkin S. G. Chem. Sustain. Development, 1995, 3, 253-260.
25. Parmon V. N. Colloids and Surfaces A., 1999, 151, 351-365.
26. Kosova N. V.; Avvakumov E. G.; Malakhov V. V.; Devyatkina E.T.; Dovlitova L. S.; Boldirev V. V.; Dokl. Akad. Nauk, 1997, 356, 350-353.
27. Golubkova G. V.; Lomovsky O. I.; Vlasov A. A.; Dovlitova L. S.; Belyev E. Y.; Malakhov V. V. J. Alloys and Compounds, 2000, 307, 131-136.
28. Malakhov V. V.; Vlasov A. A.; Boldireva N. N.; Dovlitova L. S. Proc. All-Russia conference "The chemical analysis of substances and materials", Moscow, Russia, April 16-21, 2000.
29. Hewlet Packard GC-AED System. Hewlet Packard Environmental Seminar. Irkutsk, Russia, June 15 – 21, 1990.
30. Caruso J., Heitkemper D., Sheppard B. ISP Inf. Newslett, 1991, 16, 521-523.
31. Olesik J., Kinzer J., Olesik S. Anal. Chem, 1995, 67,1-12.

Received 12 October 2001.