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Stoichiography and chemical methods of phase analysis of multielement multiphase substances and materials

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Contents

I.	Introduction	351
II.	Selective dissolution method	352
III.	Stoichiography and stoichiographic methods	353
IV.	Differential dissolution	354
V.	Strategy and technique of differential dissolution	357
VI.	Differential dissolution method in the analysis of substances and materials	363
VII.	Conclusion	368

Abstract. The problems and achievements in the determination of the phase composition of multielement multiphase inorganic solid substances are considered. The problems of theory, methodology and practical use of two chemical methods of phase analysis, *viz*., selective dissolution and reference-free stoichiographic dissolution are discussed. The unique potential of stoichiography and differential dissolution method, which allows one to overcome many limitations and difficulties typical of modern phase analysis techniques, are demonstrated. Examples of using differential dissolution for the phase analysis of diverse substances and functional materials are given. The bibliography includes 146 references.

I. Introduction

Determination of the phase composition of multielement multiphase inorganic solids is a difficult and poorly elaborated problem of analytical chemistry.[1] Effective solution of this problem is of prime importance for various fields of science and practice including physics, chemistry, materials science, geochemistry, mineralogy, processing of mineral resources, metallurgy, ecology and many other. Analytical chemistry and especially X-ray diffraction analysis traditionally use the term 'phase analysis' in a narrow sense to imply an analysis providing data on the phase composition of inorganic solids. These solids may be mixtures of solid phases of chemical elements, their compounds with either constant or variable composition, and solid solutions. However, mixtures of not only solid but also liquid and gas phases can be objects of chemical analysis. Determination of the component composition of liquid solutions, for example, extraction systems, atmospheric air, natural waters or petroleum fractions requires analysis of either individual phases or their mixtures. These phases may comprise both individual molecules, their fragments and macrostructures.

The difficulties faced by phase analysis of solids are due to a number of reasons.[2] First, compounds with ionic, covalent and metallic chemical bonds, except for molecular crystals, cannot be disintegrated down to the level of 'formula units'. Therefore, it is not mixtures of atoms, molecules or ions that are to be separated, as in the case of liquids and gases, but solid crystalline and/or amorphous macroaggregates. The selectivity of this separation by means of physical and chemical methods is rather low.

Second, there exist a great variety of phases of constant and variable composition differing in the macro- and microstructure (morphology, dispersity, porosity, the nature of interfacial surfaces) and elemental composition including the impurity elements. The key physical and chemical properties of such objects are variable; therefore, it is difficult or impossible to prepare reference samples; *i.e*., samples with exactly known parameters of composition, structure and properties adequate to these phases. The reference samples (or standards) are important: only with their use, is quantitative phase analysis possible as well as replenishment of the diffractometric and spectral databases constituting the basis of modern structural studies.

Third, there exist spatially inhomogeneous phases of variable composition, which often occur in highly dispersed or amorphous state. The composition of such phases cannot be represented by a single stoichiometric formula and no reference samples can be prepared for them. Special difficulties arise when multiphase samples may contain new, yet unknown phases.

In the general case, phase analysis of complex solid mixtures includes three main stages: separation of mixtures into individual phases; identification of the phases according to

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their stoichiometric formulas and crystal structure; and determination of the quantitative content of each phase in the mixture.[2–5] Two groups of methods for phase separation can be distinguished: non-destructive (mechanical separation in magnetic, electrical or gravitational field and flotation) and destructive methods (based on the differences between chemical, electro- or thermochemical activity of individual phases).[4,6,7] The composition and the number of phases can be determined provided that they are recovered highly selectively from mixtures. However, dependence of the reactivity of solid phases on their structure restricts the analytical scope of destructive methods. Development of such methods relies predominantly on an empirical approach based on a thorough selection of conditions for each particular system.

The predominant role of structural physical methods (mainly diffraction and spectroscopic methods[8–10]) for phase identification is indisputable and confirmed by numerous publications. However, their obvious limitations are taken as a matter-of-course. This the phase analysis of complex multielement objects with unknown phase compositions is often impossible due to relatively low selectivity of physical methods. The identification of amorphous, spatially inhomogeneous phases with variable compositions and small phases is difficult.‡ The difficulties in the preparation of reference samples almost preclude the possibility of quantitative phase analysis: publications usually present X-ray diffraction patterns and spectra that characterise the phase composition of a solid at a qualitative level. As a rule, the phase analysis of complex systems is carried out using a set of mutually complementary methods; this complicates the identification as requires intricate equipment and skilled personnel of different specialties.

This review surveys the achievements concerned with the use of chemical methods of phase analysis: the known selective dissolution (SD) method and the relatively new stoichiographic differential dissolution (DD) method. The key aspects of their theory, methodology and practical applications are considered. It is shown that the unique potential of stoichiography and the DD method allow one to overcome many limitations and difficulties characteristic of modern physical methods used for phase analysis.

II. Selective dissolution method

The selective dissolution method is the most widely used chemical method of phase analysis. A considerable contribution to its foundation and development was made by Russian analysts Dolivo-Dobrovolskii and Klimenko,[11] Filippova[12] and others.[13–16] Most publications on this issue date back to the 1950–1960s and subsequently their number started to decrease. The decay of the interest in the SD method is due to its limited scope: this method often fails to provide correct and, what is equally important, fast answers to the questions concerning phase compositions of newly obtained solids.

† In the phase analysis, the determination region of low concentrations of phases appears much earlier than the region of trace amounts in elemental analysis. For example, the most popular powder X-ray diffraction method often fails to determine phases when their contents are 5 mass %–10 mass %. These amounts can hardly be termed as trace, which accounts for the introduction of the notion 'minor phases'. The boundaries of this region are not strict. The lower boundary, $10^{-2}n$ mass %–$10^{-3}n$ mass %, corresponds to the sensitivity of chemical methods (see below) and the upper boundary is from tenths to several percent of the sensitivity of physical methods.

The essence of the SD method is as follows. Treatment of a solid analyte with specially chosen selective solvents results in quantitative dissolution of a particular form of a chemical element, which is then determined in the resulting solution, whereas other forms of the element remain in the insoluble residue. The form of the element is indicative of its belonging to a particular solid phase with either constant or variable composition.

Selective solvents used in the SD method include non-polar solvents for molecular crystals and polar solvents for ionic crystals. However, solvents that irreversibly react with the substance being dissolved are used more often; in this case, the solution contains the products of these reactions rather than the initial solids.[17] Apart from the nature of the solvents, one should take into account the conditions ensuring the selectivity of dissolution: the solvent composition, concentration and temperature, the atmosphere above the solution, the fractional composition of the dispersed sample particles, hydrodynamic dissolution conditions and duration of this process.[3,12,15]

As a measure of solubility of solid phases (more precisely, forms of chemical elements), the SD method uses the parameter α_{ij}, which is the degree of dissolution of the analyte element form under strictly specified conditions

$$\alpha_{ij} = \frac{m_{ij}}{m_i},$$

where m_{ij} is the mass of the ith form of the analyte element in the jth solvent; m_i is the mass of the ith form of the analyte element in the sample.

In each stage of the analysis of a multiphase object, it is necessary to take account of the co-dissolved forms, *i.e.*, other forms of the same element that pass to the selective solvent, to one or another extent, together with the analyte form. In this case, the selectivity of dissolution of the ith form of an element (S_{ij}) depends on the degrees of dissolution of the analyte and co-dissolved forms in the jth solvent and on their relative contents in the sample.[18] For the first form and the first solvent, the selectivity S_{11} is described by the equation

$$S_{11} = \alpha_{11} + \Sigma\beta_{i1}\alpha_{i1},$$

where

$$\beta_{i1} = \frac{m_i}{m_1}$$

is the relative (with respect to the first analyte form) content of the co-dissolved forms in the sample. The selective dissolution conditions are considered admissible if $S_{11} = 1 \pm \Delta S_{11}$ for the overall fraction of the phases co-dissolved together with the first phase to be determined $\Delta S_{11} \leqslant 0.1$; the conditions are optimal if $S_{11} \approx 1$.

The phenomenological statements of the SD method are important from the strategic standpoint, as they consider the diversity of objects of analysis, selective solvents and reactions that accompany dissolution from a common standpoint. However, the dissolution selectivity characteristics are related to the reactivity of compounds and to thermodynamics and kinetics of heterogeneous processes. These processes are significant not only for analytical, but also for inorganic chemistry and chemical engineering.[19–22]

In the development of the selective dissolution theory, it is necessary, first of all, to elaborate the system of criteria for

evaluation of the reliability and correctness of the results of phase analysis of multielement multiphase compounds; and, second, to estimate quantitatively the variation limits of the selective dissolution conditions of the phases at a specified level of validity (the systematic error level) of the final results. Unfortunately, attempts to develop such a theory provided no significant outcome.[3, 12, 16, 23, 24] This was hampered by the relatively low level of knowledge of the 1950–1960s concerning the real (distorted by defects) structure, reactivity and dissolution kinetics of solid phases. It was clear that the calculation results of selective dissolution processes have systematic errors due to both incomplete dissolution of the analyte forms of elements and co-dissolution of other forms of the same elements. It was postulated that the degree of dissolution of each phase (element forms) under fixed selective dissolution conditions remains constant and does not depend on the amount of this phase and that appropriate corrections can be introduced in the analysis results. It was thus neglected that the variations of the real macro- and microstructure of solids made the crucial uncontrollable contribution to the systematic errors, to the degree of dissolution of element forms (and phases), thus changing unpredictably the dissolution rate.

Indeed, the α_{ij} value is a function of several independent variables that characterise not only the solvent composition and dissolution conditions, but also the nature of the analyte, namely, the chemical composition, the real crystal (type and concentration of defects) or amorphous structure of single phases. It is also necessary to consider characteristics of the macrostructure of both single phases and the object as a whole: grain-size composition, morphology, porosity, specific surface area. The situation is complicated by the fact that the initial values of these parameters can change substantially upon dissolution, as this process involves continuous renewal of the reaction surface of phases including the appearance of crystal faces, change in the grain-size composition and manifestation of effects caused by mutual shielding and encapsulation of phases in their conglomerates. For example, easily soluble phases may get in contact with the solvent only after poorly soluble phases have passed to the solution if the former are encapsulated as conglomerates with the latter. The above-listed factors have a considerable influence on the recorded rate of phase dissolution. As a rule, the temporal profile of the corresponding kinetic dependences shows a chaotic set of extrema and induction periods. Examples demonstrating the dependence of the dissolution rates of iron, copper and molybdenum oxide phases on the characteristics of their real structure and preparation conditions are shown in Figs 1 and 2.[25]

Despite the fact that the popularity of the SD method decreased, it is still used. The preferred objects of SD analysis are solids with slight structural variations. Usually these are similar samples that differ only in the quantitative content of the phases.[26] The SD method is used to analyse multielement multiphase objects where the application of structural physical methods is restricted due to their too low selectivity. The SD method is little suited for analysis of porous or amorphous substances with complex or unknown phase composition, for determination of phases with variable compositions and in those cases where reference samples of the phases cannot be prepared. The SD procedures including 'wet' operations imply the use of hand labour and high skill of the analyst. These procedures are rather cumbersome and fail to be instrumentalised.

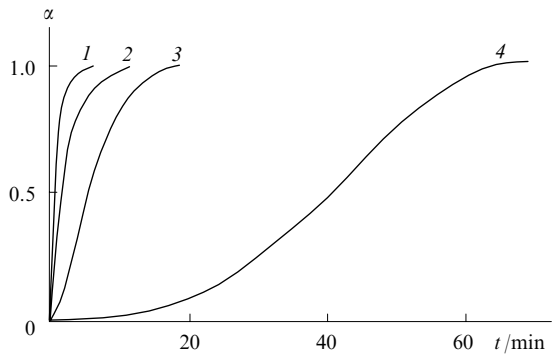


Figure 1. Kinetic curves for dissolution of α-Fe_2O_3 samples (4 M HCl, 40 °C) with a specific surface area of 170 (*1*), 62 (*2*), 39 (*3*) and 17 $m^2\ g^{-1}$ (*4*) (see [25]).
α is the degree of dissolution.

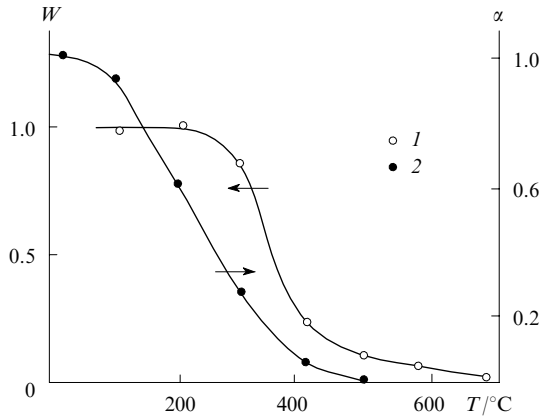


Figure 2. Relative specific rate of dissolution ($W = W_i/W_{i\max}$) of CuO in 0.25 M HCl at 20 °C (*1*) and degree of dissolution of MoO_3 in H_2O at 100 °C in 20 min (*2*) *vs.* annealing temperature of the samples.[25]

Due to the complexity of consideration of the effects of the above-listed factors on the dissolution processes of solid phases in both theoretical and experimental studies, chemists have lost interest in detailed investigation of these factors. In modern analytical chemistry of inorganic compounds, dissolution is considered as a stage of sample preparation for elemental analysis (sample digestion) and is described only qualitatively as being complete or incomplete, fast or slow, easy or difficult.

III. Stoichiography and stoichiographic methods

The stoichiography concept as a system of new views on the stoichiometry of non-steady-state hetero- and homophase mass transfer processes has appeared as a result of long-term search for effective methods for solving the problem of determination of the molecular composition of mixtures containing unknown chemical compounds.[25, 27–29] This problem does not exist in elemental analysis: all stable elements have been discovered, their total number is rather small, and methods for determination of each element in the presence of other elements are known. Meanwhile, the number of natural chemical compounds is enormous, and most have not been discovered as yet. Unlike known chemical and physical methods of molecular analysis, stoichiography provides a unique possibility of both qualitative and quantitative molecular analysis without using reference samples (standards for indi-

vidual chemical compounds), which allows also determination of unknown compounds.

The essence of stoichiography is combination of mixture separation and determination of, for example, the stoichiometry and the elemental composition of the substance flow during dissolution. On the basis of this combination, it is possible to develop fundamentally new methods of analysis and to transform classical separation methods into standard-free methods for determination of the molecular composition. These methods are based on analysis of stoichiograms, which are functions of the ratio of mass transfer rates for chemical elements *vs.* time. The mass transfer rates in hetero- or homophase systems should be expressed in mol (unit time)$^{-1}$. If a flow comprises only one compound, the ratios of the transfer rates of each two elements from this compound remain constant with time, their values corresponding to the stoichiometric coefficients that relate these elements in the empirical formula of the compound. This makes possible identification of chemical compounds based on their primary attribute, *i.e.*, the elemental stoichiometry.

A non-steady state nature of hetero- and homophase transfer processes is a necessary condition for stoichiographic methods. In the steady-state processes, the mass transfer rate is invariable. Therefore, in the transfer of mixtures rather than single compounds, stoichiograms would remain constant but differ from those corresponding to single compounds. However, under non-steady-state conditions, the stoichiograms describing the transfer of mixtures would be, conversely, variable. This follows from the kinetic features of non-steady-state processes.

The pattern of stoichiograms, which is the criterion of identification and, hence, of the results of molecular analysis, is determined by the kinetic features of mixture separation processes and are specially considered below. The non-steady-state condition (mass transfer at variable rate) is manifested in all analytical signals as peaks: in chromatograms, voltammetric and electromigration curves, mass spectrometric patterns, *etc.*

The idea of taking into account the mass ratios of elements in the dissolution or desorption processes for determination of the composition of compounds is not new.[30–33] However, the occasional early publications considered only particular examples, and this approach to chemical analysis has not been generalised or developed. It should also be noted that successful completion of stoichiographic studies depends on appropriate combination of classical chemical processes of mixture separation, the potential of modern multielement methods of chemical analysis and computing machinery. Mixtures of solid inorganic phases have become priority objects for stoichiography; for their analysis, differential dissolution method was developed.[27] Subsequently, a similar approach has been used in ion chromatography.[34, 35]

IV. Differential dissolution

The DD method allows one to determine the stoichiometric composition and the number of phases in solid multielement multiphase objects without isolating the phases in a pure state. The use of DD method, unlike SD, requires neither preliminary information on the phase composition of analytes nor reference samples. In this case, DD is a standard-free method, as measuring instruments are calibrated using standard solutions of the elements that constitute the analyte rather than reference samples of the phases.

The DD method is based on physicochemical features that dictate the course of successive dissolution of individual phases from their mixtures in a specially created dynamic regime and a change in the dissolution stoichiometry during these processes.

1. Dynamic regime of chemical reactions

Non-steady-state kinetics may give rise to numerous regimes of chemical reactions. Noteworthy is the dynamic regime, which opens up new in principle prospects for solving problems of chemical analysis and synthesis.[25] In this regime, the initial concentration of the component R in the reaction

$$A + R = P$$

is in excess and increases with time, for example, linearly or exponentially, although some R is spent for the reaction with component A. For example, to dissolve an oxide mixture in this regime, the concentration of an aqueous solution of a strong acid taken in a large excess is deliberately increased during the process.

As the concentration of the active component of the solvent (c_R), for example, protons, increases, its chemical potential μ also increases, because

$$\mu = \mu_0 + RT\ln c_R .$$

Under these conditions, the solid phases present in the mixture are dissolved consecutively as the μ value corresponding to each of them is reached. However, the solid phases are destroyed during dissolution, and the rate of dissolution may be recorded not for the whole phases but for separate elements or fragments, for example, relatively complex ions. Therefore, in the general case, except for the phases of individual elements, there appears a problem of reconstruction of the kinetic curves for the dissolution of elements into kinetic curves for the dissolution of phases that form the analyte. For solving this problem, the concept of dissolution stoichiometry was introduced for solids.[27, 28] Note that there is an analogy between the dynamic regime of dissolution and voltammetry, in particular, the inversion voltammetry: the kinetic curves for the dissolution of elements (Fig. 3), and, hence, of phases, are similar to voltammetric curves.

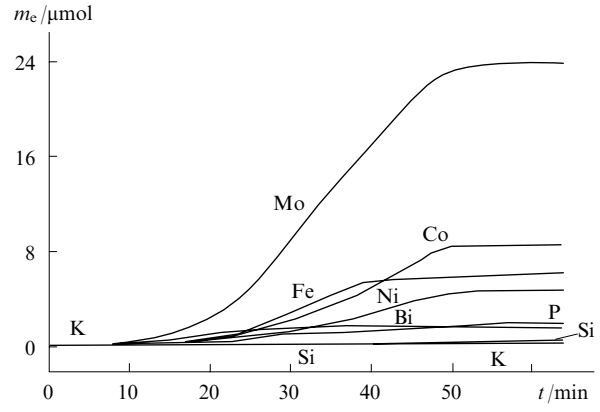


Figure 3. Kinetic curves for dissolution of elements (m_e is the element mass) present in a sample of a multicomponent catalyst for selective oxidation.
Contents of elements in the sample (mass %): Bi, 6.75; Co, 8.32; Ni, 4.49; Fe, 5.27; K, 0.04; P, 0.57; Mo, 38.2. Variation of conditions: from H_2O (pH 2), 20 °C to 4 M HCl, 60 °C.

2. Dissolution stoichiometry and stoichiograms

The dissolution stoichiometry (S) is the ratio of the amounts of every two elements that currently pass from the multielement solid phase to the solution, *i.e.*, the S value is equal to the ratio of the dissolution rates of elements present in the dissolving phases that are dissolved (the amounts of elements should be expressed in moles). For the given mixture, the total number of functions of variation of the dissolution stoichiometry with time [$S_i(t)$], stoichiograms, is equal to the number of pair combinations (without allowance for the order of elements in these combinations) of chemical elements (z) constituting the mixture

$$C_z^{(2)} = \frac{z!}{2(z-2)!}.$$

The fundamental features of the stoichiograms of individual phases with constant composition include the correspondence of their values to the stoichiometric coefficients that relate every two elements in the phase formula and the invariance of the $S_i(t)$ dependence with respect to the dissolution conditions. The latter implies that, unlike the variable kinetic curves for the dissolution of elements, the pattern of stoichiograms for the phases with the same stoichiometric composition does not depend on the dispersity characteristics and variations of the real structure of the phase, dissolution conditions (solvent composition, concentration and temperature) or on the hydrodynamic process conditions. For example, the stoichiogram of an NaCl sample with any structure remains the same, $S_{Na:Cl}(t) = 1$, during dissolution in any solvent under any conditions. The kinetic curves for Ba and Cu dissolution and the Cu : Ba stoichiogram obtained in analysis of the $YBa_2Cu_3O_\delta$ crystal are shown in Fig. 4. The dissolution of this crystal in the dynamic regime was accompanied by evolution of oxygen; when growing and being detached, oxygen bubbles shielded some of the reactive surface of the crystal. This gave rise to oscillations in the kinetic curves but the stoichiogram did not change, as $S_{Cu:Ba}(t)$ is equal to the ratio of the stoichiometric coefficients at Cu and Ba in the formula $YBa_2Cu_3O_\delta$.

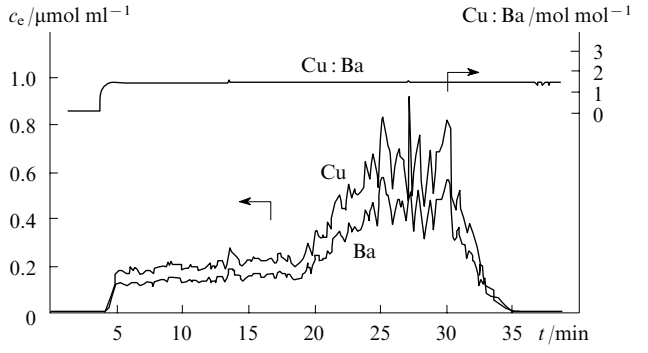


Figure 4. Kinetic curves for copper and barium dissolution and stoichiogram Cu : Ba for a crystal of the $YBa_2Cu_3O_\delta$ superconductor.
Here and below: c_e is the element concentration. Variation of conditions: from H_2O, 20 °C to 3 M HCl, 50 °C.

It should be emphasised that the invariance principle of the dissolution stoichiometry refers particularly to single phases. In the simultaneous dissolution of phases from a multielement multiphase substance, the stoichiograms can change (considerably) upon the change in the DD conditions.

The invariance principle of the dissolution stoichiometry is actually truistic, because the stoichiometry of a phase with constant composition does not depend on the amount of this phase or conditions of its existence. However, the corollaries of application of this principle to the analysis of phase mixtures are important and unexpected. First, this opens up the possibility of broad variation of the dynamic regime parameters in the search for conditions for consecutive dissolution of the phases, and, second, it is possible to determine unambiguously the degrees of phase separation during dissolution. Knowing the rules that determine the pattern of the functions $S_i(t)$ and using the DD results, it is possible to find the stoichiometric formulas and to perform quantitative determination of the phases without using reference samples. These trends were identified in the mathematical simulation of DD processes and repeatedly confirmed experimentally.

3. Modelling of the differential dissolution processes

The DD processes were studied using models of mixtures of solid phases of constant and/or variable composition and processes of their dissolution in the dynamic regime.[5, 35, 36] The developed software allowed solids to be modelled as mixtures of 2 to 8 phases each containing up to 10 elements in some stoichiometric ratios. The parameters of the kinetic equations for dissolution of each phase (rate constant, activation energy, order of reaction) and the time variation functions of the solvent concentration and temperature within the defined limits were specified. Finally, this gave kinetic dependences for the dissolution of phase elements, which could be transformed into stoichiograms, reconstructed in different ways; and the stoichiometric formulas of the phases and their contents could be calculated.

4. Mixtures of phases with constant composition

The calculations for a mixture of two phases with constant composition $A_2B_3 + AB_3$ were carried out in terms of the classical model of contracting spheres using the relevant kinetic equation for ith phase (i = 1, 2)

$$\alpha_i = 1 - \left(1 - \frac{k_i}{r_i}\tau\right)^3, \qquad (1)$$

in which α_i is the degree of dissolution of a spherical particle of the ith phase during time τ, r_i is the initial radius of the particle, k_i is the rate constant for the dissolution of this phase

$$k_i = k_i^{(0)} \exp\left(-\frac{E_i}{RT}\right) c^{n_i},$$

where E_i is the activation energy, c is concentration, n_i is the order of reaction.

The stoichiogram $S_{B:A}$ and the differential kinetic curves for the dissolution of elements A and B from phases A_2B_3 and AB_3 are presented in Fig. 5; Fig. 6 shows the reconstructed kinetic dependences of dissolution of these phases for the case where the dissolution reactions differed only in the order: $n_1 = 1$ and $n_2 = 2$. It can be seen that during dissolution of only the first phase ($t_{01} - t_{02}$), the stoichiogram remains constant $S_{B:A}(t) = 1.5$; during dissolution of the second phase ($t_1 - t_2$), the stoichiogram $S_{B:A}(t) = 3$; during simultaneous dissolution of both phases ($t_{02} - t_1$), the stoichiogram $S_{B:A}(t) \neq$ const.

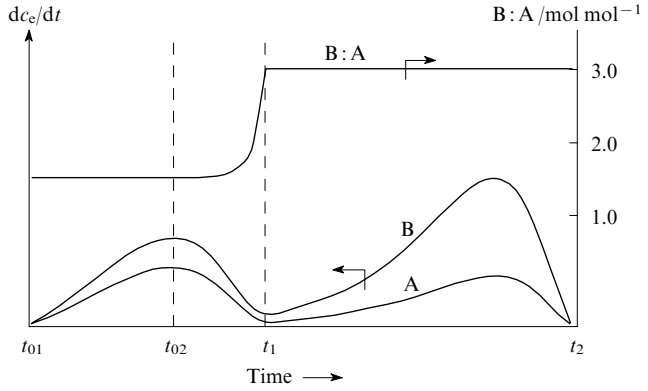


Figure 5. Kinetic curves for dissolution of elements A and B and stoichiogram B : A for a regimel phase mixture $A_2B_3 + AB_3$.

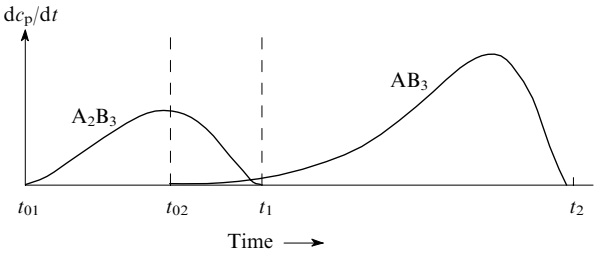


Figure 6. Kinetic curves for dissolution of phases A_2B_3 and AB_3 reconstructed from the dependences presented in Fig. 5.
Here and below c_p is the phase concentration.

In the general case,[27] when both phases AB_{c_1} and AB_{c_2} are dissolved simultaneously, the molar ratio of the elements $S_{B:A} = dB/dA$ at time instant t is

$$\frac{dB}{dA} = \frac{c_1\beta\xi + c_2}{\beta\xi + 1}, \qquad (2)$$

where c_1 and c_2 are the stoichiometric coefficients; $\beta = A_1 : A_2$, A_1 and A_2 are the numbers of moles of element A within phases AB_{c_1} and AB_{c_2}, respectively; $\xi = (d\alpha_1/dt) : (d\alpha_2/dt)$, $d\alpha_1/dt$ and $d\alpha_2/dt$ are the dissolution rates of phases AB_{c_1} and AB_{c_2}.

It is impossible to strictly describe the dissolution kinetics of a real phase mixture *a priori* without known rate constants, reaction orders, activation energies of the dissolution of each phase, the reactive surface area of each phase or the trends of its variation during dissolution. Therefore, for real substances, the form of function $\xi(t)$ in Eqn (2) is unpredictable but a change in the profile with time is a necessary feature of this function. For the model of two contracting spheres with equal radii and for $k_1 \neq k_2$ (k_1 and k_2 are rate constants for the first and second phases), the function $\xi(t)$ has the form

$$\xi(t) = \frac{6k_1^2 - 6k_1^3 t}{6k_2^2 - 6k_2^3 t} \neq \text{const}. \qquad (3)$$

The plot of this linear fractional function is a hyperbola. For simultaneous dissolution of several phases, the function $S(t)$ is also variable; evidence for this was reported.[28]

Thus, the stoichiogram profile of a mixture of phases with constant composition is determined by two major features.

1. During dissolution periods of individual multielement phases with constant composition, the molar ratios of every two elements comprised in phase, S_i remain constant in time and are equal to the ratios between the stoichiometric coefficients of the elements in the empirical formulas of the phases.

2. During periods of simultaneous dissolution of two or more multielement phases, the molar ratios between every two elements comprised in only one phase remain constant in time and are equal to the ratios between the stoichiometric coefficients of these elements in the empirical formulas of these phases, while all other molar ratios are variable.

When the stoichiometric formulas of the phases have been found, it is possible to determine also their amounts even for incomplete phase separation, as in the example considered (see Fig. 6). The rules for such stoichiographic calculations are outlined below.

5. Mixtures of phases with variable composition

Using general principles of the DD method, one can reliably interpret the results of analysis of complex mixtures of phases with constant and variable composition and solid solutions provided that the spatial concentrations of their components is not changed. This condition is typical of saturated solid solutions and before saturation, for the equilibrium state of the system as a whole. However, in the case of layer-by-layer dissolution of spatailly inhomogeneous phases of variable composition, the stoichiograms are variable rather than constant. Therefore, it is impossible to determine which of the following two cases matches the variable segments of stoichiograms: (*1*) dissolution of a mixture of phases; (*2*) dissolution of a single phase with variable composition and inhomogeneous spatial concentration of the components. It is clear that for case *1* no phase separation effect is present, while for case *2*, the phase analysis problem should be considered solved. The form of stoichiograms reflects the qualitative and quantitative character of the spatial inhomogeneity of the composition of this phase.

The intricate problem of identification of spatially inhomogeneous phases was solved upon affinity transformation of the kinetic curves of element dissolution and stoichiograms.[5] The essence of this transformation is as follows. Two or more weighed portions of the analyte must be dissolved in different dynamic regimes. As the dissolution conditions are change, the phase dissolution rates are also changed. Thus, the kinetic dependences and stoichiograms as functions of dissolution times are different for different conditions both in case *1* and in case *2*. However, the transformation of stoichiograms as functions of time to the stoichiograms as functions of the degree of analyte dissolution would give fundamentally different results. For case *1*, the transformed stoichiograms would differ from each other, while for case *2*, the transformed stoichiograms would be identical. Note that affinity transformations of kinetic dependences are used in heterogeneous chemical kinetics to prove invariability of the mechanism (the sequence of stages) of chemical reactions upon a change in reaction conditions.[20]

6. Simulation of the dissolution for spatially inhomogeneous phases with variable composition of the type $AB_{1-x}C_x$

The legitimacy of affinity transformations was proved by mathematical simulation of DD. The properties of two models of spatially inhomogeneous phases were considered: the composition of one phase belonged to the homogeneity region in the constitution diagram, while that of the other phase corresponded to a substitutional solid solution.[5] The models

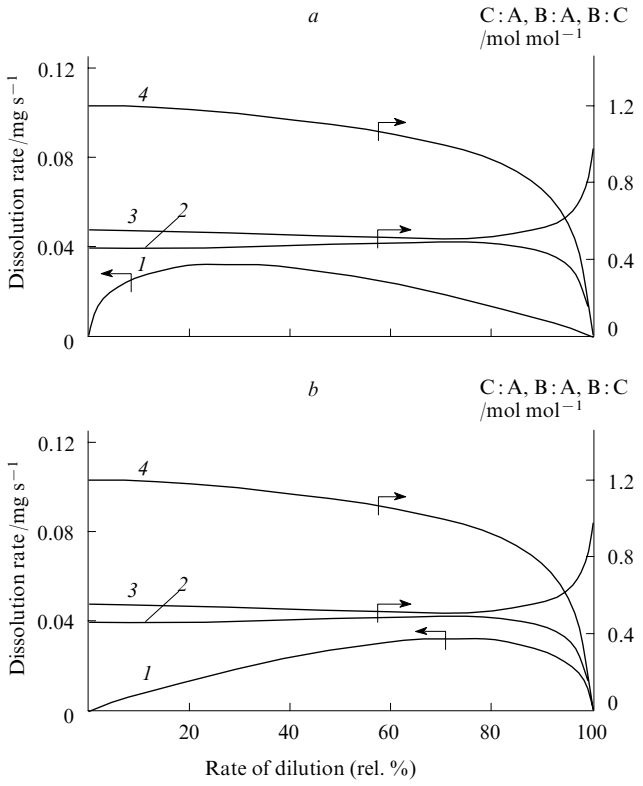


Figure 7. Kinetic curves of DD (*1*) and stoichiograms C : A (*2*), B : A (*3*) and B : C (*4*) after affine transformations depending on the degree of dissolution of spatially inhomogeneous phases of substitutional solid solution $AB_{1-x}C_x$ for $Z = 0.001$ (*a*) and 1000 (*b*).[5]
Z is the parameter determining the rate of variation of the solvent concentration.

reflected the dissolution of phases of variable composition. The kinetic curves for dissolution were monotonic and continuous, and the stoichiogram profiles were variable. These two families of time dependences became different upon a change in the dissolution conditions. However, after the affinity transformation, only the stoichiogram profiles B : A, C : A and B : C did remain the same, while the profiles of the dissolution kinetic curves were different (Fig. 7).

This important fact can be interpreted as follows. A change in the dissolution conditions results in a change in the layer-by-layer dissolution rate of, for example, the $AB_{1-x}C_x$ phase. However, as these conditions change, the layers of the spatially inhomogeneous phase of variable composition pass to the solution in the same order, though at different rates; this accounts for stoichiogram invariability in the coordinates 'ratio of chemical element mass transfer rates – degree of phase dissolution'.

A different situation is observed for affinity transformations of the kinetic plots describing the simultaneous dissolution of phases with constant composition. The profiles of all dependences differ from one another, because a change in the DD conditions for a mixture of phases with constant composition leads to a change in the separation selectivity. Hence, the profile of stoichiogram segments corresponding to the period of simultaneous dissolution of the phases is changed. This case is considered below.

V. Strategy and technique of differential dissolution

1. Stoichiograph

The efficiency of the DD method is associated with the use of high-precision highly sensitive elemental analysis and computer procedures, as the number of elementary computation operations for a substance composed of even 3 to 5 elements is larger than 10^6. About 15 years ago, an instrument that changed crucially the scope of the DD method was designed at the Institute of Catalysis of the Siberian Branch of the RAS.[37, 38] This instrument called stoichiograph (Fig. 8) has been successfully functioning up to now.



Figure 8. First laboratory stoichiograph.

The stoichiograph block diagram (Fig. 9) includes vessels *1*, *2* with solvent components (for example, with water and concentrated HCl); peristaltic pumps *4* and *5*, which pump the solvent components along the capillaries into a mixer *6* at different velocities; an electronic device *3*, which controls the flow rates by a specified programme and ensures a combined

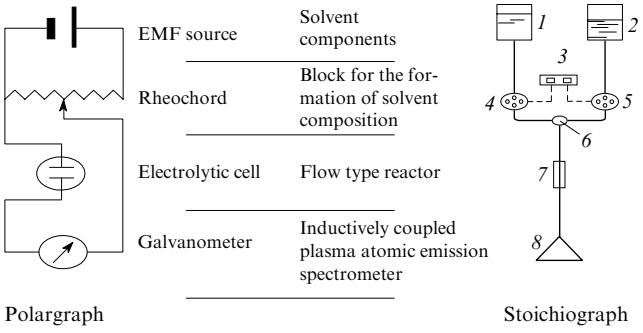


Figure 9. Scheme of the stoichiograph and polagraph (for explanations, see the text).

solvent flow from the mixer *6* to reactor *7* at a constant volume rate (~ 2 ml min^{-1}) and progressively increasing concentration. In the reactor, the sample is dissolved and the solution thus formed is fed to the analyser detector *8*. Most often, this is an inductively coupled plasma atomic emission spectrometer (ICP AES) coupled with a polychromator. The operation of the whole system is controlled and monitored by a computer.

The analyser detector allows simultaneous determination of almost all elements in the resulting solution in the required combination with a sensitivity at $n \times 10^{-3}$ μg ml^{-1}, an error at 1% – 5% and a frequency of ~ 1 s. Actually, the kinetic curves of dissolution are recorded continuously, which helps to reveal fine features of this process.

A software package has been developed to control the course of differential dissolution and to carry out the required computation. The intermediate information is obtained as kinetic curves for the dissolution of elements in unnormalised and normalised forms, integral and differential forms, and as stoichiograms. The data are output in the tabular form and as kinetic curves of phase dissolution.

The metrological characteristics of phase analysis procedures depend mainly on the analyser detector used to determine the elemental composition. With the use of ICP AES with element concentrations determined to an error of $\leqslant 5\%$, the error of determination of the stoichiometric coefficients in the empirical formulas and the quantitative contents of phases does not exceed 10%. The empirical formulas of compounds are determined to the same error using gas chromatograph – atomic force spectrometer systems.[39]

The design of a stoichiograph is similar to the classical design of the Heyrovsky polarograph (Nobel Prize in chemistry of 1959). The stiochiograph has vessels with the solvent components in place of the voltage source, an electronic device that controls the solvent composition with time instead of the rheochord, a reactor instead of the electrolytic cell, and ICP AES to replace the galvanometer. However, unlike a polagraph, which records only one voltammetric curve, the stoichiograph records 'the currents' of all elements of the substance being dissolved, which are recorded by the analyser detector. The body of information thus obtained is much greater and the information content of the results is more significant.

2. Physicochemical aspects of dissolution of the solid phase

Below we consider some features of dissolution processes that are important both to carry out the DD and to interpret the DD results.

The dissolution of solids in a flow dynamic regime in a large excess of the solvent in the solid phase – solvent system occurs under conditions far from equilibrium. Most of DD processes are irreversible because the chemical reaction products rather than initial solids pass to the solution.

For DD, the use of kinetically controlled dissolution in which the rate is determined by only the chemical nature and the crystal structure of the phase and does not depend on the diffusion factors is preferred. The occurrence of either diffusionally or kinetically controlled dissolution depends on the degree of sample grinding. When the solid particle size is < 40 μm, the DD processes are, most often, kinetically controlled, their rates being independent of either particle size or hydrodynamic conditions.[25, 38, 40]

In many cases, before the onset of matrix dissolution, it is possible to determine the composition of their surface layers by the DD method. In particular, this is true for the products of ion exchange processes that involve only the surface of solid matrices. Figure 10 shows the results of DD analysis of the product of sorption treatment of electrolytic wastes with a sapropel-based sorbent. These results were obtained by simultaneous recording of the desorption kinetics of each element in the DD regime, despite the fact that their separation selectivity (except for sodium) was relatively low.

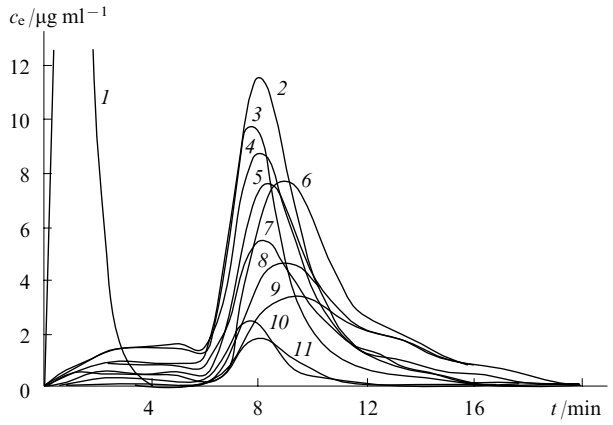


Figure 10. Kinetic curves for the dissolution of elements present in the product of sorptional treatment of electrolytic wastes (sapropel based sorbent).
(*1*) Na, (*2*) Ni, (*3*) Mg, (*4*) Co, (*5*) Cr, (*6*) Fe, (*7*) Cu, (*8*) Mn, (*9*) Zn, (*10*) Ca, (*11*) Al. Variation of conditions: from HNO_3, pH 4 to 2 M HNO_3, 20 °C.

The dissolution of homogeneous matrices is accompanied by complete destruction of the solid phase structure. The dissolution can occur either congruently or incongruently.[41] The congruent dissolution is a consequence of fast coupled elementary reactions of solvent components with the unit cell atoms of the solid phase. As a result of such macroprocess, all unit cell atoms would pass into the solution, as the not yet dissolved residue must be electrically neutral. Hence, the stoichiometric ratios of elements in the resulting solution are the same as those in the initial solid phase. Note that the condition of simultaneous dissolution of the phase components underlies the concept of the solubility product for poorly soluble compounds. The fact of conjugated dissolution of the solid phase atoms is confirmed by the equality of anion and cation transition currents in electrochemical dissolution reactions.[42] It is a general rule that conjugated bond cleavage in the reactants is more favourable for thermodynamically allowed reactions. This mechanism provides for make up for the energy spent for cleavage of the existing bonds by the energy liberated upon the formation of new bonds.[43]

The incongruent dissolution of the solid phase may complicate DD analysis. However, an experimental study of the phases susceptible for incongruent dissolution has shown that both processes (incongruent and congruent) occur in parallel at different rates. Under mild conditions, the incongruent process occurs at a high rate, while under drastic conditions, the congruent process is faster; this allows incongruent phase dissolution processes to be converted into congruent ones. Thus dissolution of minerals with layered structure (for example, chrysocolla $Cu_8[Si_4O_{10}]_2(OH)_{12} \cdot n\,H_2O$) in 1 M HCl is incongruent, dissolution of copper predominating. The dissolution of this mineral in aqueous HF (1 : 5) is congruent, copper and silicon migrating into the solution in 8 : 8 ratio according to the mineral stoichiometry. During the dissolution of the Ni – Al alloy in NaOH, only aluminium passes into the solution, while nickel remains as powdered metal (Raney

nickel). The dissolution of this alloy in 1.2 M HCl is congruent, both metals pass into the solution in the same ratio as in the solid alloy.[44]

The dependence of the dissolution rate of crystals on the contributions of their different faces to the overall reactive surface is a well-known fact. These dependences have been studied in detail in relation to etching of semiconductors. They are also manifested in DD processes and are especially clear-cut in the case of dissolution of manually unseparable phase conglomerates; in this case, the reactive surface is renewed.[17,45,46]

3. Separating power of differential dissolution

The DD models considered in previous sections are based on simple equations that neglect many circumstances affecting the separating power of real dissolution processes. Generally, it is expedient to characterise the separating power of DD by the selectivity and the efficiency, as usually done in chromatography.[44]

The selectivity of mixture separation depends on thermodynamic factors determining the possibility of phase dissolution in particular solvents at a given temperature. (Here it is pertinent to recall the old rule: like dissolves like.) The DD selectivity could be described as the difference between the chemical potentials ($\Delta\mu$) of every two neighbouring phases between the dissolution rate maxima in the kinetic curves (in the differential form). However, currently it is unclear how to measure the changes in the chemical potential in the solid–solvent system if this at all possible and potential of what system should be used for this purpose. In this situation, the selectivity can only be characterised by the Δt value, *i.e.*, the difference between the times of the dissolution rate maxima of the subsequent (t_{i+1}) and preceding (t_i) phases

$$\Delta t = t_{i+1} - t_i .$$

The selectivity of continuous processes is estimated from the ratio of the rates of reactions occurring in parallel.[43] In this case, the temporal profile of stoichiograms characterises the separating power of the DD. An invariable profile of the stoichiogram sections for phases of constant composition and spatially homogeneous phases of variable composition is an indication of selective dissolution of phases of the mixture. In the case of spatially inhomogeneous phases of variable composition, the DD selectivity can be evaluated based on the form of stoichiograms taking into account the affinity criterion.

The DD selectivity can be characterised by the degree of phase co-dissolution (A_{21}).[36] The relevant equation of the model of contracting spheres for a mixture of two phases, $AB_{c_1} + AB_{c_2}$ has the form

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

For an ith phase ($i = 1, 2$): r_i is the initial particle radius, $k_i^{(0)}$ is the preexponential factor, E_i is the activation energy, T is the process temperature, c is the solvent concentration, n_i is the order of reaction, $T(\tau_1)$ and $c(\tau_1)$ are the trends of variation of the solvent temperature and concentration, τ_1 is the time required for complete dissolution of phase 1.

Most important is the dependence of the phase co-dissolution on the form of function $c(\tau)$, *i.e.*, on the pattern of variation of the solvent concentration with time.[35,36] This function may have arbitrary form, in particular, this can be determined by the parameter Z in the equation

$$c(\tau) = kc^Z .$$

Here k is the rate constant for the variation of the solvent concentration,

$$Z = \frac{\mathrm{d}c_0/\mathrm{d}t}{\mathrm{d}c_\tau/\mathrm{d}t},$$

where $\mathrm{d}c_0/\mathrm{d}t$ is the rate of variation of the solvent concentration at an initial time instant, and $\mathrm{d}c_\tau/\mathrm{d}t$ is the same at the instant of complete dissolution of the mixture of two phases. For $Z < 1$, the solvent concentration increases rather rapidly at the initial period of dissolution and slowly in the later periods. For $Z > 1$, an opposite trend is observed. When $Z = 1$, the solvent concentration increases linearly. The results of simulation of the separation of a mixture of phases A_2B_3 and AB_3 for Z = 0.001, 1 and 1000 are presented in Fig. 11. It can be seen that a change in the pattern of the function $c(\tau)$ leads to a change in phase separation selectivity. The selectivity substantially increases with an increase in Z; hence, to ensure the possibility of complete dissolution of a previous phase before dissolution of the subsequent phase starts, the dynamic conditions should not be changed too fast.

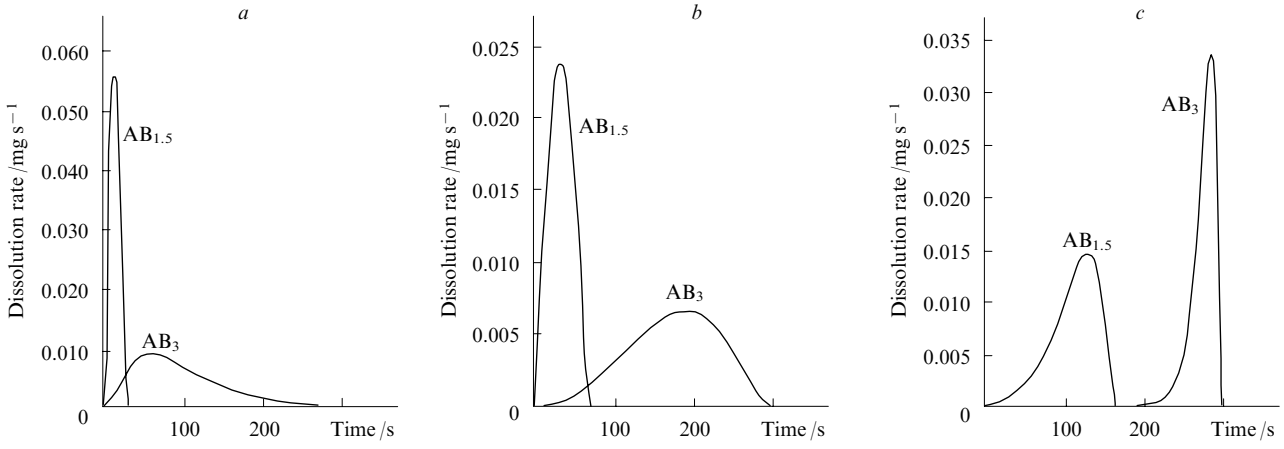


Figure 11. Results of simulation of separation processes for a mixture of phases A_2B_3 and AB_3 . $Z = 0.001$ (*a*), 1 (*b*) and 1000 (*c*).[35]

For separation, it is important what elements (the same or different) form the phases. If the number of different elements in the phases $n \geqslant 2$, then the stoichiogram segments for different elements are linear throughout the period of dissolution of these phases. In this case, the stoichiometry and the amounts of these phases can be determined without their selective isolation from the mixture. If such phases are formed by both the same and different elements, the stoichiometry can be determined only for different elements. Polymorphous modifications, α-, β-, γ-phases, dissolve under different conditions in the DD dynamic regime and can be identified in different ways, similarly to the identification of organic isomers in chromatographic separation. Phases having the same composition but differing in, for example, the degree of structure defectiveness can be determined in the same way.

The efficiency of DD depends on kinetic factors and on the factors related to the macrostructure of the phase mixture, *i.e.*, shielding (phases in the open pores of the matrix) and encapsulation (phases in the closed pores of the matrix) effects, which prevent contact of the phase with the solvent. The efficiency of DD is also determined by mass transfer rates in the stoichiograph flow system, which affect the shape and degree of smearing of the kinetic curves for phase dissolution. The resultant rate of the flow type dynamic regime of DD depends on the rates of all processes taking place in the stoichiograph. If the volume flow rate of the solvent is constant (the condition for applicability of ICP AES), then its linear velocity varies in different sections of the capillary system and in the reactor. The variation rates of the concentrations of active components and the flow temperature may be constant or variable, depending on the phase nature and content in the mixture. The velocity of discharge of the solution of phase components from the reactor is variable, because the dissolution rates of individual phases in the mixture are variable and, what is more important, unpredictable. This process was simulated using the Lovelock exponential dilution flask.[47] Note that convection and diffusion can also contribute to broadening of kinetic curves in the capillary system of a stoichiograph, as in liquid chromatographs and in flow analysis systems.

The phase shielding/encapsulation effect is manifested in different ways depending on what phases dissolve sooner and what phases dissolve later under DD conditions. The contact of the solvent with a readily dissolving phase encapsulated by a poorly dissolving one occurs only after the latter has been dissolved, *i.e.*, under more rigorous DD conditions; naturally, the former phase dissolves at a higher rate.

There are also other reasons for smearing of kinetic curves of phase dissolution, for example, the continuously changing grain size composition, renewal of the reaction surface, the crystal face effect. In this case, the kinetic dependences of DD are not smooth, thus differing from voltammograms or chromatograms. However, if these dependences reflect the dissolution of a single phase of constant composition, then the corresponding stoichiogram profiles are invariable. Figure 12 shows the stoichiograms and fragments of the family of kinetic curves for dissolution of elements of a monomineral microcline fraction. Strontium absent in the fraction to be analysed was added to the differentiating solvent. In the DD dynamic regime, the concentration of strontium linearly increased. Therefore, the observed fluctuations of the dissolution rates of elements with stoichiograms being invariable are attributable to the change in the real structure of the fraction upon dissolution rather than to instrumental effects. For phases formed by homogeneous particles, for example, for silver

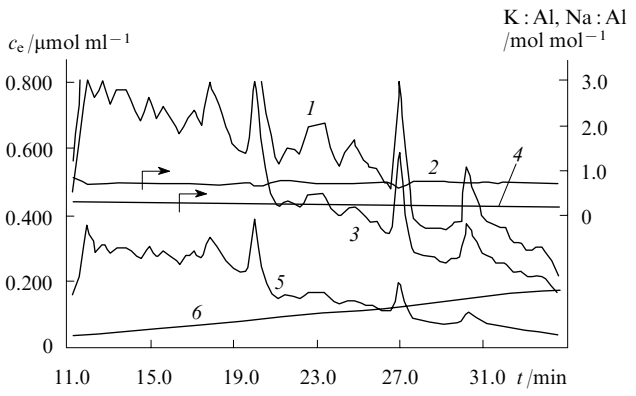


Figure 12. Stoichiograms and fragments of the family of kinetic curves for element dissolution present in the monomineral fraction of microcline. (*1*) Al, (*2*) K : Al, (*3*) K, (4) Na : Al, (*5*) Na, (*6*) Sr.

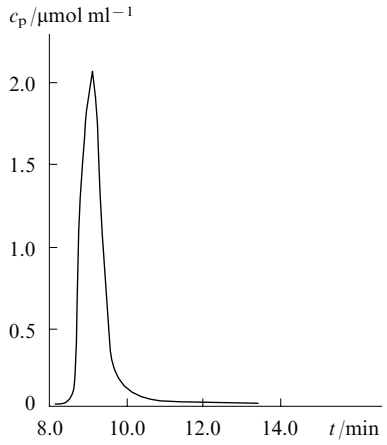


Figure 13. Dissolution of the silver phase in the Ag/Al_2O_3 catalyst.[48]

nanoparticles in the Ag/Al_2O_3 catalyst, the kinetic curves of dissolution have a number of smooth narrow peaks (Fig. 13).[48]

In most cases, variations of the macro- and microstructure of solids do not interfere with the DD analysis. Using DD one can solve seemingly unsolvable problems of phase analysis of multielement multiphase substances, as it is possible to quickly select parameters of the DD dynamic regime adequate to the real structure of each phase to be separated.

4. Conditions for dynamic regime of differential dissolution

When considering conditions for the dynamic regime of DD, one should rely on the knowledge about the ways of dissolution of inorganic solids accumulated in analytical chemistry. The solvent composition is chosen depending on the chemical analytical properties of the sample elements, some limits for time variation of its concentration and temperature being specified. Taking into account the response of the system to these conditions, they are varied in such a way that stoichiograms consist of linear segments to as large extent as possible. It is necessary to rule out the loss of elements that pass to the solution upon the formation of insoluble or volatile compounds. One should watch that the variation of DD conditions should not deteriorate the metrological characteristics of the results of analysis. Some restrictions are due to the design and functional characteristics of the stoichiograph, the resistance

of its systems to deleterious solvents, the possibility to implement the required temperature regimes and to the range of chemical elements that can be determined by the analyser detector.

The range of dissolution rates of the solid phase is rather broad, the time required for complete dissolution varying from several seconds to several hours. Too high or too low rates of dissolution hamper recording of the process; programmed temperature regime is used most often to change them in the required way. Highly dispersed water-soluble phases are dissolved at temperatures about 0 °C, while poorly soluble phases (spinels, silicates) are dissolved at ~300 °C in melts of concentrated acids. The solvents and temperatures for transition from mild to drastic conditions of the dynamic regime of dissolution used in the DD practice are summarised in Table 1.[48,49] The dissolution is started with aqueous solutions at pH 2; this prevents the undesirable hydrolysis, sorption or ion exchange. Then the solvent composition is changed towards an increase in acidic, basic or redox properties of components in an isothermal or temperature-programmed regime. The solvent concentration and temperature are varied according to either linear or exponential law. However, the optimal parameters for the dissolution of particular samples are still selected empirically. The crucial role in optimisation of DD conditions was played by the new stoichiographic titration method.[50]

Table 1. DD dynamic regime conditions for various substances.

Solid phases	Solvents	Temperature /°C
Drastic conditions		
Poorly soluble spinels	$H_2SO_4 + H_3PO_4 + HClO_4$	~ 300
Silicates		
Aluminosilicates	$H_2SO_4 + HF$	
Zeolites		
Poorly soluble oxides	$HCl + HF$	60 – 75 (aqueous solutions)
Sulfides		
Free elements, metals	$HCl + HNO_3$	
Oxides (basic, acid)	HCl, H_2SO_4, HNO_3 / NH_4OH	
Hydoxides		
Insoluble salts		
Water-soluble salts	H_2O / H_2O	~0 – 20
Mild conditions		

5. Stoichiographic titration

Titration is carried out in order to determine the amount of a known substance. The stoichiographic titration is meant for quantitative determination of known and unknown phases. The process of titration consists of coordination of the rates of variation of dynamic regime parameters with the observed rates of dissolution of elements. The parameter being monitored is not, for example, the colour of the indicator but the change in the rate of element dissolution, in particular, real-time kinetic curves are displayed at the monitor.[35] The rate coordination is done directly as dissolution proceeds while adhering to two rules.

1. If dissolution proceeds slowly or stops, the solvent concentration should be increased and/or temperature should be raised more frequently and to a higher extent.

2. If dissolution of at least one element (*i.e.*, a minimum number of elements in the phase) proceeds at a significant rate, the changes in the solvent concentration and temperature should be made less pronounced or terminated.

Analogues of stoichiographic titration include gradient elution and temperature programming in chromatography, constant-potential electrolysis in quantitative analysis and Q-mode in thermography. Stoichiographic titration differs appreciably from usual titration: it is unnecessary to measure the consumption of the titrant (differential solvent), to know the ratios in which the solvent and the solid phase react and to use fast reactions. The simple reason is as follows: the objects determined quantitatively in the stoichiographic titration are the reaction products of the titrant with the substance being titrated, *i.e.*, elements that pass to the solution.

Using stoichiographic titration, it is possible to efficiently implement conditions for increasing the selectivity of dynamic DD processes. An important advantage of this method is the possibility of extremely easy (often, in a single experiment) optimisation of the consecutive dissolution process for phases with unknown elemental composition, stoichiometry, number and amounts, real structure and dissolution rate. The unique possibilities of this new procedure are based on the invariance of the dissolution stoichiometry of individual phases with respect to dissolution dynamic regime parameters. Practically, stoichiographic titration consists of control of the operation velocity of the peristaltic pumps of the stoichiograph by means of an electronic device, resulting in the required changes in the solvent composition, concentration and temperature directly during the sample dissolution. A weighed sample is placed in the flow-type reactor of the stoichiograph and titration is carried out with observance of the above-formulated rules. The dissolution conditions are varied from mild to drastic, thus finally ensuring complete dissolution of the sample.

6. Stationary and flow regimes of differential dissolution

Phase analysis by the DD method can be carried out in stationary or flow type regime of dissolution using the corresponding reactors containing macro or micro weighed samples of the analytes (Fig. 14). The stationary type reactor is a vessel filled with a solvent taken in a large excess with respect to the sample weight. In the stationary regime, kinetic curves for element dissolution are obtained in the integral form and in the flow regime, in the differential form.

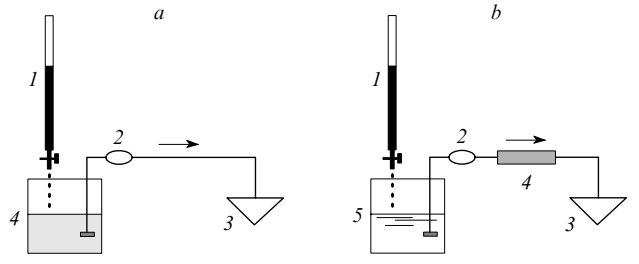


Figure 14. Diagrams for stationary (*a*) and flow type (*b*) reactors of the stoichiograph.
(*1*) Burette, (*2*) pump, (*3*) ICP AES analyser detector, (*4*) reactor, (*5*) mixer for solvent components.

Each regime has advantages and drawbacks. In the stationary regime, one can use large samples (this is especially important for preconcentration and preparative isolation of phases from mixtures) and carry out dissolution under drastic conditions. However, large volumes of the solvent result in too dilute solutions in initial stages, so that it is difficult to detect a change in the solvent volume with simultaneous sampling from the reactor and injection of additional components.

The advantages of the flow regime include more flexible process control, higher accuracy and sensitivity of analysis, minimum solvent consumption, minimisation of the effects of interaction of the solutes with the undissolved residue.

7. Preconcentration and determination of minor phases

It is often necessary to determine minor phases within complex substances. Powder X-ray diffraction is known to usually detect phases with a content of 5 mass % – 10 mass %. The DD method is more efficient in solving such problems, as it is one to two orders of magnitude more sensitive than powder X-ray diffraction.[44] In addition, using DD it is possible to carry out preconcentration of minor phases. The subsequent analysis of the isolated concentrate can be carried out by both the DD method and powder X-ray diffraction,[44, 51–54] NMR [55] or electron microscopy.[53, 56]

8. Calculations in the differential dissolution method and metrological evaluation of their results

The input information for DD analysis comprises data on time variation of both DD conditions and concentrations of the analyte elements in the resulting solution. The bulk of this information is considerable. For example, when determining to what phases 17 elements in an atmospheric aerosol belong, one must consider 153 dependences including 17 kinetic curves for element dissolution and 136 stoichiograms. Therefore, the results are processed on a PC with observance of a particular sequence and calculation rules.

The contents of elements in multielement and multiphase substances can differ by orders of magnitude; therefore, it is expedient to classify elements into major and minor. First of all, DD dependences of major elements should be considered, and fragments of the phases they form should be distinguished. The next step is to construct new families of stoichiograms characterising the dissolution rates of minor elements and the previously isolated fragments of the macrophases. The linear segments of these stoichiograms would indicate that minor elements belong to fragments of macrophases. The DD dependences of minor elements must be considered separately to reveal microphases, which may also contain small amounts of major elements.

The calculation procedure and the evaluation of the results of differential dissolution include three stages. The first one is processing of the primary information and plotting of the kinetic curves for the dissolution of sample elements. The second one includes stoichiographic calculations resulting in determination of the empirical formulas of the phases and providing data on their amount in the sample. The empirical formulas of phases would be fragmental if the phases contain elements that cannot be determined by the ICP AES analyser detector, namely, oxygen, hydrogen, carbon, nitrogen, *etc*. The fragmental formulas of an element or compound differ from the usual formulas by the subscript 1.[38] For instance, the fragmental formula for $MgCr_2O_4$ is Mg_1Cr_2, and iron(II) and iron(III) oxides and metallic iron have the same fragmental formulas: Fe_1. The fragmental nature of the formulas is due to limitations of the analyser detector used. With advances in the determination methods of elements in various forms compatible with the stoichiograph system, these limitations can be overcome. In the third stage, the results of stoichiographic calculations are correlated with conditions of the dynamic regime of dissolution and conclusions are drawn about possible ways to increase the degree of phase separation and about conditions of optimisation of the separation to make it faster and more accurate, to carry out microanalysis, microphase preconcentration or preparative isolation.

Below we present an example of stoichiographic calculations for a phase mixture $AB_{c_1} + AB_{c_2}$ (or $F_1 + F_2$). The input data consist of two groups.

1. A and B, which are the numbers of moles of elements A and B that pass to the solution in each time instant for complete dissolution of the sample. These data are derived from kinetic curves for dissolution of elements A and B.

2. c_1 and c_2, which are stoichiometric coefficients in the phase formulas. These coefficients are determined from linear segments of the stoichiogram $S_{B:A}$.

The calculations present no difficulty if the phases are completely separated during DD. The kinetic curves for dissolution of elements and stoichiograms are used. The segments corresponding to the condition $S_i(t) = \text{const}$ are distinguished in the stoichiograms and the sections matching them are distinguished in the kinetic curves. From the S_i value, the stoichiometric formulas of the phases are found in the stoichiograms, while the content of each phase is found in the kinetic curves by summing the amounts of elements that form these phases.

If complete separation of the two phases has not been achieved, then for the sections of kinetic curves corresponding to joint dissolution of elements A and B, the problem is reduced to finding the values A_{F_1} and B_{F_1} as well as A_{F_2} and B_{F_2}, *i.e*., the numbers of moles of elements A and B within each of the two phases, AB_{c_1} and AB_{c_2}. Since A and B, c_1 and c_2 are known, $B_{F_1} = c_1 A_{F_1}$ and $B_{F_2} = c_2 A_{F_2}$, for each point of the kinetic curves for element dissolution, a set of equations with two variables, A_{F_1} and A_{F_2}, should be solved

$$A = A_{F_1} + A_{F_2},$$

$$B = c_1 A_{F_1} + c_2 A_{F_2}.$$

The number of moles of each of phase F_1 and F_2 is

$$F_1 = A_{F_1},$$

$$F_2 = A_{F_2}.$$

The kinetic curves for element dissolution can be converted into curves for phase dissolution the areas under which correspond to the content of this phase in the mixture.

In the stationary-regime DD, the kinetic curves for element dissolution are recorded in the integral form; therefore, S_i for any time instant is equal to the slope ratio of the linear segments of parametric dependences (parameter – time), which relate the dissolution of every two chemical elements the amounts of which should be expressed in moles. The linear segments of the plots correspond to the dissolution of individual phases, while non-linear segments correspond to joint dissolution. Note that computer software allows solving far more complex problems than those given in this example.[5, 57]

The specific character of evaluation of metrological characteristics of the DD method and results is as follows: the stoichiometric composition and the amounts of phases are

determined in mixtures of unknown composition; statistical approach to evaluation of the results is often inapplicable as the sample is too small. Therefore, the accuracy of results of DD analysis is mainly ensured by high metrological characteristics of methods of elemental analysis of solutions and correct drawing of the balance matrix of final results.[58, 59] Apart from the overall contents of elements, the matrix also contains data about their distribution between the phases found.

One way of validation of the DD results is to compare them with the results of structural methods, *viz*., powder X-ray diffraction, IR , Raman, NMR and Mossbauer spectroscopy. Most often, this comparison showed agreement only at a qualitative level, because unlike DD, the results of physical methods are rarely quantitative.

9. Key limitations of the differential dissolution method

The following circumstances restrict the scope of DD method in the phase analysis:

— specific chemical nature and real structure of substances, resulting in either very fast or very slow phase dissolution;

— reactions of solids with solvents, giving rise to precipitates and/or gaseous products and incongruent dissolution;

— limited possibilities of the stoichiograph detector, which does not determine O, H, N and some other elements.

VI. Differential dissolution method in the analysis of substances and materials

A large body of factual knowledge concerning the practical use of the DD method has now been accumulated. The extensive use of this method was also promoted by the design of the stoichiograph, development of the stoichiographic titration technique, the unique possibility to perform phase analysis without reference samples of phases and the absence of special operations (polishing, evacuation, preliminary adjustment, *etc*.) or special requirements to analytes or analysis conditions. A large body of empirical knowledge has been accumulated on the correlations between the pattern of kinetic curves for dissolution or stoichiograms of various substances, on the one hand, and the composition and structure of the substances, on the other hand. The applications of the DD method are diverse. It is used to study catalysts, high-tech materials, natural minerals, mineral raw materials and the products of their processing, environmental objects, archaeological remains. These may occur as dispersed powders, ceramics, crystals, thin films and nano-sized systems. No less significant are the results of application of the DD method in the preparative separation of phase mixtures and in physicochemical studies of solid-phase transformations. These issues are considered in a number of reviews and survey papers (see [2, 25, 28, 29, 35, 38, 48, 60]).

1. Functional materials

The DD method was favourable for the development of the chemical studies of high-tech materials. This provides information about their phase composition and spatial inhomogeneity. Owing to high sensitivity of the method, it is possible to analyse microgram samples. Without replacing the traditional diagnostics techniques, DD allows one to obtain new data on the nature and degree of imperfection of the composition and general structure of materials.

Two procedures were used in the studies: complete dissolution of samples in the dynamic regime of DD and partial (layer-by-layer) dissolution with process termination at a specified instant of time. The residue taken out from the reactor was studied by structural methods,[53, 54, 56, 61, 62] the etch patterns on the surface of single crystals were analysed [63] or their physical and chemical properties were studied.[55] As a result, the composition – property correlations could be assigned to a particular fragment of the sample rather than to the whole sample bulk.[61, 63, 64]

a. Catalysts

The DD method has been used for the phase analysis of heterogeneous catalysts and their supports for more than two decades. Hundreds of samples containing altogether more than 60 elements have been investigated. The method proved to be efficient for the study of the formation of phase composition of catalysts at different stages of their preparation and operation and for elucidation of the nature of interaction of the catalyst active components and supports. The results of these studies were reported in more than 30 publications including reviews.[38, 48, 60] Note that the DD method was first developed just for the analysis of heterogeneous catalysts distinguished by a complex multielement composition, which is often unpredictable, and by the presence of crystalline, amorphous and highly dispersed phases. These circumstances hampered or made impossible determination of their phase composition by traditional diffraction and spectroscopic methods.

Studies of the formation features of the composition and structure of oxide catalysts provided new data on the phase composition of co-precipitated Fe(III) – Mg(II) hydroxides and Al(III) – Co(II) hydroxides as synthesis intermediates.[53, 65] The structure dynamics of reduction of copper aluminate [66] and the character of reduction – reoxidation processes for oxide copper-containing catalysts, specifically, copper chromite [67] and copper zinc hydrosilicate were studied.[68] Phase formation of vanadium titanium oxide catalysts was investigated.[69] The nature of the active component of the catalyst representing an aqueous suspension of Fe(III) oxide used for decomposition of hydrogen peroxide in alkaline media was established.[70] The phase compositions of aluminium – copper – chromium catalysts of full oxidation [71] and iron oxide block catalysts of complete combustion [72, 73] were determined by the DD method. The phase composition of SiO_2-supported eight-component molybdenum catalysts containing (mass %): 38.2 Mo, 6.75 Bi, 5.27 Fe, 8.32 Co, 4.49 Ni, 0.04 K and 0.57 P was studied. Data on the elemental composition, stoichiometry and quantitative contents of phases of complex molybdates were obtained for the first time; effects of modificaton of cobalt, nickel and iron molybdates by other elements were elucidated.[57] The study covered freshly prepared catalyst samples, those activated in a reducing environment and also spent and re-oxidised catalyst samples.

The compositions of samples of high-percentage (as regards nickel content) Ni – Al catalyst of methane decomposition at different preparation stages were determined.[74] These were mixed amorphised nickel and aluminium hydroxide precipitates dried at 120 °C, annealed at 350 °C and reduced with hydrogen at 550 °C. The phase composition of binary phosphorus – molybdenum [55] and vanadium – titanium [55, 75] oxide systems, catalysts of oxidative ammonolysis of methylpyrazine, was determined.

The DD method has been employed to study the real structure, physicochemical and catalytic properties and the nature of active components of the perovskite-based catalysts: $La_{1-x}Ca_xFeO_{3-0.5x}$,[76] $La_{1-x}Ca_xMnO_3$,[77] $La_{1-x}Sr_xCoO_3$,[78] $La_{1-x}Sr_xFeO_{3-y}$,[79] where $0 \leqslant x,\ y \leqslant 1$, including those obtained using mechanochemical activation.[80–82] For the

$La_{1-x}Ca_xFeO_{3-0.5x}$ catalysts used in extensive oxidation, a powder X-ray diffraction study has shown that a change in x results in a series of solid solutions of calcium in perovskite. The stoichiometry and the amount of each composition in the solid solution region were determined by DD; the amounts of unreacted initial lanthanum, calcium and iron oxide phases were determined (Table 2).

Table 2. Results of powder X-ray diffraction and DD phase analysis of a mixture of oxides $La_2O_3 + Fe_2O_3 + CaO$ subjected to mechanochemical activation and subsequent heat treatment at 900 °C.

Sample No.	Calculated formula	Phase formula from X-ray diffraction	DD	
			phase formula	fraction (mass %)
1	$LaFeO_3$	$LaFeO_3$	$LaFeO_3$	87.4
		La_2O_3	La_2O_3	1.56
		Fe_2O_3	Fe_2O_3	11.0
2	$La_{0.8}Ca_{0.2}FeO_{2.9}$	(La,Ca)FeO_3	$La_{1.0}Ca_{0.11}FeO_3$	72.5
		La_2O_3	La_2O_3	16.0
		Fe_2O_3	Fe_2O_3	5.5
		–	CaO	1.1
		–	$Ca_2Fe_2O_5$	4.9
3	$La_{0.2}Ca_{0.8}FeO_{2.6}$	(La,Ca)FeO_3	$La_{0.67}Ca_{0.34}FeO_3$	32.9
		La_2O_3	La_2O_3	4.0
		Fe_2O_3	Fe_2O_3	3.1
		–	CaO	2.2
		$Ca_2Fe_2O_5$	$Ca_2Fe_2O_5$	57.8

b. Heteropoly compounds

The DD method is used to study the syntheses of the solid phases of heteropoly compounds used as catalysts of various reactions. The reaction products of $[PW_{11}O_{39}]^{7-}$ with Ti(IV) were identified;[83,84] Fe(III) complexaton with As(III)–W(VI) heteropolyanions[85] and Pd(II), Cu(II), Fe(III) and V(V) complexation with $[PW_9O_{34}]^{9-}$ were studied.[86] The equilibrium of formation of lacunary As(III) heteropolytungstates[87] and the reaction of molybdophosphates with Pd(II) salts in aqueous solution were studied.[88]

c. High-temperature superconductors

The time when the stoichiograph was designed[37,38] coincided with the peak of interest in the studies of high-temperature superconductivity. Numerous works using the DD method were carried out: the major and impurity phases in the products of synthesis were determined, quantitative data on the stoichiometry of superconducting phases were obtained, doping of superconductors and degradation of their properties were investigated, the characteristic features of the structure of columnar,[56] lamellar[89] and stack structures[90] were elucidated. In most cases, the researchers were able to establish the grounds for chemical inhomogeneity of high-temperature superconductors and attribute them to either processing factors (non-equilibrium state, reactions with background impurity) or the nature of the material itself.[91] Often, defects not found by structural methods were detected in the samples.

Certain progress has been achieved in determination of the stoichiometry of major phases in the presence of impurity phases consisting of the same elements for samples of the Y–Ba–Cu–O,[58,59,92,93] Gd–Ba–Cu–O (Ref. 94) and Tm–Ba–Cu–O systems.[62] These compounds as ceramics and crystals synthesised by various methods were most often classified as single phase according to powder X-ray diffraction data. In some samples of the Y–Ba–Cu–O system, a DD study revealed the cationic non-stoichiometry for yttrium, which was first taken sceptically but later was confirmed in a detailed study of this system.[95]

A series of studies of heterophase superconducting samples of the Y–Ba–Cu–O system doped with silver[96,97] and iodine[98] demonstrated the possibility of formation of, for example, a copper-deficient $YBa_2Cu_{3-x}O_y$ phase.

Unique results were obtained in DD analysis of thin films of the Y123 superconducting phase applied on sapphire, strontium titanate and silicon substrates.[99,100] It was found that the detected gross stoichiometry of films does not ensure their single-phase character. The results of DD analysis of a ~600 Å-thick heterophase film in which microquantities of impurity phases were detected in addition to the major $YBa_2Cu_3O_y$ phase are shown in Fig. 15.[29]

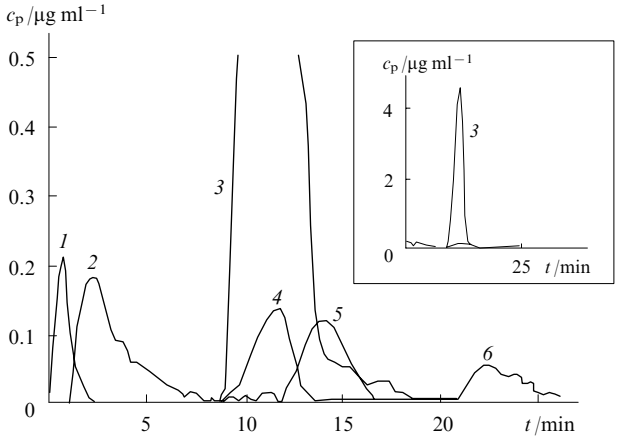


Figure 15. Kinetic curves for dissolution of the phases of thin (~600 Å) superconducting film Y123.[29]
Variation of conditions: from H_2O to HCl (1 : 10), 20 °C. Phase composition of the film (the content of the phase in μg is given in parentheses): (*1*) BaO (0.54), (*2*) Ba_2CuO_x (1.37), (*3*) $YBa_2Cu_3O_x$ (28.2), (*4*) Y_2O_3 (0.95), (*5*) BaO (0.90), (*6*) CuO (0.64).

The DD method proved to be efficient in a study of heterodiffusion processes in the Y123–sapphire film–substrate system. It was fond that a considerable aluminium flow from the substrate to the film surface is probable only for polycrystalline films and is absent if the films have strictly stoichiometric composition and are single-crystalline.[100] The results of DD analysis were significant for the production of qualitative and spatially homogeneous Y123 films on sapphire with high functional properties (T_c = 89 K, the width of the temperature transition of the film material into the superconducting state is 1 K, current density is 0.6×10^7 A cm^{-2}). Thus, the view that degradation of the superconducting properties of these films is caused by aluminium diffusion into the superconducting phase, existing in the early 1990s, was refuted.

Using the DD method, the process of formation of the Y123 phase in the films deposited by laser ablation technique onto various substrates at temperatures from 25 to 800 °C has been studied in detail. The formation of the Y123 amorphous phase was detected even at 100 °C and then, with increasing temperature, it transformed gradually from the amorphous (undetectable by powder X-ray diffraction) into crystalline state. The temperature of the onset of crystallisation of this

phase is 500 °C but the phase becomes single-crystalline only at 775 °C. The dectecion of the Y123 amorphous phase in the films by DD analysis gave grounds for the assumption that it is formed from oxide clusters, *i.e.*, polymeric structures $(MO)_n$ (M = Y, Ba, Cu; $n = 1-13$); subsequently, this has been confirmed by direct mass spectrometric studies.[101]

The DD method has been used to determine the phase composition of the superconductors of the Bi–Sr–Ca–Cu–O system, in particular, with Al, Ag, Pb, Ba and Nd additives.[90, 102–104] The results of a detailed DD study of the real stoichiometry of crystalline samples of the given system produced in different ways have been reported.[90, 91]

d. Materials with specific magnetic and electrical properties

The causes for the magnetic phase transition in the structurally low-dimension $LiCuVO_4$ phase ‡ have long been obscure and have been debated.[105, 106] In a DD study of this phase the type and concentration of the defects in the copper magnetic sublattice were determined. In combination with other methods, it was shown that the magnetic properties of the compounds $Li_{1-x}Cu_{1+y}VO_{4-z}$ are related, in a complicated manner, to lithium and oxygen deficiency with an excess of copper ions arranged in the Li sublattice.[107, 108] Unlike crystals, in the case of $Li_{1-x}Cu_{1+y}VO_{4-z}$ powders (x, y and z vary from 0.1 to 0.3), broadening of the magnetic phase transition is caused, in addition to the non-stoichiometry and disorder, by the spatial phase and chemical inhomogeneity (Fig. 16).

The composition of manganese ferrite nanoparticles was determined and their low content in the bulk of borate glasses was established by DD analysis using preconcentration. These glasses are promising as materials for memory devices with high data recording density.[109] It was shown [53, 110, 111] that nanoparticles represent mixtures of phases of variable composition, $Mn(Fe_{1-x}Al_x)_2O_4$, where $0 \leqslant x \leqslant 1$. As the particle composition changed, their real structure caused by second-order microstresses and packing defects also changed, as was established by high-resolution transmission electron microscopy and synchrotron X-ray diffraction. This gave correlations between glass magnetisation and the crystallite size, packing and mutual orientation in the nanoparticles.

In a DD study of the electrical properties of crystalline samples having the gross composition $Fe_{0.29}Mn_{0.71}S$, the stoichiometry of these objects was determined and impurity phases were detected at the microlevel.[112]

e. Optical materials

A DD study of $LiInS_2$ and $LiInSe_2$ crystals,[89, 113, 114] promising materials for non-linear optics, resulted in identification of the non-stoichiometry and cationic disorder and heterophase nature of some samples. The nature of the detected imperfections was confirmed by studies of optical properties of these defective crystals.[89] This resulted in recommendations on how to eliminate the factors responsible for deterioration of the mechanical strength and transparency and for colour change.[113, 114] The results of a DD study of the spatial inhomogeneity of $LiInS_2$,[89] Na_2S/Ce_2S_3 (new-generation red inorganic pigment) [63] and rare earth element disulfide [115, 116] powders demonstrated a pronounced defectiveness of the surface layers of the powder grains. For example, higher concentration of sodium sulfide in the Na_2S/Ce_2S_3 surface layers changes the pigment colour, an excess of lithium sulfide

‡ The properties of this phase are determined by one- or two-dimensional fragments of its three-dimensional structure.

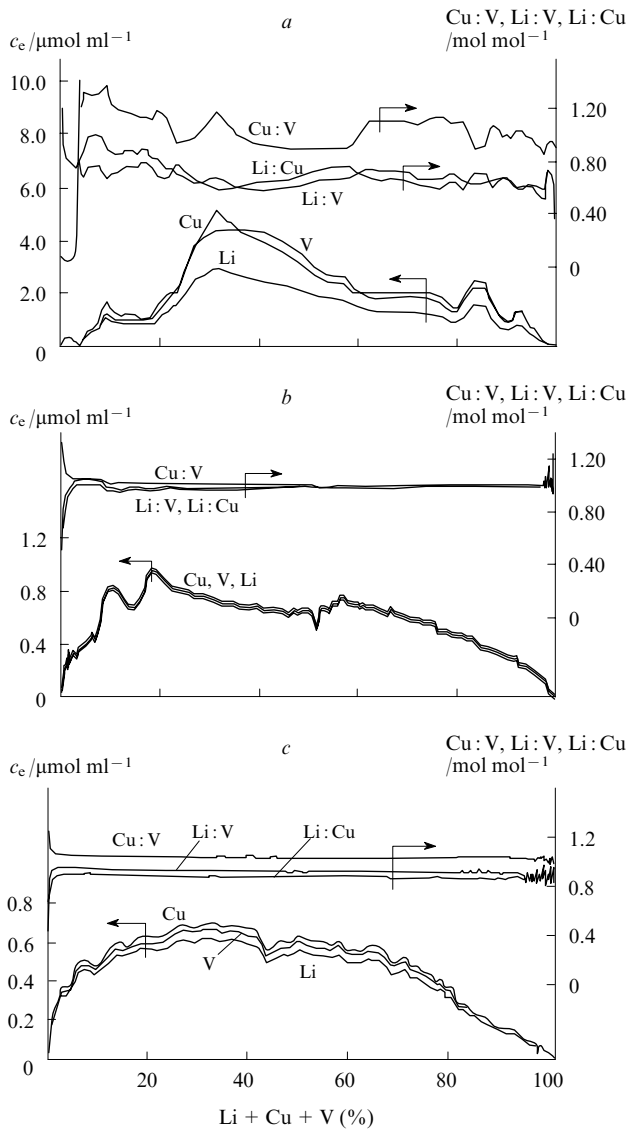


Figure 16. Kinetic curves for element dissolution and stoichiograms of samples of the Li–Cu–V–O system.[107]
Variation of conditions: from H_2O to HCl (1 : 10), 20 °C. (*a*) $Li_{0.72\pm0.23}Cu_{1.07\pm0.25}V_{1.00}$ powder phase, (*b*) $Li_{0.99\pm0.03}Cu_{1.00\pm0.01}V_{1.00}$ crystal, (*c*) $Li_{0.93\pm0.02}Cu_{1.05\pm0.01}V_{1.00}$ crystal.

makes $LiInSe_2$ powders air-unstable, and excessive concentration of near-surface sulfur in rare earth metal disulfides has a pronounced effect on the semiconductor properties.

f. Luminophores

A number of publications [56, 117, 118] demonstrated the efficiency of the DD method in detection of non-equilibrium supersaturated solid solutions in the surface layers of CVD-produced $Mn_{1-x}Zn_xS$ and $Eu_{1-x}Zn_xS$ films (Fig. 17). For the ZnS–EuS system, DD provided data on low ($\leqslant$0.05 at.%) solubility of EuS in ZnS, demonstrated the specific character of formation of the EuS phase in the ZnS matrix. The specific character is caused by the formation, under definite deposition conditions, of low-dimension EuS clusters coated by organic shell consisting of decomposition products of the ligands of volatile metal complexes, which rules out the possibility of cluster coalescence. Powder X-ray diffraction does not detect the EuS phase until, under other conditions of synthesis, the

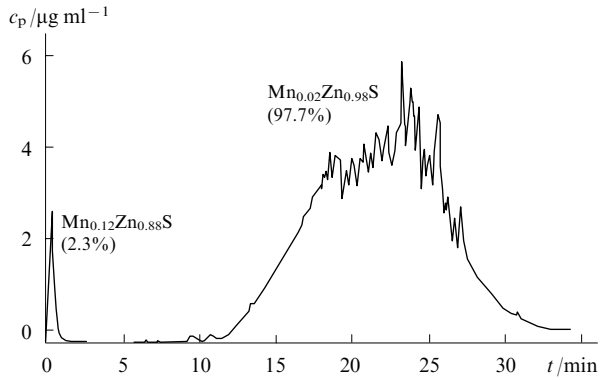


Figure 17. Phase composition of non-equilibrium supersaturated solid solutions in the $Mn_{1-x}Zn_xS$ thin film.[60]

coalescence of clusters becomes more favourable than their reaction with the gaseous organic products. The obtained information was used to select the conditions of synthesis of homogeneous $Eu_{1-x}Zn_xS$ films and to elucidate the mechanism of the CVD process.

g. Thermochromic materials

The heterometallic solid phases $Fe_xM_{1-x}(NH_2trz)_3(NO_3)_2$ [NH_2trz is 4-amino-1,2,4-triazole, M = Fe(II) and Ni(II)] exhibit a thermochromic effect: on heating their pink colour changes to white. The intensity of this effect depends on the x value. The results of DD analysis of a $Fe_{0.6}Ni_{0.4}(Htrz)_3.(NO_3)_2 \cdot H_2O$ sample (Htrz is 1,2,4-triazole) are shown in Fig. 18. According to gross elemental analysis, the overall Fe : Ni ratio in this compound corresponds to the given formula. Meanwhile, the Fe : Ni stoichiogram attests to the formation of one spatially inhomogeneous phase with variable composition in which x varies over a broad range.[119, 120]

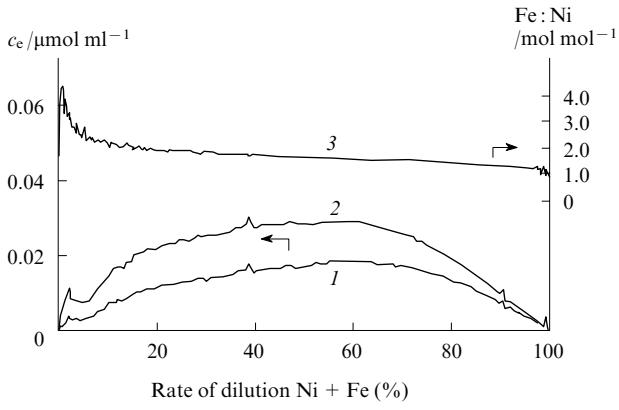


Figure 18. DD kinetic curves for Ni (*1*), Fe (*2*) and stoichiogram Fe : Ni (*3*) of a sample of the spatially inhomogeneous $Fe_{0.6}Ni_{0.4}(Htrz)_3.(NO_3)_2 \cdot H_2O$ heterometallic phase.[119]
Conditions DD: HCl, pH 2, 35 °C.

h. Nanodispersed composite sorbents

The DD method was used to determine the phase composition of composite sorbents of carbon dioxide [121] and water.[122–124] These sorbents are prepared by dispersing inorganic salts (alkali and alkaline earth metal sulfates, chlorides and bromides) into the pores of matrices, namely, meso- and microporous silica gels, γ-alumina or porous carbonaceous materials. The formation of sorbent properties is affected by both dispersion of their components down to nano dimensions and the physicochemical interactions between the components. The active components of these sorbents are most often amorphous. Using the DD method, the phase composition of sorbents was determined and the reaction products of the salts with the substrate surface were identified. For example, the sorbents consisting of magnesium sulfate on meso- and microporous silica gels were found to contain, apart from the magnesium sulfate phase, magnesium adsorbed on the silica gel surface (most likely, this is a result of ion exchange with the protonated silica gel surface). Analogous surface forms of the active components were also found in sorbent samples containing copper sulfate and calcium chloride. Note that structural methods did not provide this kind of data.

i. Fuel cell materials

The dissolution kinetics of caesium hydrogen sulfate incorporated in composites with high proton conductivity in the temperature range of 100–250 °C, which are promising materials for fuel cells, was studied by the DD method. Specific features of dissolution of this salt from composites with different composition and degree of dispersion were identified.[125]

j. Mechanochemical synthesis and mechanochemical activation products

The products of mechanochemical synthesis often have unknown phase composition and defective crystalline or amorphous structure. Application of diffraction or spectroscopic methods of phase analysis to these compounds is often of low efficiency. The DD method has helped to solve many problems arising in the studies of mechanochemical synthesis products in 20 different systems.[126, 127]

For samples of extensive oxidation catalysts, the perovskites $La_{1-x}Ca_xFeO_{3-0.5x}$ ($x = 0-1.0$), the results of phase analysis of the products of mechanochemical synthesis carried out by powder X-ray diffraction and DD were compared (see Table 2).[76] It can be seen that DD analysis, as opposed to powder X-ray diffraction, provides knowledge about the exact stoichiometry and the quantitative content of phases in these products even when they are present in minor amount.

The DD method was used to study activated samples of the Fe–Si system formed in the synthesis of iron silicides. This is an example of analysis of amorphous substances for which quantitative data about the phase composition have been obtained at different stages of their mechanochemical activation and subsequent annealing (Table 3).[128] The sequence of reactions of formation of the silicide $FeSi_2$ was established. The DD method was also used for analysis of the mechanochemical activation products in the Fe–Si system with a minor Co

Table 3. Phase composition of samples of the Fe–Si system after mechanochemical activation and annealing (mass %).

Phases	Activation time, temperature		
	15 min, 20 °C	35 min, 20 °C	35 min, annealing at 900 °C
Si	22.7	20.6	9.6
Fe	1.2	1.2	–
$FeSi_{0.17}$	38.3	–	–
FeSi	35.6	13.4	–
$FeSi_2$	–	64.8	90.4

additive.[129] The qualitative and quantitative composition of the products, including the solid solution $Fe_{0.92}Co_{0.09}Si_2$ was determined. Data on the phase composition for a series of samples of the Cu – Zn – O catalysts prepared by mechanochemistry were reported.[130] Using the DD method, phase formation during mild mechanochemical synthesis of calcium titanate was studied for the first time.[131] The crystalline and amorphous $CaTi_4O_9 \cdot n\,H_2O$ and $CaTiO_3$ phases and active TiO_2 were identified and determined quantitatively in the products of synthesis.

2. Minerals, ores, products of their processing, atmospheric aerosols

a. Minerals

The DD method was first applied to minerals to analyse clay samples[25] and later to study the composition of the monomineral fractions of biotite, olivine, pyroxene, microcline, muscovite,[61, 132] vivianite with isomorphous elements[133] and a white suspension of river water.[134, 135] It was found that, according to mineralogical analysis, sandine $(K,Na)_1Al_1Si_3$ and glauconite $K(FeAlMg)_2[AlSi_3]$ form the basis of monomineral fractions of microcline and muscovite. General aspects and specific features of DD analysis of minerals have been discussed.[60, 136]

By means of DD, new data on the phase composition of vanadium slags from the Nizhnii Tagil metallurgical plant were obtained.[60] A phase of constant composition, $Ca_2Si_1O_x$ (6.24%), and two phases of variable composition, $Ca_1V_{0.18}Si_{0.21}O_x$ (44.7%) and $Fe_1Mg_{0.43}Ti_{0.083}Cr_{0.019} \cdot Mn_{0.19}V_{0.029}$ (41.1%), were found in one sample and quantitatively determined. These results could not be obtained by other methods of phase analysis including powder X-ray diffraction, which was applied to study these products in parallel with DD.

b. Atmospheric aerosols

Atmospheric aerosols are the challenge for phase analysis by any method. Usually, these unpredictable structures are characterised by inhomogeneity of the elemental and phase compositions and present in minor quantities. This restricts the application of diffraction or spectroscopic methods for their phase analysis.§

Using the DD method, it was possible to gain unique information about the elemental and phase compositions of aerosols.[138 – 141] In an aerosol sample collected on a filter in a district of Novosibirsk, the contents of 15 elements, Na, K, Mg, Cu, Ca, Sr, Ba, Zn, Cd, Al, Si, S, Fe, Co and Ni, were determined by the DD method. The specificity of analysis was that the dissolution of both major and minor elements of aerosol microphases in the flow regime of stoichiograph operation took place in a minimum solvent volume, which decreased the detection limits of all elements by 1 to 2 orders of magnitude. The initial kinetic curves for the dissolution of elements present in the aerosol sample, which characterise the degree of dissolution of each element, were reported in the integral form.[140] This representation allows one to present, on the same scale, the plots for all elements with absolute contents in the aerosol differing by 3 or 4 orders of magnitude. The kinetic curves for phase dissolution derived from these plots are given in the differential form.

§ Note, however, that a great potential of the Auger spectroscopy for the study of the composition of surface layers of aerosols was demonstrated.[137]

Table 4. Ratio of the contents (in moles) of alkaline earth elements in aerosol phases.

Phase No.	Phases	Ca : Mg : Sr : Ba
1	water-soluble	1 : 0.11 : 0.00027 : 0.00032
2	calcium carbonate	1 : 0.078 : 0.00078 : 0.0010
3	calcium sulfate	1 : 0.063 : 0.00019 : 0.0013
4	silicates	1 : 2.44 : 0.0027 : 0.0033

Using the DD method, it is possible also to obtain other types of unique information on the chemical composition of aerosols. For example, the data presented in Table 4 refer to the relative contents of four alkaline earth metals in three phases with predominant content of calcium and in two silicate phases where magnesium predominates. It can be seen that the relative contents of all these elements in the phases are substantially different. Data of this type may be useful for identification of the sources of aerosols.

3. Archaeological findings

The DD method was used to determine the composition of various archaeological findings from the Mountain Altay.[133 – 135] In two graves the age of which was estimated as ~2500 years, bags with unknown powders were found on the belts of buried pazyryk woman and man. The stoichiometric formula of the blue powder from woman's grave was determined by the DD method to be $(Fe_{0.96}Mg_{0.03}Mn_{0.001})_3(PO_4)_2$. This corresponds to the composition of the mineral vivianite, which was used by Mountain Altay's women back in the 4 century B.C. as a beauty aid, blue dye (the bag contained a metallic mirror together with vivianite). This mineral was described by British mineralogist J G Vivian in 1817; currently it is used in the manufacture of paint and fertilizers.[142]

According to DD data, the powder found in the man's bag was mainly a silicate with the fragmental formula Al_1Si_2. This fragment is encountered in various minerals, but, most probably, this was pyrophyllite $Al_2[Si_4O_{10}](OH)$, an analogue of talc.[134, 135] The same results were obtained in analysis of contamination of the dress fabric of a man from another grave. If this was also pyrophyllite, it was probably mined from the same deposit and used by ancient horsemen in the same way as talc, *viz*., as a dusting powder.

The DD method has been extensively used for identification of inorganic components in the studies of unique archaeological textile sample from the frozen graves of the Mountain Altay (5 – 2 centruries B.C.).[134, 135] Note that phase analysis of the ancient fabric could not be carried out by powder X-ray diffraction due to the complex multielement composition of the inorganic textile material, its low content (fractions of percent) and a low mass of the material to be analysed (several milligrammes). Totally, elemental analysis of more than 100 fragments of ancient textile, parts of domestic stuff or dresses of pazyryks, was carried out. These included shirts, trousers, petticoats, fur coats, belts, felt, rugs, lacing, tie-strings, ropes, quivers, horse harness parts. Seven standard samples of modern fabrics stained by ancient procedures were also analysed by DD method. The mordant dyeing has been known from times immemorial. The mordants include oxide and hydroxide derivatives of aluminium, calcium, tin and some other elements. The results of DD analysis confirmed the presence of the mordand key components in the standard samples as individual compounds of aluminium, calcium, potassium and chromium. The archaelogical fabrics were found to contain silicates whose elemental composition is

quite close to the composition of white suspension of water from the Ak-Alakha river, which flows in the habitat area of ancient pazyryks. This suspension, which is a mixture of dispersed and hydrated silicate and aluminosilicate minerals, could have been used for natural mordant staining.

4. Differential dissolution method in solid-state kinetic studies

The quality and quantity of knowledge about the kinetics of transformations in multielement systems

solid + solid = solid

is far inferior to analogous data obtained by, *e.g.*, chromatographic or mass spectrometric techniques for liquid and gaseous systems. The main reason for poor knowledge of the solid-phase kinetics is the absence of adequate methods for quantitative determination of phase composition of both the complex initial solids and the products of their solid-phase transformations, especially those containing unknown phases, phases of variable composition and amorphous phases. Therefore, the application of DD for solving problems of this type appears quite promising.

First, DD was used to study the kinetics of phase formation of calcium titanate from calcium hydroxide and hydrated titanium dioxide upon mild mechanochemical synthesis.[131] In a system with the initial molar ratio $Ca(OH)_2 : TiO_2 \cdot n\,H_2O = 1:1$, the $CaTi_4O_9$ phase is formed in an early period and the formation process of the main $CaTiO_3$ phase has an induction period. Thus, these two phases are formed along independent routes. By the onset of formation of the $CaTiO_3$ phase, the active form of TiO_2 has been accumulated in the system; in the final stage of the synthesis, the remaining unreacted titanium dioxide is converted into this form. The presence of induction period in the formation of the $CaTiO_3$ phase can be attributed to the necessity of accumulation of active TiO_2.

The phase formation in the Mo–V–Nb–O system was studied by the DD method.[143, 144] Recently, unique results have been obtained in such study of the Mo–Te–V–Nb–O system.[145] For this complex multielement multiphase system containing amorphous spatially inhomogeneous phases with variable compositions, complex phase formation and destruction processes taking place both with and without temperature programming were quantitatively characterised. Figure 19

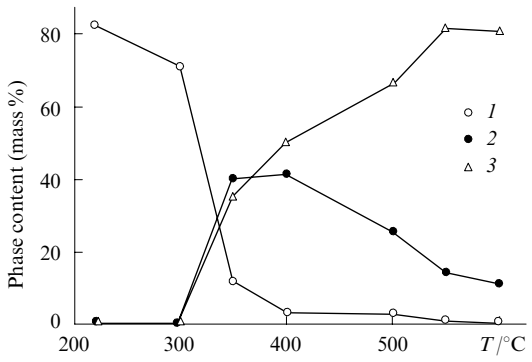


Figure 19. Kinetic plots for the formation and destruction of phases *1–3* in the Mo–Te–V–Nb–O system obtained with temperature programming in time.
The composition of phases *1–3* is given in Table 5.[145]

Table 5. Formation of the phase composition in the Mo–Te–V–Nb–O system.[145]

T /°C	Phase 1	Phase 2	Phase 3
20	$MoV_{0.21}Te_{0.22}Nb_{0.06}$	–	–
25	$MoV_{0.27}Te_{0.15}Nb_{0.03}$	–	–
220	$MoV_{0.13}Te_{0.10}$	–	$MoV_{0.11}Te_{0.02}Nb_x$
300	$MoV_{0.13}Te_{0.13}$	$MoV_{0.20}Te_{0.25}$	$MoV_{0.19}Te_{0.02}Nb_{0.12}$
350	$MoV_{0.14}Te_{0.07}$	$MoV_{0.43}Te_{0.43}$	$MoV_{0.20}Te_{0.04}Nb_{0.13}$
400	$MoV_{0.14}Te_{0.05}$	$MoV_{0.35}Te_{0.28}$	$MoV_{0.25}Te_{0.05}Nb_{0.13}$
500	$MoV_{0.14}Te_{0.04}$	$MoV_{0.28}Te_{0.30}$	$MoV_{0.27}Te_{0.08}Nb_{0.12}$

shows kinetic data for these processes, while Table 5 contains data on stoichiometry changes for phases with variable compositions in this system.

VII. Conclusion

The information presented in the review indicates that the difficulties of determination of the phase composition of multielement multiphase objects are due to the complex chemical composition and real macro- and microstructures of the analysed substances. These difficulties are typical of both structural physical and chemical methods of phase analysis. The scope of physical methods for determination of amorphous phases, phases with variable composition including spatially inhomogeneous phases and minor phases is limited. The complexity of preparation of reference samples (or the lack of them) hampers analysis of substances with unknown phase composition and almost rules out the possibility of quantitative phase analysis by physical methods. Chemical methods including the most frequently used selective dissolution method have the same limitations. The interpretation of selective dissolution results is complicated or impossible if composition and structure characteristics of particular phases in real samples differ considerably from these characteristics of reference samples.

Unlike fast instrumental physical methods, the 'wet' selective dissolution method cannot be instrumentalised. Finally, the actual monopoly of physical methods resulted in not only rejection of cumbersome and 'leisurely' chemical methods but also in the loss of interest of analytical chemists in phase analysis problems. Indeed, analytical chemistry textbooks give no data about the theoretical aspects and determination methods of either stoichiometric composition or content of each phase in solid multiphase mixtures; meanwhile, this is a field of inorganic analysis of enormous scope and diversity of objects rather than a number of specific issues.

The situation in the phase analysis of complex substances crucially changed with the advent of the stoichiographic DD method. The long-term practice demonstrated that this is the only reference-free method for quantitative determination of the phase composition of multielement and multiphase substances. It has appreciable advantage over reference diffraction and spectroscopic methods in the qualitative and quantitative analysis of substances of unknown phase composition, in determination of the amorphous phase modifications, phases of variable composition and in phase microanalysis. In view of the unique potential of the DD method, it has come into use for the detection and interpretation of the nature of spatial chemical inhomogeneity of samples of different complexity and dimensionality. No less significant are the results of application of this method in preparative-scale separation of

phase mixtures and in physicochemical studies of solid-phase transformations. There is every ground to describe the fast instrumental highly sensitive quantitative DD method as a full-scale technique that meets the criterion 'sample – result of analysis' with inherent theory, strategy, instruments, terminology and an extensive and topical field of application.

It is important that the stoichiographic approach to molecular analysis is not restricted to dynamic dissolution processes. It is in principle possible to extend this approach to other separation methods used in analytical chemistry, as has already been done, for example, in ion chromatography – stoichiography.

We would like to note the following. Somewhat more than 200 years ago, an outstanding event occurred in the history of chemistry: in 1793, German chemist I W Richter formulated the law or multiple proportions, the first quantitative law of chemistry. Richter was among the first chemists to use mathematics in studies. Although integral calculus has been fully developed at that time, in the Introduction to his famous book *Anfangsgrunde der Stochiometrie oder Messkunst chemischer Elementen*, Richter explained to chemists: 'if one number is added to another, the sign '+' (called plus) should be placed between them; if we wish to subtract, the sign '−' (called minus) is placed between the numbers.' Historians note with good feeling that Richter might have judged too harshly the mathematical knowledge of chemists but there is a chance that they really needed such guidance.[146] Perhaps, for this reason, Richter's discovery has not been recognised by contemporaries and has remained unnoticed for a relatively long period of time (~20 years). However, Richter was perspicacious when drew the attention of chemists to the two arithmetic operations, as stoichiometric calculations soon started to play the same role in chemistry as the addition and subtraction in mathematics.

Currently, the statements of stoichiometry are considered so important, clear and complete that they are learned at school at the start of learning chemistry and one can hardly imagine something new found in this field. After the discovery of rhenium, the last stable element of the Periodic Table, in 1925, romanticism of the quest for new elements has left analytical chemists. However, the world of chemical compounds is inexhaustible. One can hope (to rehash Richter) that stoichiography as an 'art of measuring chemical compounds' would help chemists to perceive this world.

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References

1. Yu A Zolotov *Analiticheskaya Khimiya: Problemy i Dostizheniya* (Analytical Chemistry: Problems and Achievements) (Moscow: Nauka, 1992)
2. V V Malakhov *Zh. Anal. Khim.* **52** 790 (1997) [a]
3. B S Khristoforov *Izbiratel'nye Rastvoriteli v Veshchestvennom Analize* (Selective Solvents in Material Analysis) (Novosibirsk: Siberian Branch of Academy of Sciences of the USSR, 1964)
4. Yu A Klyachko, O D Larina *Zh. Vsesoyuz. Khim. O-va im. D I Mendeleeva* **25** 681 (1980) [b]
5. V V Malakhov, A A Vlasov, L S Dovlitova *Zh. Anal. Khim.* **59** 1126 (2004) [a]
6. Kh Z Brainina *Inversionnaya Vol'tamperometriya Tverdykh Faz* (Inversion Voltammetry of Solid Phases) (Moscow: Khimiya, 1972)
7. O A Songina, V A Zakharov, in *Vol'tamperometriya Organicheskikh i Neorganicheskikh Soedinenii* (Voltammetry of Organic and Inorganic Compounds) (Moscow: Nauka, 1985)
8. L V Vilkov, Yu A Pentin *Fizicheskie Metody Issledovaniya v Khimii* (Physical Methods of Investigation in Chemistry) (Moscow: Vysshaya Shkola, 1987)
9. I M Zharskii, G I Novikov *Fizicheskie Metody Issledovaniya v Neorganicheskoi Khimii* (Physical Methods of Investigation in Inorganic Chemistry) (Moscow: Vysshaya Shkola, 1988)
10. Yu D Tretyakov *Usp. Khim.* **72** 731 (2003) [*Russ. Chem. Rev.* **72** 651 (2003)]
11. V V Dolivo-Dobrovol'skii, Yu V Klimenko *Ratsional'nyi Analiz Rud* (Efficient Analysis of Ores) (Sverdlovsk, Moscow: Metallurgizdat, 1947)
12. N A Filippova *Fazovyi Analiz Rud i Produktov ikh Pererabotki* (Phase Analysis of Ores and Products of Their Processing) (Moscow: Khimiya, 1975)
13. B S Khristoforov, E D Glotko *Veshchestvennyi Analiz Produktov Svintsovogo Proizvodstva* (Material Analysis of Products of Lead Production) (Novosibirsk: Siberian Branch of Academy of Sciences of the USSR, 1963)
14. M N Fedorova, K S Krivodubskaya, G N Osokina, T I Kostousova *Fazovyi Khimicheskii Analiz Rud Chernykh Metallov i produktov ikh Pererabotki)* (Chemical Phase Analysis of Ferrous Metal Ores and Products of Their Processing) (Moscow: Nedra, 1972)
15. R S Young *Chemical Phase Analysis* (London, High Wycombe: Griffin and Co., 1974)
16. N N Maslenitskii, M N Fedorova, R S Mil'ner, N V Budnikova *Khimicheskii Fazovyi Analiz Alyuminievogo Syr'ya i Nemetallicheskikh Poleznykh Iskopaemykh* (Chemical Phase Analysis of Aluminium Ores and Non-Metal Mineral Resources) (Moscow: Nedra, 1983)
17. *The Electrochemistry of Semiconductors* Ch. 6 (Ed. P J Holmes) (New York: Academic Press, 1962)
18. V V Malachov *Tagung Festkörperanalytik* Bd. 1 (Karl-Marx-Stadt: Technische Hohschule, 1979)
19. B Delmon *Introduction a la Cinetique Heterogene* (Paris: Technip, 1969)
20. P Barret *Cinetique Heterogene* (Paris: Gauthier Villars, 1973)
21. G A Aksel'rud, M A Al'tshuler *Vvedenie v Kapillyarno-Khimicheskuyu Tekhnologiyu* (Introduction in Capillary Chemical Technology) (Moscow: Khimiya, 1983)
22. E M Vigdorchik, A B Shein *Matematicheskoe Modelirovanie Neprerynykh Protsessov Rastvoreniya* (Mathematical Simulation of Continuous Dissolution) (Leningrad; Khimiya, 1971)
23. V V Dolivo-Dobrovol'skii *Zap. Leningr. Gorn. In-ta* **42** 3 (1963)
24. Kh K Ospanov *Fiziko-Khimicheskie Osnovy Izbiratel'nogo Rastvoreniya Mineralov* (Physicochemical Foundations of Selective Dissolution of Minerals) (Moscow; Nedra, 1993)
25. V V Malakhov *Zavod. Lab.* **56** 1 (1990)
26. G V Ostroumov, G A Sidorenko, L N Lyubimova *Zh. Analit. Khim.* **43** 360 (1988) [a]
27. V V Malakhov *Dokl. Akad. Nauk SSSR* **290** 1152 (1986) [c]
28. V V Malakhov *Zh. Analit. Khim.* **44** 1177 (1989) [a]
29. V V Malakhov *Zh. Analit. Khim.* **49** 349 (1994) [a]
30. V V Dolivo-Dobrovol'skii *Nauchn.-Tekhn. Inform. Byul. In-ta Mekhanoobr.* (5) 11 (1956)
31. N A Rudnev, I V Melikhov, A M Tuzova *Zh. Analit. Khim.* **28** 635 (1973) [a]
32. I V Melikhov, M S Merkulov *Sokristallizatsiya* (Cocrystallisation) (Moscow: Khimiya, 1975)
33. D V Tarasova, V A Dzis'ko, L G Karakchiev, V V Malakhov, L S Melekhova, F I Bondarevskaya, V G Shinkarenko *Kinet. Katal.* **13** 207 (1972) [d]
34. V V Malakhov, A A Vlasov, N N Boldyreva, L S Dovlitova, in *VI Konferentsiya 'Analitika Sibiri i Dal'nego Vostoka-2000' (Tezisy Dokladov)* [The VIth Conference 'Analytics of Siberia and the Far East-2000' (Abstracts of Reports)] (Novosibirsk: Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 2000) p. 21

35. V V Malakhov *Zh. Anal. Khim.* **57** 1029 (2002) [a]
36. A A Vlasov, V V Malakhov, in *Proceedings of the International Congress on Analytical Chemistry, Moscow, 1997* Vol. 1, B-12
37. RF P. 2075338; *Byul. Izobret.* (8) 136 (1997)
38. V V Malakhov, A A Vlasov *Kinet. Katal.* **36** 503 (1995) [d]
39. R Buffington *GC-Atomic Emission Spectroscopy Using Microwave Plasmas* (Avandale, USA: Hewlett-Packard, 1988)
40. H Lux *Anorganisch-Chemische Experimentierkunst* (Leipzig: J Ambrosius Barth, 1959)
41. P Atkins *Physical Chemistry* (London: Oxford University Press, 1978)
42. I G Gorichev, N A Kipriyanov *Zh. Fiz. Khim.* **55** 2734 (1981) [e]
43. G K Boreskov *Geterogennyi Kataliz* (Heterogeneous Catalysis) (Moscow: Nauka, 1986)
44. V V Malakhov, in *Razdelenie i Kontsentrirovanie v Analiticheskoi Khimii i Radiokhimii. Materialy II Mezhdunarodnogo Simpoziuma, Krasnodar, 2005* (Separation and Preconcentration in Analytical Chemistry and Radiochemistry. Proceedings of the Second International Symposium, Krasnodar, 2005) p. 56
45. V V Malakhov, A A Vlasov, I G Vasilyeva, L S Dovlitova, in *Aktual'nye Problemy Analiticheskoi Khimii (Tezisy Dokladov Vserossiiskoi Konferentsii), Moskva, 2002* [Topical Problems in Analytical Chemistry (Abstracts of Reports of the All-Russian Conference), Moscow, 2002] Vol. 1, p. 23
46. S M Repinskii, S F Devyatova, O I Semenova, L L Sveshnikova, in *Problemy Fizicheskoi Khimii Poverkhnosti Poluprovodnikov* (Problems of Physical Chemistry of Semiconductor Surface) (Novosibirsk: Nauka, 1978) p. 87
47. D A Vyakhirev, A F Shushunova *Rukovodstvo po Gazovoi Khromatografii* (Handbook on Gas Chromatography) (Moscow: Vysshaya Shkola, 1975) p. 275
48. V V Malakhov *J. Mol. Catal., A* **158** 143 (2000)
49. V V Malakhov, A A Vlasov, N N Boldireva, L S Dovlitova, in *Proceedings of the International Congress on Analytical Chemistry, Moscow, 1997* Vol. 1, p. 24
50. RF P. 2056635; *Byul. Izobret.* (8) 261 (1996)
51. V V Malakhov, in *Razdelenie i Kontsentrirovanie v Analiticheskoi Khimii. Materialy Mezhdunarodnogo Simpoziuma, Krasnodar, 2002* (Separation and Preconcentration in Analytical Chemistry. Proceedings of International Symposium, Krasnodar, 2002) p. 15
52. V V Malakhov, N N Boldyreva, A A Vlasov *Zh. Anal. Khim.* **47** 484 (1992) [a]
53. I G Vasilyeva, L S Dovlitova, V I Zaikovskii, V V Malakhov, I S Edel'man, A S Stepanov, K S Aleksandrov *Dokl. Akad. Nauk* **401** 349 (2005) [c]
54. O P Krivoruchko, E K Duplishcheva, V V Malakhov, N N Boldyreva, S M Paramzin, L M Plyasova *Kinet. Katal.* **31** 431 (1990) [d]
55. V M Bondareva, T V Andrushkevich, O B Lapina, V V Malakhov, L S Dovlitova, A A Vlasov *Kinet. Katal.* **41** 736 (2000) [d]
56. I G Vasilyeva, E N Ivanova, A A Vlasov, V V Malakhov *Mater. Res. Bull.* **38** 409 (2003)
57. V V Malakhov, A A Vlasov, N N Boldyreva, L S Dovlitova, L M Plyasova, T V Andrushkevich, T G Kuznetsova *Kinet. Katal.* **37** 457 (1996) [d]
58. I G Vasilyeva, N N Boldyreva, O V Potapova, V V Malakhov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (1) 38 (1990)
59. I G Vasilyeva, L P Kozeeva, V V Malakhov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (1) 45 (1990)
60. V V Malakhov *Eurasian Chem. Technol. J.* **3** 141 (2001)
61. V V Malakhov, L L Petrov, A A Vlasov, L S Dovlitova, in *Vtoroi Mezhdunarodnyi Sibirskii Geoanaliticheskii Seminar 'Intersibgeochim 2001' (Tezisy Dokladov), Irkutsk, 2001* [The Second International Siberian Geoanalytical Seminar 'Intersibgeochim 2001' (Abstracts of Reports), Irkutsk, 2001] p. 57
62. I G Vasilyeva *Vestn. Kazakh. Nats. Un-ta im. Al'-Farabi* (3) 23 (2003)
63. I Vasilyeva, V Malakhov, in *Proceedings of the 8th European Conference on Solid State Chemistry, Oslo, 2001* p. 029
64. I G Vasilyeva, B M Ayupov, A A Vlasov, V V Malakhov, P Macaudiere, P Maestro *J. Alloys Compd.* **268** 72 (1998)
65. E A Taraban, V V Malakhov, O P Krivoruchko, L M Plyasova, N N Boldyreva *Zh. Neorg. Khim.* **36** 875 (1991) [f]
66. L M Plyasova, T M Yur'eva, I Yu Molina, T A Kriger, A M Balagurov, L P Davydova, V I Zaikovskii, G N Kustova, V V Malakhov, L S Dovlitova *Kinet. Kat.* **41** 472 (2000) [d]
67. L M Plyasova, I Yu Molina, T A Kriger, L P Davydova, V V Malakhov, L S Dovlitova, T M Yur'eva *Kinet. Kat.* **42** 139 (2001) [d]
68. T M Yurieva, T P Minyukova, G N Kustova, L M Plyasova, T A Krieger, M P Demeshkina, V I Zaikovskii, V V Malakhov, L S Dovlitova *Mater. Res. Innovations* **5** 74 (2001)
69. G A Zenkovets, G N Kryukova, S V Tsybulya, E M Al'kaeva, T V Andrushkevich, O B Lapina, E B Burgina, L S Dovlitova, V V Malakhov, G S Litvak *Kinet. Kat.* **41** 628 (2000) [d]
70. A A Lysova, A O Kuz'min, V N Parmon *Kinet. Kat.* **44** 95 (2003) [d]
71. Z R Ismagilov, D A Arendarskii, O A Kirichenko, G B Barannik, E M Moroz, V A Ushakov, V V Malakhov, N N Boldyreva *Kinet. Katal.* **30** 918 (1989) [d]
72. V A Sazonov, N A Prokudina, Z R Ismagilov, N N Boldyreva *Zh. Prikl. Khim.* **70** 94 (1997) [g]
73. N A Prokudina, V A Sazonov, Z R Ismagilov, N N Boldyreva *React. Kinet. Catal. Lett.* **60** 251 (1997)
74. O V Goncharova, L B Avdeeva, V B Fenelonov, L M Plyasova, V V Malakhov, G S Litvak, A A Vlasov *Kinet. Katal.* **36** 293 (1995) [d]
75. V M Bondareva, T V Andrushkevich, N N Chumachenko, R I Maksimovskaya, L M Plyasova, V V Malakhov, L S Dovlitova, E B Burgina, G S Litvak *Kinet. Kat.* **41** 245 (2000) [d]
76. L A Isupova, S V Tsybulya, G N Kryukova, G M Alikina, N N Boldyreva, A A Vlasov, O I Snegurenko, V P Ivanov, V N Kolomiichuk, V A Sadykov *Kinet. Katal.* **43** 140 (2002) [d]
77. L S Isupova, S V Tsybulya, G N Kryukova, G M Alikina, N N Boldyreva, I S Yakovleva, V P Ivanov, V A Sadykov *Solid State Ionics* **141 – 142** 417 (2001)
78. L S Isupova, G M Alikina, S V Tsybulya, N N Boldyreva, G N Kryukova, I S Yakovleva, V A Sadykov *Int. J. Inorg. Mater.* **3** 559 (2001)
79. I S Yakovleva, L S Isupova, S V Tsybulya, A V Chernysh, N N Boldyreva, G M Alikina, V A Sadykov *J. Mater. Sci.* **39** 5517 (2004)
80. L A Isupova, I S Yakovleva, S V Tsybulya, G N Kryukova, N N Boldyreva, G M Alikina, V A Rogov, A A Vlasov, V A Sadykov *Khim. Inter. Ustoich. Razvitiya* **10** 77 (2002) [h]
81. L S Isupova, G M Alikina, S V Tsybulya, F N Salanov, N N Boldyreva, E S Rusina, I A Ovsyannirova, V A Rogov, R V Bunina, V A Sadykov *Catal. Today* **75** 305 (2002)
82. L S Isupova, Yu Yu Tanashev, I V Kharina, E M Moroz, G S Litvak, N N Boldyreva, E A Paukshtis, E B Burgina, A A Budneva, A N Shmakov, N A Rudina, V Yu Kruglyakov, V N Parmon *Chem. Eng. J.* **107** 163 (2005)
83. L G Detusheva, M A Fedotov, L I Kuznetsova, A A Vlasov, V A Likholobov *React. Kinet. Catal. Lett.* **59** 367 (1996)
84. L G Detusheva, M A Fedotov, L I Kuznetsova, A A Vlasov, V A Likholobov *Izv. Akad. Nauk, Ser. Khim.* 914 (1997) [i]
85. L G Detusheva, L I Kuznetsova, V A Likholobov, A A Vlasov, N N Boldyreva, S G Poryvaev, V V Malakhov *Koord. Khim.* **25** 611 (1999) [j]
86. L G Detusheva, L I Kuznetsova, M A Fedotov, V A Likholobov, L S Dovlitova, A A Vlasov, V V Malakhov *Koord. Khim.* **27** 890 (2001) [j]
87. L G Detusheva, L I Kuznetsova, L S Dovlitova, V A Likholobov *Izv. Akad. Nauk, Ser. Khim.* 354 (2003) [i]
88. L G Detusheva, L I Kuznetsova, M A Fedotov, L S Dovlitova, A A Vlasov, V A Likholobov, V V Malakhov *Zh. Neorg. Khim.* **48** 1835 (2003) [f]
89. L Isaenko, I Vasilyeva, A Yelisseyev, S Lobanov, V Malakhov, L Dovlitova *J. Cryst. Growth* **218** 313 (2000)

90. I Vasilyeva, V Malakhov, L Dovlitova, H Bach *Mater. Res. Bull.* **34** 81 (1999)
91. L G Kozeeva, I G Vasilyeva, V P Shaburova, A Ya Royak, N A Podberezskaya, S A Gromilov *Zavod. Lab.* **56** 28 (1990)
92. L P Kozeeva, M Yu Kameneva, N V Podberezskaya, I G Vasilyeva, N V Kurat'eva, D Yu Naumov, V A Nadolinnyi, V E Fedorov *Zh. Strukt. Khim.* **45** 268 (2004) [k]
93. I Vasilyeva, A Vlasov, V Malakhov, in *Proceedings of the IVth International Workshop on Chemistry and Technology of High Temperature Superconductors, Moscow, 1995* p. 92
94. I G Vasilyeva, in *Proceedings of the International Symposium, Krakow, 1994* p. 120
95. T N Kol'tsova, G D Nipan *Zh. Neorg. Khim.* **41** 1944 (1996) [f]
96. N F Zakharchuk, I G Vasilyeva, in *Materialovedenie Vysokotemperaturnykh Sverkhprovodnikov. Materialy I Mezhgosudarstvennoi Konferentsii, Khar'kov, 1993* (Materials Science of High Temperature Superconductors. Proceedings of the First International Conference, Kharkov, 1993) Vol. 3, p. 57
97. B A Kolesov, N F Zakharchuk, I G Vasilyeva, L I Yudanova, L P Koseeva, S A Gromilov, M A Starikov *Solid State Commun.* **84** 645 (1992)
98. A P Nemudry, B B Bokhonov, S S Shatskaya, V V Boldyrev, I G Vasilyeva, N F Zakharchuk *Physica C (Amsterdam)* **211** 366 (1993)
99. I G Vasilyeva, A A Vlasov, Ya I Gibner, V V Malakhov *Dokl. Akad. Nauk* **324** 596 (1992) [c]
100. I G Vasilyeva, A A Vlasov, V V Malakhov, M R Predtechensky *Thin Solid Films* **292** 85 (1997)
101. A V Bulgakov, M R Predtechensky, A P Mayorov *Appl. Surf. Sci.* **96**–**98** 159 (1996)
102. I G Vasilyeva, B V Reddi, N N Boldyreva, I N Kuropyatnik, A I Romanenko, V V Malakhov *Sverkhprovodimost: Fiz., Khim., Tekhnol.* **3** 2608 (1990)
103. B V Reddi, I G Vasilyeva, A I Romanenko, V V Malakhov *Bull. Mater. Sci.* **14** 291 (1991)
104. I Vasilyeva, J Zhu, T Shilkina, Ya Gibner, T Kuropyatnik, S Gromilov, V Malakhov *Mater. Res. Bull.* **26** 255 (1991)
105. A N Vasil'ev *JETP Lett.* **69** 876 (1999)
106. A N Vasil'ev, L A Ponomarenko, H Manaka, I Yamada, M Isobe, Y Ueda *Physica B: Condens. Matter* **284**–**288** 1619 (2002)
107. A V Prokofiev, I G Vasilyeva, V N Ikorskii, V V Malakhov, I P Asanov, W Assmus *J. Solid State Chem.* **177** 3131 (2004)
108. A V Prokofiev, I G Vasilyeva, W Assmus *J. Cryst. Growth* **275** 2031 (2005)
109. B Jeyadevan, K Tohji, K Makatsuka, A Narayanasamy *J. Magn. Magn. Mater.* **217** 99 (2000)
110. I G Vasilyeva, in *Trudy 10-go Mezhdunarodnogo Simpoziuma 'Poryadok, Besporyadok i Svoistva Oksidov', Rostov-na-Donu, 2007* (Proceedings of the 10th International Symposium 'Order, Disorder and Properties of Oxides', Rostov-on-Don, 2007) Vol. 1, p. 103
111. I G Vasilyeva, D A Sychev, V V Malakhov, in *Digest Reports of the XVIth International Synchrotron Radiation Conference, Novosibirsk, 2006* p. 36
112. J B Romanova, L I Ryabinkina, N V Volkov, G A Petrakovsky, V V Sokolov, I G Vasilyeva *Phys. Met. Metallogr.* **99** 573 (2005)
113. L Isaenko, I Vasilyeva, S Lobanov, A Yelisseyev *J. Cryst. Growth* **275** 217 (2005)
114. I G Vasilyeva *J. Alloys Compd.* **323**–**324** 34 (2001)
115. I G Vasilyeva, in *Handbook on Physics and Chemistry of Rare Earths* (Amsterdam, London, New York, Oxford, Paris, Shannon, Tokyo: Elsevier, 2001) p. 573
116. I G Vasilyeva *Zh. Fiz. Khim.* **80** 2068 (2006) [e]
117. V G Bessergenev, E N Ivanova, Yu A Kovalevskaya, S A Gromilov, V N Kirichenko, S M Zemskova, I G Vasilieva *Mater. Res. Bull.* **30** 1393 (1995)
118. V G Bessergenev, E N Ivanova, Yu A Kovalevskaya, I G Vasilieva, V L Varand, S M Zemskova, S V Larionov, B A Kolesov, B M Ayupov, V A Logvinenko *Mater. Res. Bull.* **32** 1403 (1997)
119. O V Shakirova, Yu G Shvedenkov, D Yu Naumov, N F Beizel', L A Sheludyakova, L S Dovlitova, V V Malakhov, L G Lavrenova *Zh. Strukt. Khim.* **43** 649 (2002) [k]
120. O G Shakirova, L G Lavrenova, Yu G Shvedenkov, V A Varnek, N F Beizel', O S Aristova, L S Dovlitova, V V Malakhov, in *XX Mezhdunarodnaya Chugaevskaya Konferentsiya po Koordinatsionnoi Khimii, Rostov-na-Donu, 2001* (The XXth Chugaev International Conference on Coordination Chemistry, Rostov-on-Don, 2001) p. 493
121. A G Okunev, V E Sharonov, A V Gubar', I G Danilova, E A Paukshtis, E M Moroz, T A Kriger, V V Malakhov, Yu I Aristov *Izv. Akad. Nauk, Ser. Khim.* 343 (2003) [i]
122. L G Gordeeva, S I Glaznev, V V Malakhov, Yu I Aristov *Zh. Fiz. Khim.* **77** 2048 (2003) [e]
123. L G Gordeeva, I S Glaznev, E V Savchenko, V V Malakhov, Yu I Aristov *J. Colloid Interface Sci.* **301** 685 (2006)
124. L G Gordeeva, A V Gubar', L M Plyasova, V V Malakhov, Yu I Aristov *Kinet. Katal.* **46** 780 (2005) [d]
125. V G Ponomareva, G V Lavrova, V V Malakhov, L S Dovlitova *Neorg. Mater.* **42** 1223 (2006) [l]
126. V V Malakhov, L S Dovlitova, A A Vlasov, N N Boldireva, in *Proceedings of the Vth International Conference on Mechanochemistry and Mechanical Alloying, Novosibirsk, 2006* p. 88
127. V V Malakhov, L S Dovlitova, A A Vlasov, N N Boldyreva *Khim. Inter. Ustoich. Razvitiya* **15** 117 (2007) [h]
128. G V Golubkova, O I Lomovsky, A A Vlasov, L S Dovlitova, E Y Belyev, V V Malakhov *J. Alloys Compd.* **1**–**2** 131 (2000)
129. G V Golubkova, O I Lomovsky, Y S Kvon, A A Vlasov, A L Chuvilin *J. Alloys Compd.* **351** 101 (2003)
130. H L Sastricum, V V Malakhov, T M Yurieva, H Bakker, E K Poels, in *Proceedings of the Russian–Dutch Workshop. Catalysis For Sustainable Development, Novosibirsk, 2002* p. 186
131. N V Kosova, E G Avvakumov, V V Malakhov, E T Devyatkina, L S Dovlitova, V V Boldyrev *Dokl. Akad. Nauk* **356** 350 (1997) [c]
132. V V Malakhov, L L Petrov, A A Vlasov, L S Dovlitova *Spectrochim. Acta, Part B* **58** 373 (2003)
133. V V Malakhov, A A Vlasov, I A Ovsyannikova, L M Plyasova, I L Kraevskaya, S V Tsybulya, V G Stepanov, in *Fenomen Altaiskikh Mumii* (Phenomenon of Altay Mummies) (Eds A P Derevyanko, V I Molodin) (Novosibirsk: Institute of Archaeology and Ethnography, Siberian Branch of the Russian Academy of Sciences, 2000) p. 162
134. V V Malakhov, A A Vlasov, I L Kraevskaya, L S Dovlitova, in *Kostyum i Tekstil' Pazyryktsev Altaya (IV–III vv do NE)* [Dress and Textile of the Altay Pazyryks (4–3 centuries B.C.)] (Novosibirsk: INFOLIO, 2005) p. 198
135. N V Polos'mak, L P Kundo, G G Balakina, V I Mamatyuk, V G Vasil'ev, E V Karpova, V V Malakhov, A A Vlasov, I L Kraevskaya, L S Dovlitova, E A Korolyuk, E G Tsareva, *Tekstil' iz Zamerzshikh Mogil Gornogo Altaya IV–III vv. do NE. Opyt Mezhdistsiplinarnogo Issledovaniya* (Textile from Frozen Graves of the Mountain Altay of the 4–3 centuries B.C. Attempt of International Investigation) (Novosibirsk: Siberian Branch of the Russian Academy of Sciences, 2006)
136. I G Vasilyeva, V V Malakhov, in *Book of Abstracts of the XVth International Conference on X-Ray Diffraction and Crystal Chemistry of Minerals, St Petersburg, 2003* p. 56
137. V P Ivanov, S N Trukhan, D I Kochubei, K P Kutsenogii, V I Makarov *Khim. Inter. Ustoich. Razvitiya* **14** 449 (2006) [h]
138. V V Malakhov, A A Vlasov, N N Boldyreva, L S Dovlitova, S G Pushkin *Khim. Inter. Ustoich. Razvitiya* **3** 253 (1995) [h]
139. V N Parmon *Colloids Surf., A* **151** 351 (1999)
140. V V Malakhov, A A Vlasov, L S Dovlitova *Khim. Inter. Ustoich. Razvitiya* **10** 643 (2002) [h]
141. V V Malakhov, L S Dovlitova, A A Vlasov, N N Boldyreva, in *Analiz Ob'ektov Okruzhayushchei Sredy (Tezisy Dokladov VI Vserossiiskoi Konferentsii), Samara, 2006* [Analysis of Environmental Objects (Abstracts of Reports of the VIth All-Russian Conference), Samara, 2006] p. 145

142. A A Godovikov *Mineralogiya* (Mineralogy) (Moscow: Nedra, 1975)
143. V M Bondareva, T V Andrushkevich, G I Aleshina, R I Maksimovskaya, L M Plyasova, L S Dovlitova, E B Burgina *React. Kinet. Catal. Lett.* **88** 183 (2006)
144. V M Bondareva, T V Andrushkevich, G I Aleshina, L M Plyasova, L S Dovlitova, O B Lapina, D F Khabibulin, A A Vlasov *React. Kinet. Catal. Lett.* **87** 377 (2006)
145. T V Andrushkevich, G Ya Popova, G I Aleshina, L M Plyasova, Y A Chesalov, V V Malakhov, L S Dovlitova, M L Khramov, in *Mekhanizmy Kataliticheskikh Reaktsii (Tezisy Dokladov VII Rossiiskoi Konferentsii), St Peterburg, 2006* [Mechanisms of Catalytic Reactions (Abstracts of Reports of the VIIth Russian Conference), St Petersburg, 2006] Vol. 2, p. 7
146. F Szabadvari, A Robinson *A History of Analytical Chemistry* (Amsterdam: Elsevier, 1980)

[a] — *J. Anal. Chem. (Engl. Transl.)*
[b] — *Mendeleev Chem. J. (Engl. Transl.)*
[c] — *Dokl. Phys. Chem. (Engl. Transl.)*
[d] — *Kinet. Catal. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[f] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[g] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[h] — *Chem. Sust. Develop. (Engl. Transl.)*
[i] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[j] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[k] — *J. Struct. Chem. (Engl. Transl.)*
[l] — *Inorg. Mater. (Engl. Transl.)*