

Determination of chemical composition of solid inorganic substances and materials using the principles of stoichiography and voltammetry

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Abstract The state of the art in determination of the phase composition of complex inorganic solids by chemical and electrochemical methods is discussed. The theoretical and practical essentials of stoichiography and the new stoichiographic method of differential dissolution (DD) are reported. The unique feature of this method is that reference samples of the analyzed solid phases are not necessary. The development of this stoichiographic method was strongly affected by voltammetry. The application of the DD method for determining the chemical composition of various substances and materials is presented. The complementary use of voltammetry and DD for the detection, identification, and quantitative determination of inhomogeneity of the chemical composition of high-temperature superconductors was shown to be efficient.

Keywords voltammetry · stoichiography · phase composition of solids

Introduction

The term “chemical composition of a substance” is not strictly defined in the chemical literature. This term is taken as self-evident, indicating chemical elements and their compounds. Meanwhile, variations of the composition are classified as elemental, molecular, phase, surface, bulk, matrix, extrinsic, ionic ones, etc. The composition is characterized also by different forms of elements (speciation): They can belong to some chemical compounds, be soluble or insoluble, volatile or non-volatile, mobile, strongly or weakly bound,

catalytically active, toxic, etc. Elements are distinguished by their oxidation state; they can constitute different structural groups—clusters, clathrates, nanostructures, and others. Structural forms and composition of solid multielement multiphase substances are multivarious. Such substances can be represented by the sum of individual particles of phases with constant or variable composition or by the mechanically inseparable aggregations of these phases. In the aggregations, there are interfaces between phases. However, in the bulk of individual phases, there can be regions with inhomogeneous composition and/or structure that have no interfaces.

Regions with inhomogeneous composition and/or structure without interfaces can be present in the bulk of individual phases. Phases can be mutually encapsulated in the closed pores or shielded by other solid phases in the open pores. Adsorbed, ion-exchange, and covalently bound components can exist on the phase surface, whereas the bulk of phase aggregations may include the boundary structures having composition which differs from the composition of contacting phases.

Many problems and tasks of analytical chemistry are caused by the fact that open systems are always at non-equilibrium in the formation of substances and materials. As driving force of the processes increases, the nature of transformations occurring in such systems may change drastically (bifurcations, deterministic chaos). This inevitably leads to changes in the number and features of the processes and, accordingly, alters the chemical composition of such systems. In the absence of transport connections between local volumes of solid systems, the newly emerging chemical processes also deviate a system from spatial uniformity of the composition. Thus, the term “compositional inhomogeneity” reflects a more general—spatial—concept of the chemical composition of substances and materials, which is not adequate to conventional notions of their gross composition, content of admixtures, purity levels, etc.

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The composition of multielement solid substances is often characterized as “quite complicate”; however, this declaration can hardly reveal the essence of problems accompanying the development of methods and techniques for analysis of such objects. The theory of analytical chemistry does not provide any exact principles and rules for the detection, identification, and quantitative determination of all variants of the chemical composition of solid inorganic substances. Their composition is commonly characterized by the data of gross elemental analysis, inhomogeneity being leveled using the so-called representative samples.

Determination of spatial and local inhomogeneity is of prime importance for studying the composition, structure, and properties of various materials. Such studies form a highly developed and fast-moving field of science and practice with the dominance of structural physical methods: X-ray diffraction (XRD), infrared (IR), nuclear gamma resonance (NGR, the Mössbauer effect), electron microscopy, secondary ion mass spectrometry (SIMS), laser ablation techniques, etc. The role of analytical chemistry methods in this field is minor, being restricted mainly to gross analysis.

Chemical and electrochemical methods of phase analysis

Nevertheless, chemical and electrochemical methods are applied to some extent for the separation and determination of solid phases [1–4]. For separations, the possibilities of these methods strongly depend on the variable reactivity of individual phases related to their real structure. Thus, practical applications of these methods are based mainly on an empirical approach, which requires careful selection and observance of the separation conditions for each system under analysis.

Chemical and electrochemical methods of determination are based on performing selective chemical reactions. Two situations are possible. In the first case, a phase to be determined remains in the undecomposed residue of the sample, where it can be identified and quantitatively determined by appropriate methods. In the second case, products of selective decomposition of the analyzed phase are transferred to the solution or gas phase, where one of the elements of this phase is quantitatively determined by elemental analysis. Chemical methods, especially the method of selective dissolution, were widely employed in the middle of last century, but now they are used only rarely.

Voltammetric techniques are virtually also chemical methods, where the selectivity of the interaction is achieved by controlling the electrochemical reactions of solid phases. The field of application of electrochemical methods is restricted to determinations of phases capable of undergoing redox reactions and possessing a sufficient electronic conductivity. Electrochemical methods are instrument-based, which enhances their analytical power.

At present, in a general flow of studies with predominance of physical structural methods, the role of chemical and electrochemical methods is modest, as they cannot solve the entire scope of problems related to phase analysis. Such problems proved to be actually irresolvable by the most known chemical method of selective dissolution (SD). Any non-chemist would manage to separate a mixture of sodium chloride and gold dust by dissolution. However, some questions cannot be answered even by a professional chemist, in particular: how to separate a mixture of non-identified solid phases if it is known only that the mixture consists of, say, 10–15 chemical elements. Due to difficulties with separation of solid phases, analytical chemists have lost interest in solving such problems. Meanwhile, this concerns not only some specific problems and tasks! Determination of chemical compounds in multielement inorganic solid mixtures is a topical field of inorganic analysis considering a wide range of objects. Unfortunately, this field has dropped out from the realm of interest of analytical chemistry. This subject is not considered in the university manuals of analytical chemistry. There are no specialists professionally working in phase analysis (the term “phase analysis” here is meant in the sense of identifying and quantifying different phases in a solid sample); papers on the subject disappeared from analytical chemistry journals. This situation is due to insurmountable difficulties in phase analysis of solid objects, which are related primarily with radical differences in the chemical–analytical features of inorganic solids and those of liquid and gaseous substances.

First, solid substances with their infinite spatial structures of ionic, covalent, or metallic nature (molecular crystals being an exception) cannot be dispersed into elementary chemical–structural objects—“the formula units”. Thus, methods of solid mixture separation radically differ from the methods used to separate gaseous and liquid mixtures, where components are divided on the atomic–molecular level. In the case of solid mixtures, their crystal and amorphous macrostructures should be divided. The known methods for separation of liquid and gaseous substances (e.g., chromatographic and electrophoretic techniques) are unacceptable for solids.

Second, solid phase samples with identical stoichiometric composition but different prehistory (natural or synthetic samples subjected to thermal, mechanical, or radiation action) always differ in their real structure. Such phases are represented by amorphous and crystal modifications with the crystal structure defects of different type and concentration and they differ in the morphology and dispersity—size and geometry of dispersed particles, pore structure, specific surface area, and features of interfaces. These factors underlie the variability of all properties of the solid phases with identical stoichiometry and different real structure. It is virtually impossible to prepare and use standard samples of such objects of analysis.

Third, there exist phases of variable composition, which are represented by numerous natural and synthetic samples differing in the relative content of main and impurity chemical elements. For such phases, the preparation and use of standard samples are also impossible.

Thus, it can be stated that separation of solid phases is the principal and practically unresolved problem of phase analysis, whereas determination of the stoichiometry of pure phases is a trivial task of elemental analysis.

Stoichiography

The concept of stoichiography is a system of new ideas on the stoichiometry of non-steady-state hetero- and homophase mass transfer processes. Stoichiography (and stoichiographic methods) resulted from a long search for new efficient ways of solving a general problem of chemistry—how to determine the composition of mixtures containing unknown chemical compounds [5–8]. This problem does not exist in elemental analysis: All stable elements have already been discovered; their total number is relatively small, and methods for determining each element in the presence of other elements are known. On the contrary, chemical compounds are uncountable, and most of them are still undiscovered.

The problem of chemical analysis is most topical for the mixtures of inorganic solids. Physical diffraction and spectroscopic methods prevail here: XRD, IR, Raman spectroscopy, NGR, nuclear magnetic resonance (NMR), and electron microscopy. Chemical methods of phase analysis play only a minor part now.

The essence of chemical stoichiographic methods is the combination of mixture separation processes (chromatography, electromigration, dissolution, extraction, etc.) and determination of the time-varying stoichiometry of elemental composition of the substance flow being separated. Stoichiographic methods are distinguished from all known chemical and physical methods of analysis by their ability to perform molecular analysis without reference samples of chemical compounds. This unique and fundamental feature is based on specific calibration procedure: Measuring instruments are calibrated against standard samples of the elements constituting the analyte, whereas reference samples of the compounds are not used. However, results of analysis are presented as the stoichiometric formulas of compounds being identified and as the quantitative data on their content in the objects under consideration. This refers also to earlier unknown chemical compounds that are discovered for the first time.

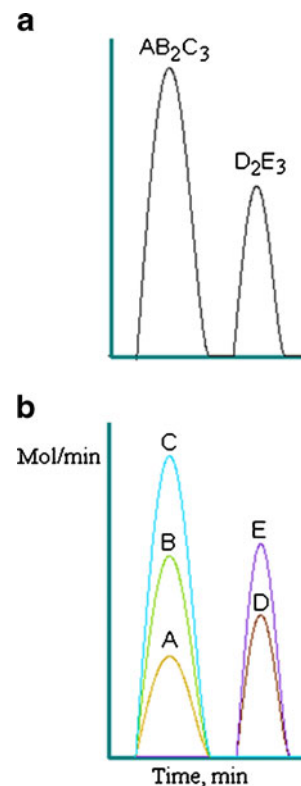
To formulate the stoichiography postulates, it was necessary to introduce some new terms (*italicized*), which are defined in the text.

The idea and principles of stoichiography and stoichiographic methods are very simple. This can be explained by a

chromatographic example. Figure 1a displays a model chromatogram of a mixture of two compounds, AB_2C_3 and D_2E_3 , which can be obtained using a conventional chromatographic detector. Such detectors record the appearance of chemical compounds in chromatograms as individual peaks. Figure 1b shows a chromatogram of the same mixture recorded with the use of so-called *absolute detector* [5], which can record all chemical elements of the Mendeleev's Periodic Table in a mobile phase flow. Unfortunately, such a detector has not been developed as yet, but advanced inductively coupled plasma atomic emission (ICP AES) and inductively coupled plasma mass spectrometers can perform most of the necessary functions.

The intensities of the analytical signals recorded by an absolute detector should be expressed in moles. In this case, molar ratios of every two elements at each point of their separated peaks will be equal to coefficients that relate these elements in the simplest stoichiometric formulas of compounds to be separated. This allows finding such formulas immediately. In our example, these will be AB_2C_3 and D_2E_3 . At the same time, the total peak area of the elements corresponds to the content of each of two compounds in the sample. Thus, stoichiographic methods provide simultaneous detection, identification, and quantitative determination of chemical compounds by their primary feature—the stoichiometry of elemental composition.

Fig. 1 Model chromatograms of a mixture of AB_2C_3 and D_2E_3 with conventional detector (a) and absolute detector (b)



Stoichiographic method of differential dissolution

For a long time, there was no method similar to chromatography for separation of solid phase mixtures. Such a method was developed in 1986 and called (as an alternative to SD), the differential dissolution (DD) method [7]. The DD method is based on two physicochemical regularities that determine (1) the course of successive passing of individual phases from their mixtures into solution in a specially created dynamic dissolution regime and (2) changes in the dissolution stoichiometry during these processes.

The DD dynamic regime [8, 9]

Kinetic analysis of the chemical reaction $A+R=P$ commonly implies that initial concentration of substance A and reactant R in the reaction system decreases, whereas the concentration of product P increases. If reactant R in this system is present in a large excess, its concentration is assumed to remain constant in the course of reaction; the concentration of A decreases, and that of P increases. These two regimes can be characterized as stationary ones in distinction to non-stationary dynamic regime of the reaction under consideration. In the dynamic regime, the concentration of reactant R taken in a large excess grows with time, for example, linearly, although a part of R is consumed upon interaction with A; accordingly, the concentration of A decreases, and that of P increases. To provide such dissolution regime for a solid substance, e.g., a mixture of oxides, the concentration of solvent, e.g., strong acid, is to be increased intentionally in the process; this should be accompanied by recording the rate of chemical elements passing into solution from the sample.

The essence of the dynamic regime consists in increasing the chemical potential μ with an increase in the concentration of active components of the solvent—protons, reductants, or oxidants. Under such non-stationary dynamic conditions, various solid phases successively pass into solution when μ values corresponding to each phase are attained. Such effect resembles voltammetry, first of all stripping voltammetry. Respectively, the dynamic kinetic curves for dissolution of multiphase solid substances have the form of well-known voltammetric dependences; see Fig. 2. No works were found in the chemical literature on the analysis of dynamic regime from this point of view. This may be explained by a seeming uselessness of such regime: Why increase the concentration of reactant which already has a large excess in the system? However, a large excess of solvent increases the chemical potential in the dynamic regime of differential dissolution, when a negligible part of the solvent is spent for dissolution of solid phases.

The dissolution stoichiometry [8]

Solid phases are destroyed upon dissolution; so, it is possible that dissolution rate is recorded, not for the entire phase, but only for the constituting elements or some fragments. A problem arises of reconstructing the kinetic curves of element dissolution into kinetic curves of phase dissolution. To solve this problem, the notion of dissolution stoichiometry of solids was introduced.

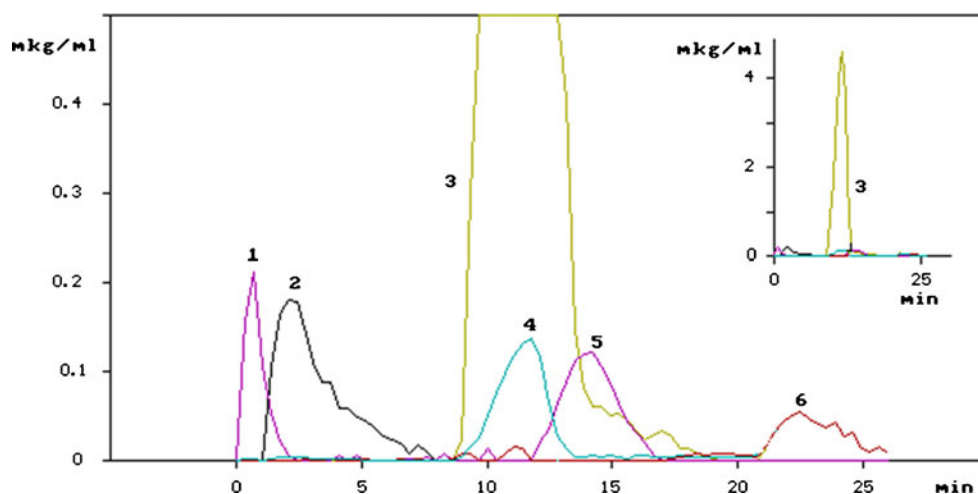
The dissolution stoichiometry S is characterized by a family of stoichiometric (molar) ratios, where elements at each time point pass from a solid substance into solution, i.e., S is equal to the dissolution rate ratio of the element. It seems reasonable to transform the differential kinetic curves of elements' dissolution into the time functions of molar ratios of dissolution rates for each two elements of the substance under analysis, $S(t)$. Such functions are called *stoichiograms*. Their total number is equal to the number of pair combinations of elements constituting the substance. An essential feature of stoichiograms is that, upon dissolution of individual phases of a constant composition, the stoichiograms retain constant values equal to stoichiometric coefficients relating the respective two elements in each individual phase.

It is known that the dissolution rate of each individual phase is determined, on one hand, by its chemical nature and real structure, i.e., by the crystal structure (defects taken into account) and dispersity—linear dimensions of solid particles, their pore structure, and specific surface area, which determine, in particular, the area of reacting surface. On the other hand, the dissolution rate of solids depends on the chemical composition and concentration of solvents, and on the temperature and hydrodynamic conditions of dissolution. Of principal importance is that the dissolution stoichiometry of individual phases of constant or variable composition is invariant to changes in all these characteristics and parameters (*the invariance principle of dissolution stoichiometry*). The dissolution stoichiometry of a NaCl sample with any real structure remains equal to a constant molar ratio $Na/Cl=1$ over the entire period of dissolution in any solvent under any constant or time-varying conditions. Principles for determination of phases with a variable composition are reported elsewhere [10].

In general, the invariance principle of dissolution stoichiometry is trivial, because stoichiometry of a phase with constant composition is independent of the amount of this phase and conditions of its existence. However, the application of this principle to analysis of phase mixtures has important and unexpected consequences. First, this opens a way to broad variation of the dynamic regime parameters when searching for conditions of successive phase dissolution; second, a degree of phase separation upon dissolution can be fixed unambiguously. This is reflected by the time profile of stoichiograms rather than by kinetic curves of element dissolution. The regularities that determine the form

Fig. 2 Kinetic curves for phase dissolution and their content (in micrograms) in a 700 Å thick Yb-Ba-Cu-O film:

1 – BaO (0.54), 2 – Ba₂CuO_x (1.37), 3 – YBa₂Cu₃O_x (28.2), 4 – Y₂O₃ (0.95), 5 – BaO (0.90), 6 – CuO (0.64). The DD conditions: H₂O + HCl (1:10), 20°C [11]



of $S(t)$ functions make it possible to perform phase analysis without reference samples of the phases. Such regularities were revealed at mathematical modeling of DD processes and verified by many experiments. The theory, methodology, and instrumentation of the DD method were reported in numerous publications and a review [8]; a brief overview is presented below.

Experimental procedure [11]

When phase composition of a substance is unknown, it is natural that all parameters determining the dissolution rate of each constituting phase are also unknown. During the dissolution, it is possible to specify and control the composition and concentration of solvents, the temperature, and, to some extent, the hydrodynamic conditions. However, the dissolution kinetics of a substance under analysis cannot be described a priori, since there are no data on the reacting surface area of individual phases and its changes during the dissolution, on the rate constants, order of the reactions, or activation energy for dissolution of each phase of the mixture. Besides, these and other parameters can change in the dynamic regime. However, when choosing the conditions of successive phase dissolution, it is not necessary to know these characteristics and parameters, since separation conditions for each sample can be found quite easily in experiments from the shape of stoichiograms.

The composition of differentiating solvents, starting from water, is usually arranged in the following order: NaOH ← NH₄OH ← H₂O → HCl, HNO₃, H₂SO₄ → (HCl+HNO₃) → (HCl+HF) → (H₂SO₄+HF) → (H₂SO₄+H₃PO₄+HClO₄). This simple series of solvents allows analyzing various substances of different nature; see Table 1.

Stoichiograph ([8, 12], patent)

Efficiency of the DD method is related to the use of precise and highly sensitive multielement methods of elemental analysis, which are computerized because the number of

elementary computing operations exceeds 10⁶ for DD analysis of a substance comprising, e.g., five elements. About 20 years ago, a device that strongly enhanced the possibilities of DD method was devised at the Borekov Institute of Catalysis SB RAS, Novosibirsk. This device, called stoichiograph, successfully operates until now.

A scheme of the stoichiograph, as shown in Fig. 3a, includes vessels 1 and 2 with the solvent components (for example, water and a concentrated solution of HCl), peristaltic pumps 4 and 5 delivering the solvent components through capillaries to mixer 6 at different rates, and electronic device 3 controlling flow rates of the solvent components by a preset program and providing a joint solvent flow from mixer 6 to reactor 7 with a constant volumetric rate (~2 ml min⁻¹) and progressively increasing concentration of the solvent. A sample is dissolved in the reactor, and the resulting solution goes directly to analyzer detector 8—an ICP AES. Operation of the entire system is controlled by a computer.

A microprocessor electronic device for controlling the solvent flow rate is incorporated into the casing of a pump. This device is used to program the pumping of solvents to the mixer with a decreasing rate from one vessel and with an increasing rate from another one given that the volumetric flow rate of solvent from mixer is constant. The ICP AES analyzer detector allows simultaneous determination of the majority of elements in the resulting solution with periodicity of ≥1 s. Recording of kinetic dissolution curves is actually continuous, which makes it possible to reveal fine effects during the process. A software package was developed to control the course of differential dissolution and make necessary calculations.

As seen from Fig. 3b, design of a stoichiograph formally resembles the classical design of the J. Heyrovský polarograph (the 1959 Nobel Prize). In the stoichiograph, the vessels with the solvent components correspond to the voltage source of a polarograph, an electronic device controlling the solvent composition—reochord, the reactor – to electrolytic cell, and ICP AES – to galvanometer.

Table 1 Conditions of the DD analysis

Phases	<i>Severe conditions</i>	
	Solvents	Temperature, °C
Difficult-soluble spinels	$\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4 + \text{HClO}_4$	~ 300
Silicates	↑	↑
Alumosilicates	$\text{H}_2\text{SO}_4 + \text{HF}$	
Zeolites	↑	
Difficult-soluble oxides	$\text{HCl} + \text{HF}$	$60 - 75$
Sulfides	↑	(Water-solutions)
Metals	$\text{HCl} + \text{HNO}_3$	↑
Oxides	↙ ↘	
Hydroxides	HCl NH_4OH	
Nonsoluble Salts	↔	
Water-soluble Salts	H_2SO_4 HNO_3	$0 - 20$
	↙ ↘	
	H_2O	
		↑
		<i>Mild conditions</i>

However, in distinction to the polarograph that records a single voltammetric dependence, the stoichiograph records the “current” of all elements of the substance being dissolved, which are determined by the analyzer detector. The fundamental distinction between these analytical systems is that electron flux used in voltammetry is replaced in stoichiograph by the flows of protons, reducing or oxidizing reactants, which allows not only redox, but also the acid–base reactions to be involved in dissolution process. Accordingly, stoichiography provides a much greater body of data and more significant information as compared with voltammetric analysis. Figure 3c displays a photo of the first lab-scale stoichiograph.

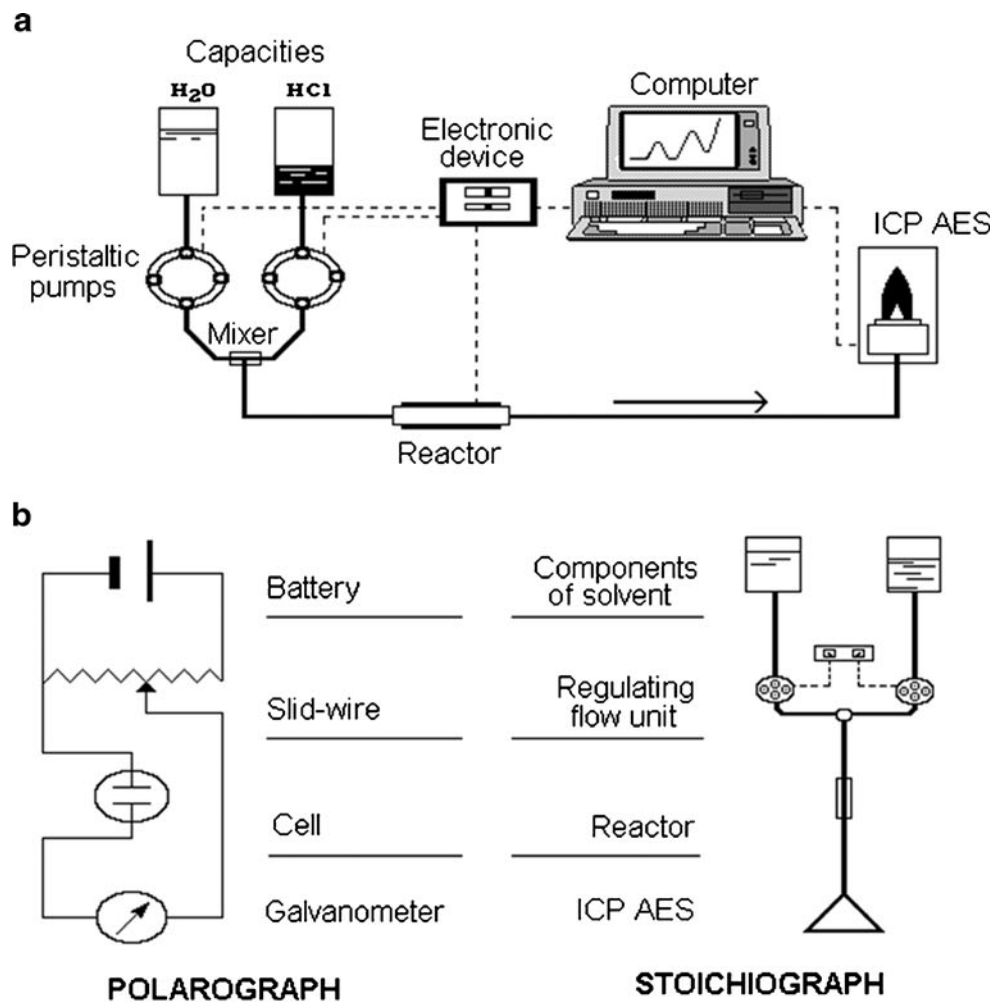
Stoichiographic titration ([8, 13], patent)

Optimal parameters for dissolution of particular objects can be chosen only empirically, because data necessary for preliminary calculations are usually lacking. A key role in selection of DD conditions was played by *stoichiographic titration*. This method can form parameters of dynamic

regime corresponding to a real structure of each phase being separated and, which is most important, makes it in situ—on a real-time basis—directly in the DD process. The titration process matches the rates of changes in dynamic regime parameters with the observed dissolution rates of elements constituting the analyzed substance. At that, one should monitor changes not in the color of indicator, but rather in the rate of element dissolution. This can be done easily, as the kinetic curves of element dissolution are displayed at the stoichiograph monitor on a real-time basis. Parameters of the dissolution process are adjusted immediately according to two rules.

1. If dissolution proceeds slowly or stops, the concentration of solvent components and/or temperature should be increased more frequently and to a greater extent.
2. If dissolution of at least one element (i.e., a minimum number of elements in the phase) proceeds at a significant rate, variation of the solvent concentration and temperature should be decreased or terminated.

Fig. 3 Schemes of the stoichiograph (a), the polarograph and stoichiograph (b) and the first lab-scale stoichiograph (c)



In practice, such titration consists in controlling the operation rate of peristaltic pumps in stoichiograph by means of an electronic device, which provides the desired changes in parameters of dynamic dissolution regime. The main advantage of stoichiographic titration consists in extremely fast (often, in a single experiment) optimization of successive dissolution and determination of solid phases with unknown elemental composition and stoichiometry, number and quantitative content in the analyzed object, real structure, and dissolution rates. The unique potential of this new procedure is based on invariance of the dissolution stoichiometry to changes in the parameters of dynamic DD regime of this process.

Stoichiographic calculations [8, 14]

The calculation and estimation of differential dissolution results include three steps. The first step is the processing of primary data and plotting of kinetic curves for dissolution of elements of the analyzed sample. The second step includes stoichiographic calculations leading to the simplest empirical formulas of the phases and providing data on their amount in the sample. At the third step, results of the stoichiographic calculations are correlated with the conditions of the dynamic dissolution regime to reveal possible ways for increasing the degree of phase separation and optimization of the separation process aimed at its acceleration, higher accuracy, microanalysis, concentration, or preparative isolation of microphases.

An example of stoichiographic calculations for a mixture of phases $AB_{c_1} + AB_{c_2}$ (or $F_1 + F_2$) is considered below. There are two initial groups of data.

1. A and B are the number of mole elements A and B passing into solution at each time point upon complete dissolution of the sample. These data are extracted from kinetic curves for dissolution of elements A and B .
2. Stoichiometric coefficients c_1 and c_2 in the phase formulas, which are determined from linear segments of stoichiogram $S_{B:A}$.

The calculations are not difficult if phases are separated completely in the course of differential dissolution. If separation of two phases is incomplete, then the problem for a segment of kinetic curves corresponding to joint dissolution of A and B is reduced to finding the values of A_{F_1} and B_{F_1} , A_{F_2} and B_{F_2} , i.e., the number of mole elements A and B in each of two phases $AB_{c_1} + AB_{c_2}$. Taking into account that A and B and c_1 and c_2 are known, $B_{F_1} = c_1 A_{F_1}$ and $B_{F_2} = c_2 A_{F_2}$, a set of two equations with two unknown A_{F_1} and A_{F_2} is solved for each point of the element dissolution kinetic curves:

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

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

Accordingly, the number of moles F_1 and F_2 for each of the two phases 1 and 2 is found as

$$F_1 = A_{F_1}$$

$$F_2 = A_{F_2}$$

Ultimately, kinetic curves of element dissolution can be reconstructed as *phase dissolution curves*, areas under the curves being equal to the content of phases in the mixture; see Fig. 4. Note that the stoichiograph software allows solving more complicated problems as compared with the example considered above [14].

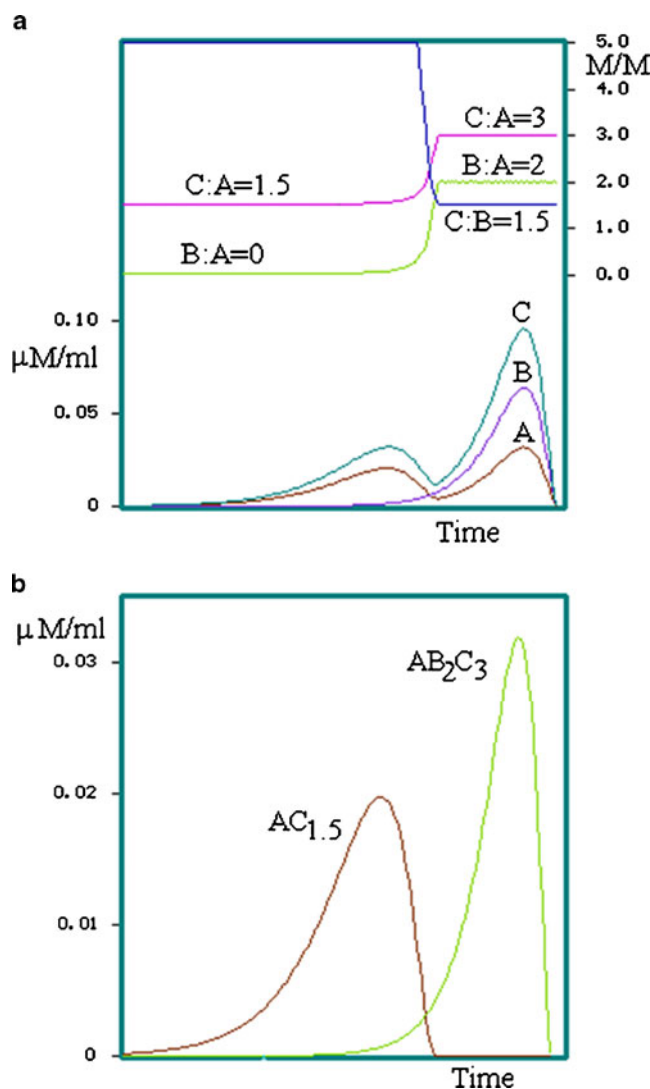


Fig. 4 Model mixture of two phases $AC_{1.5}$ and AB_2C_3 : kinetic curves of A , B , C elements dissolution and their stoichiograms as the $C:A$, $B:A$, $C:B$ ratios being constant during single-phase dissolution and variable during dissolution of two the phases (a); reconstructed from the kinetic curves (a) of $AC_{1.5}$ and AB_2C_3 phases dissolution with the ranges of the single phase dissolution and joint dissolution of two the phases (b)

The metrology of differential dissolution [8, 14]

The specificity of estimating the metrological characteristics of DD techniques and results consists in the necessity to analyze mixtures with unknown phase composition. So, the accuracy of DD analysis data and its sensitivity are provided mainly by metrological characteristics of elemental analysis of the solutions formed in the DD processes.

The reliability of DD data is confirmed by comparing them with the data obtained by structural methods, e.g., XRD, IR, CS, NMR, and NGR. However, the agreement of DD and structural data is often revealed only on a qualitative level, because, in distinction to DD, data of structural physical methods can almost never be quantitative. In many cases, such a comparison cannot completely confirm or disprove the DD data. The reason is that the DD method acquires unique data at determination of amorphous modifications of phases and stoichiometry of compounds with a variable composition as well as at determination of small phases and phase microanalysis.

Voltammetry and stoichiography

The voltammetric methods played a special role in the development of stoichiography. They were used to study the dissolution kinetics of solid phases; various theoretical and methodological aspects of voltammetry served as examples for creating the scientific bases of the DD method.

Continuous recording of the dissolution kinetics of solid phases [15]

There are virtually no publications reporting systematic investigations of the dissolution of disperse substances, i.e., samples widely differing in characteristics of dispersity—granulometry, specific surface area, pore structure, and in the atomic structure type—crystal (taking into account also defects) or amorphous. Data on the effect of composition and concentration of solvents, temperature, and hydrodynamic conditions on the dissolution of such samples would be important here. For such studies, we synthesized samples of oxides and hydroxides of Cu, Fe, Ni, Co, Mo, V, and other elements with different real structures. The samples were subjected to thermal treatment in a wide range of temperatures, from 110 °C to 1,000 °C (with increments of 100 °C), with subsequent preparation of fractions with particle sizes of 1.00 to 0.05 mm. The structure of the samples was characterized by XRD and electron microscopic methods; specific surface area was measured by the BET method, and mercury porosimetry was used to determine the pore structure.

In the studies of dissolution processes, kinetic dissolution curves are commonly presented in the integrated form

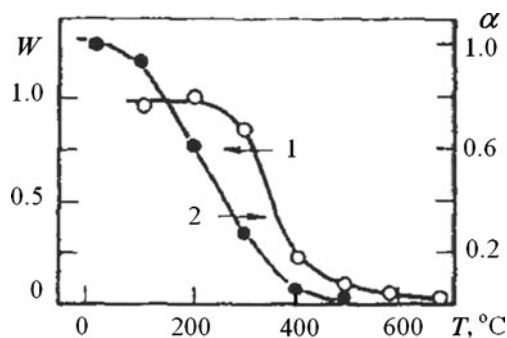


Fig. 5 Relative specific rate of dissolution (W) and degree of dissolution (α) versus the calcination rate of samples: MoO₃ in H₂O (1) and CuO in HCl (2)

plotted with discrete points. Such form inevitably leads to losses of information about essential features of the dissolution processes, which show up at a continuous recording of kinetic dependences. However, there are only a few analytical methods that can be adapted for real dissolution conditions to provide continuous recording of kinetics of these processes. Among such methods is polarography, which was used in our studies. Dissolution was performed directly in the electrolytic cell of a polarograph with a dropping mercury electrode, the background electrolyte serving as solvent was mainly made of solutions of strong acids with different concentrations. A solid-phase suspension was mixed by a stirrer with adjustable rotational speed. Changes in the limiting current of metal ions from solid phases at a corresponding constant potential of the mercury

Fig. 6 Voltamperograms of the α -Fe₂O₃ (1) and CuO (2) mixture in a 1 M Na₂SO₄ background at linear variation of Hg electrode potential with time (A) and in the regime of current accumulation (B)

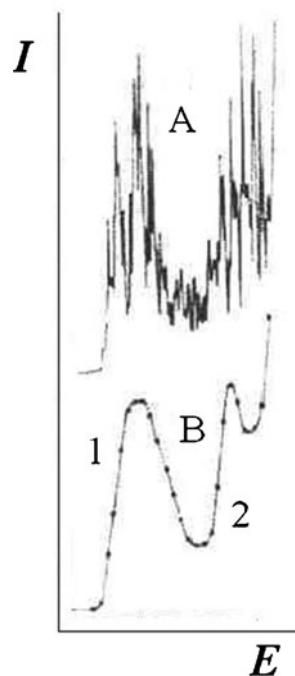
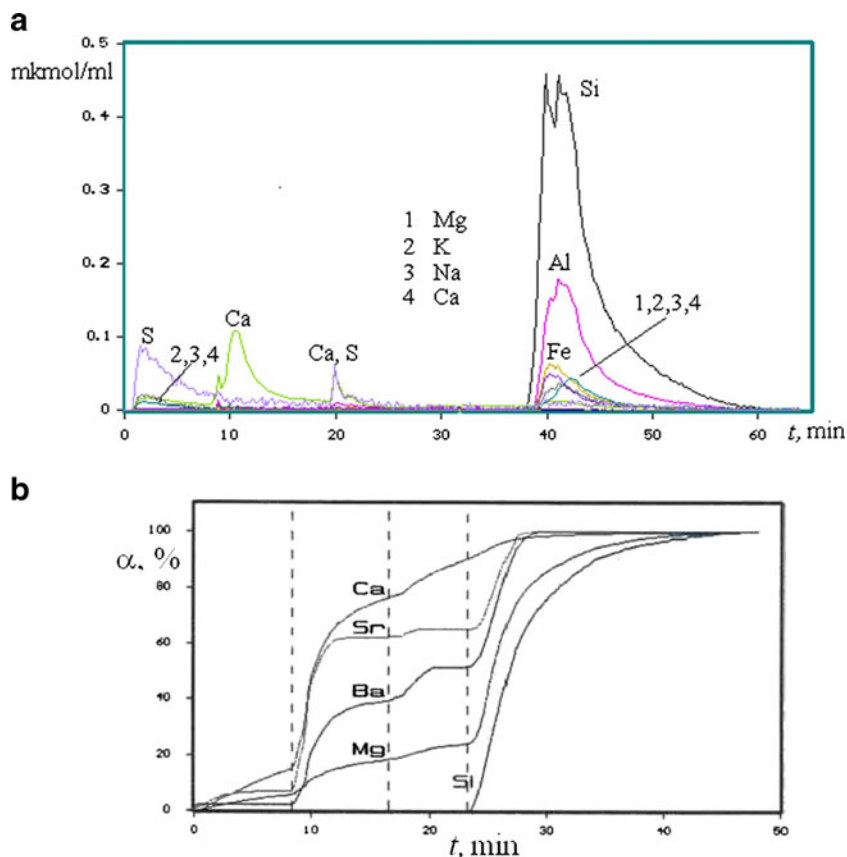


Fig. 7 Results of DD analysis of an atmospheric aerosol: kinetic curves for dissolution of all elements constituting the aerosol (a); time dependences of the Ca, Sr, Ba, Mg, and Si dissolution degree (b). Dotted lines indicate the dissolution periods of phases with composition shown in Table 2



electrode were recorded over the entire dissolution process. Upon termination of dissolution, an aliquot of standard metal solution was introduced in the solution, and quantitative calculations were performed with respect to the obtained response.

Our studies provided a great body of information on the dissolution kinetics of samples in solvents with different composition and concentration, at different temperatures and hydrodynamic conditions of dissolution [9–15]. Some of the results are depicted in Fig. 5. The main conclusion of

the studies is that clear functional dependences can be obtained for the series of samples at successive variation of their structural characteristics and dissolution conditions. The dissolution behavior of a random sample with unknown structural features is unpredictable.

Polarography of insoluble suspensions

The pioneering works of Micka [16] and his disciples demonstrated that disperse suspensions of oxides, chalcogenides,

Fig. 8 Phases and their content (in weight percent) determined by DD for vanadium-containing slag: 1 - the only phase with constant composition $\text{Ca}_2[\text{SiO}_4]$ (6.24); the phases of variable composition 2 - $\text{Ca}_1\text{V}_{0.18}\text{Si}_{0.21}$ (44.7) and 3 - $\text{Fe}_1\text{Mg}_{0.43}\text{Ti}_{0.083}\text{Cr}_{0.019}\text{Mn}_{1.19}\text{V}_{0.029}$ (41.1)

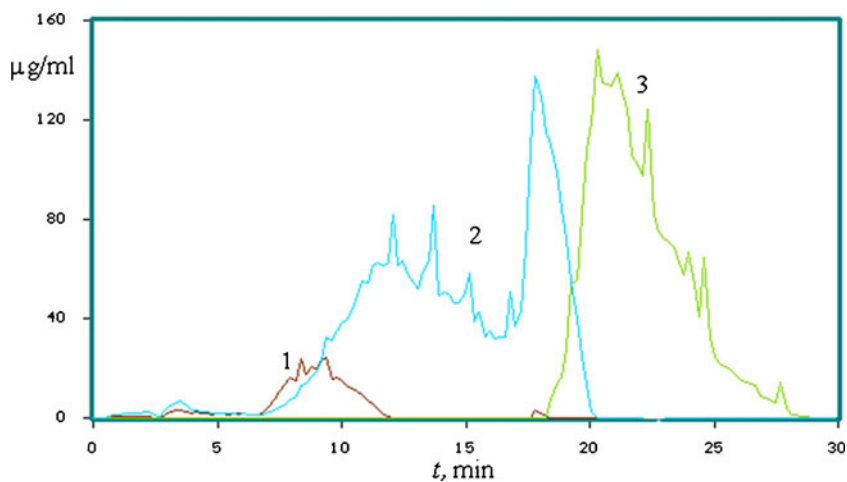
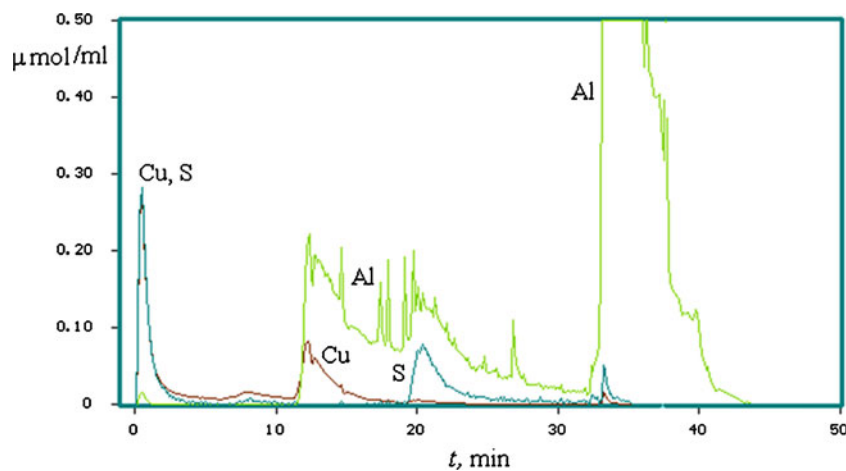


Fig. 9 Result of DD analysis of a composite sorbent $\text{CuSO}_4/\gamma\text{-Al}_2\text{O}_3$. The nanopore structure of alumina was found to include copper sulfate and absorb species Cu^{++} and SO_4^-



halogenides, and other insoluble compounds of at least 30 elements (Cu, Ag, Cd, Hg, In, Tl, Ge, Sn, Pb, V, Nb, As, Sb, Bi, Cr, Mo, W, O, S, Te, Mn, Re, Cl, Br, I, Fe, Co, Ni) are capable of electrochemical reactions on a mercury electrode [17]. Micka was the first to suppose that polarography of suspensions could be used for phase analysis of inorganic solids and compete with X-ray diffraction method. However, these hopes deceived, mainly due to extremely poor reproducibility of polarograms from suspensions. In distinction to smooth classical polarographic waves obtained on the dropping mercury electrode, voltamperograms of suspensions are characterized by numerous peak currents statistically distributed over some region of potentials. Such form of polarograms, as in Fig. 6a, made them improper for rigorous quantitative calculations.

However, we managed to devise quite an efficient method for obtaining smooth and reproducible polarograms of suspensions—current signals were accumulated and averaged (during the formation of 20–50 mercury drops) at discrete changes in potential of the dropping mercury electrode [15]. Such polarograms were distinct and reproducible, as in Fig. 6b, which allowed us to investigate solid suspensions with different composition and structure and reveal the effect of various factors on potentials and intensity of the peak currents of suspensions. It was found that peak currents for the reduction of oxides of different elements are reproducible, but their intensity strongly depends on numerous features of atomic and macrostructure of disperse solids. The current intensity at potentials of polarographic maxima depended to a great extent on granulometric characteristics and specific surface area of suspensions—their crystal (taking into account structural defects) and amorphous species. Results of the studies allowed a conclusion that polarography of suspensions can be used only for *qualitative* phase analysis. Unfortunately, this method is absolutely inappropriate for quantitative analysis, since it is impossible to prepare standard samples of phases adequate to those being analyzed.

Theory and methodology of voltammetry and differential dissolution

The chemical potential μ_i , which determines the possibility of phase dissolution under certain conditions of dynamic DD regime, depends on the concentration of active components of solvents and temperature. The DD selectivity can be characterized by the difference in chemical potentials $\Delta\mu$ between maxima of the dissolution kinetic curves for phases (and their elements)—each two adjacent peaks on the total kinetic curve for dissolution of a phase mixture. However, it is not clear whether it is possible to measure changes of the chemical potential μ in the system “solid substance–solvent”, how it could be made, and the potential of which system should be used as a reference. The separation selectivity can

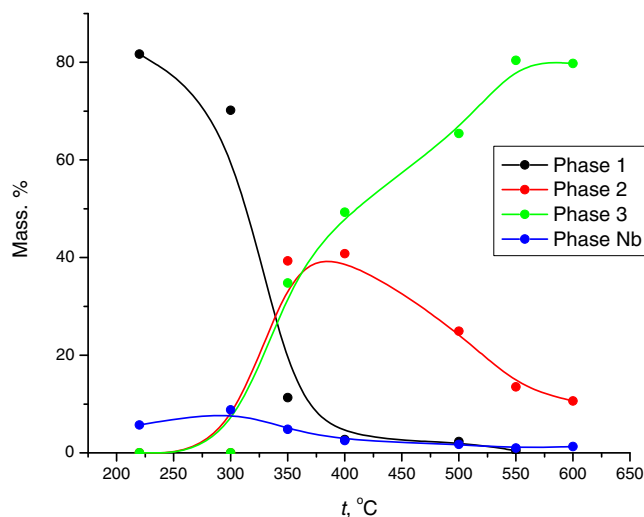


Fig. 10 Temperature dependence of the phase content during thermal treatment of a sample in the Mo-V-Te-Nb-O system. According to XRD data all the products are amorphous, whereas DD analysis found to be amorphous 1, 2, 3 phases with a variable composition (see Table 3). The end product, phase 3, turns into the crystal state only at temperature above 500°C

Table 2 Alkali-earth elements in aerosol phases

No.	Phases	Molar ratio Ca/Mg/Sr/Ba
1	Water-soluble	1:0.11:0.00027:0.00032
2	Ca carbonate	1:0.078:0.00078:0.0010
3	Ca sulfate	1:0.063:0.00019:0.0013
4	Silicates	1:2.44:0.0027:0.0033

be estimated most easily from the time profile of stoichiograms, with the narrow and well-resolved peaks of each two adjacent phases corresponding to a high selectivity. If peak maxima are resolved quite well, but their wings are diffuse and overlap the adjacent peaks, this indicates low efficiency of phase separation.

Voltammetry commonly employs a parametric linear dependence of the indicator electrode potential on time. At that, voltamperograms reflect a logarithmic dependence of current strength on the concentration of electroactive components of the system. Evidently, if in dynamic DD regime a linear time dependence of the chemical potential of solvent is approached, the solvent concentration should increase exponentially with time ($\mu = \mu^0 + RT \ln C_R$), thus changing by orders of magnitude rather than several fold. Such changes in the concentration of, say, protons are possible when going from neutral water to acid solutions with $\text{pH} \approx 2$. However, in this range of pH variation, only the dissolution of readily soluble solid phases can occur. Most of the phases require much more severe conditions. When going to more concentrated solutions of acids, there appear obstacles to smooth exponential changes in the solvent concentration. First, fast changes of the concentration in this region drastically diminish the separation selectivity of different phases. Second, peristaltic pumps of the stoichiograph cannot provide the required high pumping rates of the solvent components. These obstacles can be overcome using a stepwise variation of the solvent concentration during stoichiographic titration. At stoichiographic titration, each next phase is titrated with a much more concentrated solution, the end of capillary being

transferred from a flask with low-concentrated solvent to a flask with solution having a higher concentration.

Application of stoichiography for determining the chemical composition of substances and materials

Differential dissolution was initially developed as a method of phase analysis. But soon it was found that the dynamic dissolution regime could provide additional information on the chemical composition of solid substances. Indeed, the advancement of the dissolution reaction front from the surface to the center of dissolving particles is accompanied by a continuous recording of stoichiometric ratios between each pair of elements constituting the particles. Under relatively mild conditions, such information can be acquired for particles of a single phase; using more severe conditions, this can be done successively for other phases of a complex mixture. In such processes, changes in the time profile of stoichiograms characterize the homogeneity of the elemental composition of successively dissolving phases as well as their nonstoichiometry, whereas changes in the shape of the kinetic curves for dissolution of elements (and phases) characterize the homogeneity of the macro- and microstructure of these phases.

There are many examples of DD analysis of crystalline and amorphous substances—from natural minerals to high-tech objects. The DD method is used to study the mechanism and kinetics of solid-phase reactions and characterize the reactivity of solid phases with identical composition and different real structure. A preparative version of the method is applied in synthetic chemistry for precise correction of the phase composition of substances and materials.

The complementary use of voltammetry and DD proved efficient for the detection, identification, and quantitative determination of inhomogeneities in the chemical composition of heterophase ceramic samples of $\text{YBa}_2\text{Cu}_{3-x}\text{Ag}_x\text{O}_y$ superconductors [18]. In such samples, the ratios of impurity phases and the main phase 123, the cationic and anionic stoichiometry of phases, and the content of copper and oxygen

Table 3 Fragment of the table with data on temperature dependence of the composition and phase content in samples of the Mo-V-Te-Nb-O system

No.	$T, ^\circ\text{C}$	Phase 1	%	Phase 2	%	Phase 3	%	Nb, %
1	25	$\text{MoV}_{0.21}\text{Te}_{0.22}\text{Nb}_{0.06}$	87.0	–	–	–	–	4.4
2	220	$\text{MoV}_{0.27}\text{Te}_{0.15}\text{Nb}_{0.03}$	81.7	–	–	–	–	5.7
3	300	$\text{MoV}_{0.13}\text{Te}_{0.10}$	70.2	–	–	–	–	8.8
4	350	$\text{MoV}_{0.13}\text{Te}_{0.13}$	11.3	$\text{MoV}_{0.20}\text{Te}_{0.25}$	39.3	$\text{MoV}_{0.19}\text{Te}_{0.02}\text{Nb}_{0.12}$	34.8	4.8
5	400	$\text{MoV}_{0.14}\text{Te}_{0.07}$	2.7	$\text{MoV}_{0.43}\text{Te}_{0.43}$	40.8	$\text{MoV}_{0.20}\text{Te}_{0.04}\text{Nb}_{0.13}$	49.3	2.5
6	500	$\text{MoV}_{0.14}\text{Te}_{0.05}$	2.3	$\text{MoV}_{0.35}\text{Te}_{0.28}$	24.9	$\text{MoV}_{0.25}\text{Te}_{0.05}\text{Nb}_{0.13}$	65.4	1.7
7	550	$\text{MoV}_{0.14}\text{Te}_{0.04}$	0.45	$\text{MoV}_{0.28}\text{Te}_{0.30}$	13.5	$\text{MoV}_{0.27}\text{Te}_{0.08}\text{Nb}_{0.12}$	80.4	0.99
8	600	–	–	$\text{MoV}_{0.30}\text{Te}_{0.31}$	10.6	$\text{MoV}_{0.28}\text{Te}_{0.08}\text{Nb}_{0.12}$	79.8	1.3

in anomalous charge states in phase 123 were determined quantitatively. Figures 7, 8, 9, and 10 and Tables 2 and 3 illustrate the DD analysis of various objects to characterize this method from different points of view. The necessary explanations are presented in the figure captions.

Conclusion

Inorganic analysis of solid substances is based mainly on the methods of elemental analysis and physical methods of structure analysis (like X-ray, neutron and electron diffraction, etc.). However, since all stable chemical elements have already been discovered, elemental analysis can be considered as a past stage in the development of analytical chemistry. In organic chemistry, this type of analysis is applied only to determine the stoichiometric formulas of pure compounds, as it would be absurd to characterize the composition of a complex mixture of organic compounds by the content of carbon, hydrogen, nitrogen, or other elements. The molecular, in particular, chromatographic analysis of such mixtures is necessary. However, the composition of inorganic solids—from mineral objects to high-tech materials—is characterized almost always by the results of gross elemental analysis. Although such data are of fundamental importance, it should be noted, in modern science and engineering, it becomes more essential to obtain information on chemical compounds that determine the composition of various solid substances and materials, on fine variations in the spatial structure and composition of such objects. The long history of DD application for analyzing multivarious substances and materials gives good reasons to suggest that the role of DD method in analysis of mixtures of solid inorganic phases can be similar to the role of chromatography in analysis of molecular mixtures of organic compounds. The DD method can be used to analyze crystalline and/or amorphous mixtures of phases with constant or variable composition represented by powders, ceramics, crystals, thin films, and nanostructured species. It can be applied also for analysis of mineral objects and products of

their processing, functional materials, in particular, catalysts and sorbents, environmental objects, archeological findings, and many others. The place of DD among other analytical methods is related to its unique reference-free nature, the possibility to determine in a single experiment, rapidly and with high sensitivity the stoichiometric formulas and quantitative content of phases in solid multielement multiphase objects. Phase composition of such objects may be obscure and include new, yet unknown phases.

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References

1. Malakhov VV (1997) *Zh Analit Khim* 52:790–797
2. Zakharchuk NF, Smirnova TP, Fedorov VF (2010) *J Struct Chem* 51(Supplement 1):171–177
3. Brainina HZ (1972) Stripping voltammetry of solid phases. Khimiya, Moscow
4. Songina OA, Zakharov VA (1985) Voltammetry on solid electrodes. In: Agasyan PK, Zhdanov S (eds) Voltammetry of organic and inorganic compounds. Nauka, Moscow
5. Malakhov VV (1994) *Zh Analit Khim* 49:349–360
6. Malakhov VV (2002) *J Analyt Chem* 57:869–876
7. Malakhov VV (1986) *Dokl Akad Nauk SSSR* 290:1152–1156
8. Malakhov VV, Vasilyeva IG (2008) *Russ Chem Rev* 77:351–372
9. Malakhov VV (2009) *J Analyt Chem* 64:1097–1107
10. Malakhov VV, Vlasov AA, Dovlitova LS (2004) *J Analyt Chem* 59:1016–10
11. Malakhov VV, Boldyreva NN, Vlasov AA, Dovlitova LS (2011) *J Analyt Chem* 66:458–464
12. Russian Patent, No. 2075338
13. Russian patent, no. 2056635
14. Malakhov VV, Vlasov AA (2011) *J Analyt Chem* 66:262–268
15. Malakhov VV (1979) Chemische analyse von katalysatoren und Tragermaterialien. In 2. Tagung Festkörperanalytik, Technische Hochschule Karl-Marx-Stadt 1: 113–130
16. Micka K (1960) *Advances in polarography* 3. Pergamon Press, London, UK
17. Dausheva MR, Songina OA (1973) *Russ Chem Rev* 42:323–342
18. Vasilyeva IG, Zakharchuk NF (1994) *Supercond Phys Chem Eng* 7:1269–1278