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Microwave radiation in analytical chemistry: the scope and prospects for application

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Abstract. The key aspects of the effect of microwaves on the physicochemical processes in solutions and heterogeneous systems are analysed. Good prospects for the use of microwave radiation for intensifying various types of interaction are demonstrated in relation to dissolution, hydrolysis of organic and inorganic substances, complex formation by metal ions in solution and in the sorbent phase, oxidation of organic compounds, and synthesis of coordination and organic compounds. Specific features of analytical operations with microwave treatment are considered and the trends of development of analytical methods using microwaves are discussed. The bibliography includes 137 references.

I. Introduction

In recent years, a breakthrough has taken place in the development of instrumental methods used in inorganic and organic analysis, such as electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission spectrometry (ICP AES), inductively coupled plasma mass spectrometry (ICP MS), chromatographic and GC/MS techniques, *etc*. This is due to the need for more stringent control of technological processes, development of the analytical groundwork for the search for new raw material sources, aggravation of the environmental problems related to industrial environment pollution. Meanwhile, traditional methods used to prepare samples for analysis, which are time-consuming, comprise many stages and require large amounts of reagents, held up the elaboration of modern quick analytical procedures and hampered implementation of the most important parameters of instrumental methods. Development of more advanced methods for preparing a substance for determination of its composition has become a highly topical task in modern analytical chemistry.

The efficiency of analysis is largely determined by the rate and completeness of the underlying physicochemical processes. The search for ways of affecting these processes and controlling them in various fields of chemistry and technology has resulted in extensive use of physical fields [1] and in the design of photochemical, catalytic and ultrasonic methods. Nevertheless, an increase in temperature has the most crucial effect on reactions in solutions and heterogeneous systems. However, slow heat transfer from the source to the sample and within the sample creates insurmountable obstacles which preclude substantial acceleration of processes under conditions of conventional (thermal) heating. An alternative way of raising the temperature of reaction mixtures is fast bulk heating on exposure to electromagnetic radiation of the microwave range.

Microwave heating differs from the traditional one by the greater volume and time gradients involved and by the fact that solutions and components of heterogeneous systems differing in composition possess unequal abilities to absorb the energy of radiation. In addition, charged species and dipoles present in the solution become oriented in the electromagnetic microwave field, which has an influence on their interaction.[2] This changes the yields of reaction products [3] and gives rise to some specific effects [2] observed only under microwave heating conditions. No unambiguous interpretations of these phenomena have been proposed; an approach to investigation of chemical processes induced by microwave radiation (MW) includes comparison of the reaction rates, the compositions and yields of the resulting compounds, and the activation energies of reactions proceeding under thermal and microwave heating.[4]

This review describes systematically the available data on the use of MW for the intensification of chemical reactions, first of all, those which underlie analytical operations.

II. Some aspects of the influence of electromagnetic fields on solutions

Numerous chemical reactions proceed in aqueous solutions or, at least, in the presence of water.[5] The processes taking place in solutions, in particular, in aqueous ones, are mediated by interactions of the reactants with the solvent. These electrostatic interactions result in the formation of ions, solvation shells and assembled structures; this may prevent the initial substances from reacting with each other. The application of external physical fields, including electromagnetic fields, not only activates diffusion and mass transfer in solutions but also gives rise to additional effects upon electrostatic interactions, namely, it changes the degree of ordering of the solvent and the structure of solvation shells of ions, deforms the electron shells of atoms and molecules, facilitates reactions between species, increases the reaction efficiency, and accelerates chemical reactions. These phenomena can be of different natures such as the influence of the field on

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electrostatic interactions in solutions (an additional effect of external field), an increase in the system's intrinsic energy due to heating or the direct effect on charged species. An increase in temperature and the electric field effect have the most pronounced influence on the structure of water and solutions. Under exposure to MW, these factors are closely interrelated.

Now we consider the mechanisms of microwave heating in more detail. Microwave radiation is a form of non-ionising electromagnetic radiation whose frequency is intermediate between the infrared (IR) and radio-frequency ranges, namely, 300 to 30 000 MHz (wavelengths from 1 m to 1 cm). Since these waves are actively used in radio- and telecommunications, for industrial purposes, in science and in medicine, four frequencies are stipulated by international rules, a frequency of 2450 MHz (12.2 cm) being utilised most often. In recent years, radiation of this type is so widely employed to accelerate chemical processes and to solve applied analytical problems that some researchers have spoken about a new line of research called microwave chemistry;[2,6] nevertheless, the data on the chemical aspects of the action of MW on reaction systems are sparse.

The mechanism of interaction of MW with matter involves absorption of the electromagnetic radiation energy by the material and scattering of the energy as heat. Although the microwave frequency corresponds to the rotational movement of molecules, in the condensed state where no free molecular rotations take place, as opposed to the gas phase, the absorption of energy immediately results in its redistribution between molecules and homogenous heating of the medium. Thus, microwave heating is a bulk phenomenon; the physical aspects of the effect of MW on a substance are described in detail in monographs dealing with the theory of dielectrics (see references in Ref. 2) and in some other studies.[7–9]

As MW passes through solutions, the transfer of energy occurs by two mechanisms, namely, due to re-orientation of the solvent dipoles in an alternating electric field and due to migration of ions of the solute, *i.e.*, through dipole rotation and ion conduction. The induced thermal motion is superimposed onto the solvent structure disordering, which is due to the orienting action of the field. The significance of each factor is dictated by the nature of the process and the reactants. It is worth noting that back in 1933, Bernal and Fowler,[10] introduced the notion of 'structural temperature', according to which the influence of ions (*i.e.*, charged species which form some electric field) on water (solvent) can be likened to the action of an increase or decrease in temperature. These views can be useful for the understanding of the specific features of chemical reactions under microwave heating when the same outcome is attained at the same or even lower temperature than upon thermal heating.[2]

The mechanism of dipole rotation is the major one in the case of pure water or other solvents with low degrees of dissociation. The heating rate and the temperature that can be obtained largely depend on the radiation frequency, the initial temperature of the solution and on the solvent properties, in particular, the dielectric constant. Figure 1 shows the experimental curves characterising the microwave heating of water and some organic solvents.

The dielectric properties of free and bound (present as aggregates in a substance) water molecules are somewhat different;[11] as a consequence, they possess different capacities for absorbing the microwave radiation energy. This difference can be clearly seen when examining drying in a microwave oven of ferrimanganese concretion samples (FMC),[12] which are layered structures binding water molecules in different ways. When dried under conventional conditions, FMC initially lose the absorbed water and then the water incorporated in the structure of the minerals.[13] A similar stepwise removal of water also occurs in a microwave field, and the curves for the loss of weight by the samples during microwave heating for several minutes reveal the presence of different H_2O forms. This selectivity in the absorption of the radiation energy by the solvent molecules bound in different ways has also been used [11, 14, 15] in microwave extraction techniques.† The stepwise pattern of variation of the absorptivity of aqueous solutions of alcohols, indicating the presence of different molecular structures, has also been noted in other publications.[16, 17]

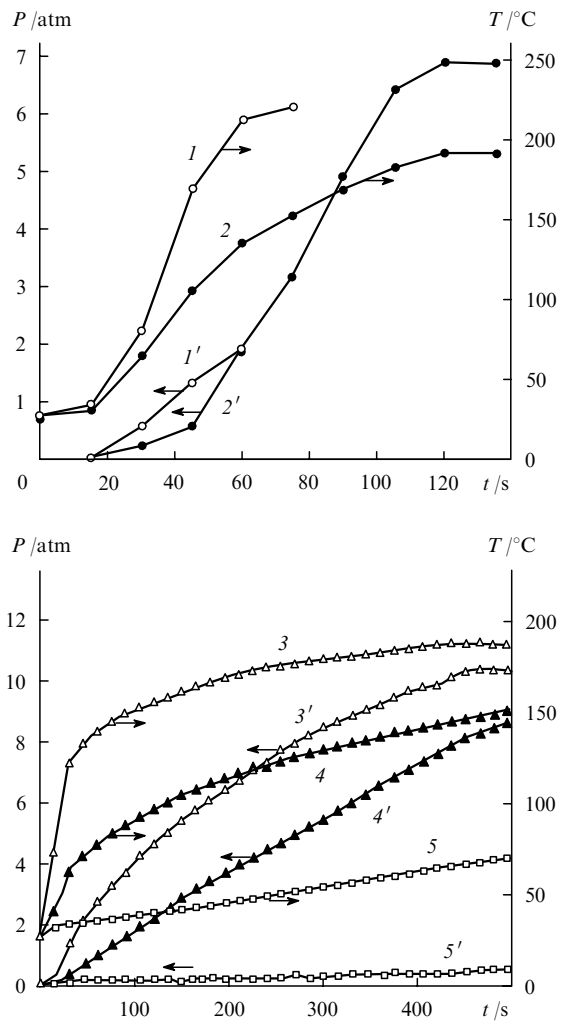


Figure 1. Effect of microwave radiation on the variation in the temperature (T) of solvents ($1-5$) and the pressure (P) of the vapour ($1'-5'$) in a closed vessel: (1, $1'$) dimethyl sulfoxide; (2, $2'$) water; (3, $3'$) propan-2-ol; (4, $4'$) dichloromethane; (5, $5'$) hexane (t is the time of microwave treatment).

Yet another mechanism of the microwave heating is related to the effects of conduction, which may be due to electrophoretic ion migration in solution or the transfer of charged species in a solid upon application of an electromagnetic field. The contribution of the ion conduction mechanism in solutions is determined by the sizes, charges and the electrical conductivity of ions;[8] in addition, this value depends on the interaction of ions with solvent molecules. The ion conductivity depends on the concentration, ion mobility and the solution temperature. Compounds with high dissociation constants absorb efficiently the microwave energy.

The relative contribution of each of the two mechanisms of transformation of the MW energy (dipole rotation and ion conduction) depends substantially on the temperature. For small molecules such as water molecules or molecules of other solvents, the dielectric loss caused by the contribution of the dipole rotation

† The term 'microwave extraction' is often used in the literature to describe the extraction of useful components of different natures by any solvent on exposure to MW. Here, this term is used to imply the extraction of organic components by organic solvents.

decreases with an increase in the temperature.[8, 18] Conversely, the dielectric loss due to ion conduction increases with an increase in the sample temperature, and the effect of MW on charged species becomes more significant. Due to the diversity of factors which influence the warming-up of a solution exposed to MW, modelling of this process is currently considered to be impossible,[2] although a physical model that allows the calculation of the change in the solution temperature in an open system has been proposed, the mechanisms of gaining and losing energy through the solution have been analysed,[19] and the theoretical aspects of the microwave heating of solids have been considered.[20, 21]

It is generally believed among the analysts who use laboratory microwave systems mainly for the routine digestion of samples that fast heating is the major or the only consequence of action of a microwave field on solutions. Indeed, the MW frequency approximately corresponds to the frequency of the rotation of molecules but the energy of a quantum per mole ($\sim$1 J mol^{-1}) is too low to cleave not only chemical bonds (the energy of a C–H bond is 350 kJ mol^{-1}) but also hydrogen ($\sim$20 J mol^{-1}) and even van der Waals bonds (2.5 J mol^{-1}).[11] However, regarding chemical transformations, the changes in the structures of the solvent and solvated ions are especially important because, as noted above, it is the solvation shells that hamper the occurrence of reactions involving ions and molecules; the electron density redistribution in molecules and conformational changes induced by an electromagnetic field are equally important.

It can be seen from Fig. 2 that an electromagnetic field brings about a substantial change in the state of the ion shell; as a consequence, the ion should become much more reactive and accessible for a nucleophilic attack. The electron density shifts very rapidly (in 10^{-14} s)[23] (electron polarisation), and then it is 'fixed' in the field with the given frequency over a period of 2.5×10^{-9} s; the positions of the ions and molecules themselves change to a much lesser extent. During the indicated period, a field-activated ion present in aqueous solution can participate in $10-10^3$ collisions. This is important, for example, when microwave heating is used to accelerate substitution in the inner coordination spheres of complexes with inorganic ligands or in the molecules of organic compounds where steric factors and configurations of the reacting species are rather significant. In particular, acceleration of complexation caused by microwave treatment has been observed for various elements and sorbents in different sorption regimes at the same temperature as in the case of traditional heating.[24–26] Note that the displacement of the electron density in an electromagnetic field does not depend on the temperature and can be attributed to so-called non-thermal effects.

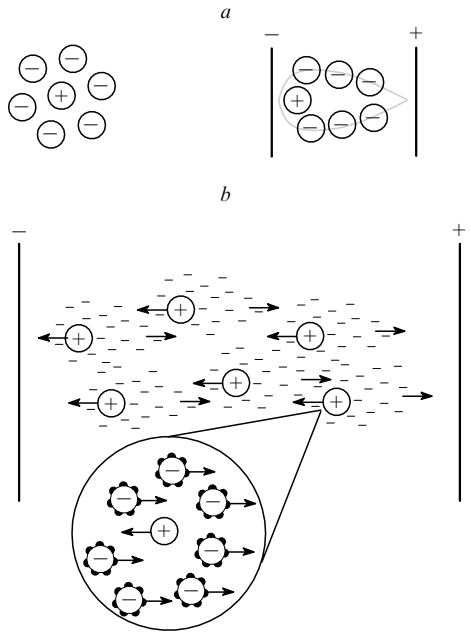


Figure 2. Change in the state of the ionic environment in a microwave field (*a*) and electrophoretic effect (*b*).[22]

Direct evidence for the change in the state of solvated (hydrated) species in a microwave field has also been obtained. Circular dichroism measurements provided experimental data on the change in the spatial structure of protein molecules, which is known to be largely formed due to hydration of polar groups in the polypeptide chains by water molecules. Experiments carried out‡ at different temperatures with either thermal or microwave heating of an aqueous solution of erythropoietin demonstrated that thermal heating at 65 °C is equivalent to exposure to MW at 45 °C over a period of time which makes only 7% of the overall experiment duration (recall the Bernal and Fowler's structural temperature).

We have also observed destruction of colloid particles of soil in an MW field; thus the microstructure of the particles formed by hydrated layers was identified; the solution temperature did not exceed 50 °C.

Microwave treatment can induce additional thermal effects related to the nature of the influence of the radiation on the system. In the case of conventional heating, the number of boiling centres in the solution bulk is much smaller than that near the surface. The microwave heating takes place from the inside, uniformly throughout the whole bulk; therefore, the temperature of the solution is higher than the temperature of the surroundings (vessel walls, the gas phase above the solution, *etc.*).[27] As a result, the solution can be heated to a temperature exceeding its boiling point under atmospheric pressure, which has been shown experimentally using various physical methods[2, 3] (Table 1).

Table 1. Change in the boiling point (b.p.) of liquids of different natures under microwave radiation conditions.[2, 3]

Solvent	b.p. /K		Δb.p. /K
	traditional heating	microwave heating	
Water	373	377	4
Methanol	338	357	19
Ethanol	352	376	24
Propan-2-ol	355	373	18
Tetrahydrofuran	339	354	15
Dichloromethane	313	328	15
Acetonitrile	354	380	26
Acetone	329	354	25
Diglyme	435	448	13
Ethyl acetate	351	368	17
Dimethylformamide	426	443	17
Diisopropyl ether	342	358	16

One more mechanism of interaction of MW with the matter is possible in heterogeneous systems, which is due to interface phenomena (interfacial polarisation). The thermal effects thus arising are used to heat mixtures of dielectrics with compounds that poorly absorb the MW energy.[28] The non-uniformity of heating caused by different abilities of substances to absorb the MW energy gives rise to non-trivial results upon bulk removal of water, synthesis on solid surfaces and the preparation and use of catalysts.[2, 29] The difference in the ability of the initial reactants

‡ We carried out these studies together with N V Bovin (Institute of Bioorganic Chemistry, Russian Academy of Sciences).

and reaction products to absorb the MW energy can give rise to self-catalysed reactions.[30]

The course of chemical processes and the composition of the resulting products are influenced by one more important factor, the time gradient of heating ($\Delta T/\Delta t$), which is much higher in the case of microwave treatment than in the case of conventional heating of solutions. When several competing reactions with different rate constants take place simultaneously, the probabilities of formation of particular products in the very narrow temperature range under the action of MW can differ appreciably from those observed under conventional heating. The same is true for equilibrium processes in which the rate constants for the forward and back reactions are different. This fact has been considered [31] as the reason for the higher selectivity of some processes of organic synthesis under microwave heating.

III. Specific features of chemical reactions in a microwave field

This Section covers the main types of reactions widely used in analytical practice.

1. Hydrolysis of inorganic and organic compounds

The effect of MW on reaction systems is most pronounced in the case where the radiation energy is absorbed directly by a reactant. In some cases, a reactant acts simultaneously as the reaction medium. Evidently, MW should have a substantial influence on hydrolysis because water efficiently absorbs energy of electromagnetic radiation.

Hydrolysis induced by MW has been used to synthesise organic compounds,[32, 33] to cleave the peptide bonds in proteins when determining their amino acid composition,[34, 35] and to study the composition of a number of other natural compounds.[35, 36]

Hydrolysis of inorganic compounds in a microwave field has been studied [37] in relation to the exceptionally stable polynuclear iridium sulfate complexes. The uncertainty in elucidation of the composition of these complexes is the main cause for the analytical problems arising during determination of iridium in sulfate solutions by various methods. The mononuclear chloride complex of iridium was prepared upon hydrolysis and destruction of the iridium sulfate complex on exposure to MW with subsequent transformation of the resulting aqua hydroxo complex into the chloride complex on treatment with NaCl in HCl. Microwave irradiation accelerates deprotonation and hydrolysis. The degree of transformation of sulfate complexes of iridium into the chloride complexes is linearly dependent on temperature, which indicates a substantial contribution of thermal effects to acceleration of the reaction. However, it has not yet been explained why the metal is stabilised in the higher oxidation state under the action of MW.

The rigorous conditions of hydrolysis, namely, concentrated acid and elevated temperature, ensure the cleavage of most of hydrolysable bonds in organic compounds. However, in many cases, these conditions also promote undesirable side processes, in particular, destruction of either initial compounds or reaction products. The efficiency of using microwave treatment for performing such reactions was first demonstrated by Majetich and Hicks.[38] Of special importance is the choice of conditions for mild and, simultaneously, selective hydrolysis for the removal of protective groups. Under microwave heating, the occurrence of these reactions is markedly facilitated.[33]

Microwave-enhanced hydrolysis has been used for analytical purposes in the synthesis of macrocyclic compounds [39] that have found application as reagents for determination of metals. Acid hydrolysis of *p*-toluenesulfonyl protective groups under conditions of thermal or microwave heating has been studied in relation to a number of macrocyclic compounds and their linear fragments.[40, 41] The possibility of stepwise hydrolysis under the action of radiation and, hence, targeted control of reaction products has been demonstrated. Compounds have been synthesised that could not be prepared in the given reaction system upon thermal heating. The achieved effects are caused, most likely, by the sharp increase in the temperature of the reaction mixture under conditions of microwave heating (to 200 °C for 2 min), which is due, to some extent, to the absorption of the radiation energy by the substrate;[4] according to some views,[42] this substantially activates the reactions.

2. Complexation of metal ions with organic reagents

The kinetic inertness of the coordination compounds of a number of metals towards substitution is often an obstacle hampering the practical use of complexation reactions.[43] The use of MW for the solution of various problems related to complexation has been described only in a few publications. For example, it was demonstrated that coordination compounds of transition and noble metals, in particular, chromium, ruthenium, iridium, platinum and gold, with organic ligands can be synthesised efficiently under microwave heating.[44, 45] The analytical aspects of complexation of inorganic ions in solutions and in the phase of complexing sorbents under the action of MW (sorptional collection of palladium and rhodium [46] and chromium [26] using nitrogen-containing sorbents, the formation of complexes by the platinum metal and chromium in solutions) have been considered.[25, 47–50] A reaction with microwave heating between cadmium or cobalt ions and immobilised reagents, bromothiazo- and 1-(2-pyridylazo)-2-naphthols,[51] prepared using MW, has been described.[52] The possibility of synthesising coloured compounds of platinum metals for spectrophotometric determination of metals in a flow system on exposure to radiation has been demonstrated.[53, 54] A study [55] has been devoted to the targeted synthesis of binuclear tetraacetate, the initial compound for the coulometric determination of rhodium, in the solution to be analysed. The general regularities of MW-assisted complexation identified for the above-listed systems are considered below.

a. Complex formation in solutions

The reactions of metal ions with nitrogen-, sulfur- or oxygen-containing reagents under routine conditions can involve ligand desolvation and conformational changes, hydrolysis and desolvation of metal ions, changes in the metal oxidation state (usually, reduction to a more labile state), and the formation of a complex (metal – ligand interaction), which is complicated in some cases by the formation of polynuclear complexes.[47, 49, 56] For complexation under microwave heating conditions, it is most often impossible to separate the contributions of thermal effects and the field effects on the electrostatic interactions of particles. According to the Arrhenius equation, the rate constants of the slowest reactions increase most appreciably as the temperature rises. The orienting action of the field can play a crucial role in the case of sterically hindered transformations, for example, those involving large molecules of organic compounds which react with metal ions according to the nucleophilic substitution mechanism.

The most comprehensive information on the intensification of complexation under the action of MW has been obtained for platinum metal compounds (Table 2) some chemical forms of which are extremely inert towards ligand substitution.[43] It was found that radiation substantially intensifies the reduction of metals (at the same temperature),[25, 50, 57] markedly shortens the reaction time and often makes it possible to exclude the use of stabilising additives. The composition of complexes thus formed does not change. The labilising action of MW is so pronounced that the efficiency of complexation does not depend on the initial form of the metal. This allows the use of MW for reagent-free activation of inert coordination compounds.[58]

b. Complex formation in the sorbent phase

The sorption of metal ions on sorbents with fixed complexing groups depends not only on the chemical reaction but also on the diffusion of metal ions both from the solution to the sorbent (outer diffusion) and in the sorbent pores (inner diffusion). It was noted that in the reaction of cobalt ions with the modified silicic

Table 2. Effect of microwave radiation on the time (t) of metal complexation with organic reagents in solution.

Metal	Reagent	Hypothetical composition of the complex	t /min		Ref.
			usual conditions	microwave treatment	
Pd(II)	chlorophosphonazo-mN	PdR_2	1	0.5	54
Rh(III)	5-chloro-2-pyridylazo-2,4-diaminobenzene	unknown	does not react	0.5 [a]	53
Ru(III)	the same	the same	the same	0.5 [a]	53
Os(IV)	"	"	"	0.5 [a]	53
Ir(IV)	"	"	"	0.5 [a]	53
Pt(IV)	"	"	"	0.5 [a]	53
Ir(IV)	2,2′-bipyridine	$[Ir(H_2O)R_3]^{2+}$	220	10	47–49
Os(IV)	1,10-phenanthroline	$[OsR_3]^{2+}$	180	15	47
Ru(IV)	the same	$[RuR_3]^{2+}$	45	6	47
Ru(IV)	sulfochlorophenolazorhodanine	$[RuCl_4R_2]^-$	30 [b]	4	25, 48
Al(III)	sulfonaphtholazorhodanine	$[AlR_3]^{3+}$	60 [b]	4	25, 48

[a] Complexation in the presence of a reducing agent. [b] Complexation in the presence of an acetate buffer solution.

acid xerogel, microwave heating increases the rates of both the outer and inner diffusion.[51] Acceleration of diffusion processes on treatment with physical fields of various natures has also been described in other publications.[20, 21, 59–61]

The extraction of noble metals by the POLYORGS IV sorbent containing 3(5)-methylpyrazole groups has been studied under static conditions.[12, 46] The action of MW substantially accelerates the process (which takes place at the solution boiling point) both for rhodium, which reacts with sorbent groups by a complex-formation mechanism,[62] and for palladium and platinum (which react by the ion-exchange mechanism §). Similar results have been obtained for sorption on POLYORGS XI-H,[24] the degree of rhodium collection in a microwave field being higher than that with conventional heating. The observed acceleration of sorption has been explained by the influence of the electromagnetic field on the state of the complex ion and electrostatic interactions in solution. Under conventional conditions, similar results can be attained by adding alkali metal salts, which destroy the structure of the solvation shells of ions; however, the effect of a microwave field is much greater.[12]

Microwave treatment has markedly enhanced the efficiency of collection of chromium ions, especially Cr(VI), by the DETATA sorbent.[26, 63] Almost complete separate extraction of Cr(III) and Cr(VI) from solutions with pH 7 and 3, respectively, can be attained only using MW. An EPR study of the possible changes in the Cr(III) coordination sphere during the reaction with the aminocarboxy groups of the sorbent showed that the spectra of the complexes obtained at room temperature with conventional heating and in a microwave field are identical. This indicates that the same complex spieces of Cr(III) are formed under different conditions and that the factors influencing the reaction rate make the predominant contribution to the increase in the efficiency of sorption extraction of chromium on exposure to MW. Obviously, the same factors increase the efficiency of preconcentration of chromium ions by sorption in a flow regime and make it possible to increase the solution flow rate from 0.4–0.5 to 10 ml min^{-1}. Similar results have been obtained in a study of the reaction of cadmium ions with silicic acid xerogels modified by organic reagents.[51]

3. Oxidation of organic compounds by inorganic acids

Oxidation of an organic matrix with nitric acid is a widely used analytical operation. Study of the mechanism of oxidation of organic compounds including natural products in a microwave field [64–67] showed that, as in the case of traditional heating, the major reaction products include, apart from carbon dioxide and water, nitro-substituted aromatic acids, which decompose at temperatures above 260 °C. The same composition of the oxidation products obtained in the conventional and microwave heating modes suggests that the reactions follow the same pathways. However, the rates of oxidation are substantially different: decomposition of organic matrices at the same temperature is much faster with microwave heating than with traditional heating both in open and closed systems.[67, 68] No unambiguous interpretation of this fact can be found in the literature; therefore, it seems important to compare the quantitative characteristics, for example, the activation energies (E_a) of the processes that take place under different conditions. The first attempt to solve this complicated experimental problem was made by Pratt,[69] who showed that the E_a values for the oxidation of amino acids (phenylalanine and tryptophan) with nitric acid under conditions of conventional and microwave heating are equal.¶

Bacci *et al.*[71] were the first to use heating of the reaction system by microwave radiation when determining the thermodynamic functions and kinetic parameters. Microwave heating at a rate of 6.0–7.5 K min^{-1} was combined with simple photometric recording of the absorbance of the resulting complex. This technique appears efficient because the experiment can be carried out quickly and no temperature gradients exist in the solution; however, special experimental equipment is required.

In recent years, continuous temperature variation [72] has been used to estimate the activation energies of various processes ranging from enzymic reactions to evaporation of atoms in electrothermal atomic-absorption spectrometry (dynamic method). This method is based on a logarithmic dependence of a parameter proportional to the concentration of an element or a substance in the analytical volume on the reciprocal temperature. This dependence is used to calculate the activation energy of the process using the Arrhenius equation from the slope of the straight line plotted in the $\ln P - T^{-1}$ coordinates, where P is the sought-for parameter (in particular, pressure) and T is absolute temper-

§ Acceleration of cation exchange processes has also been described by Mingos and Baghurst.[7]

¶ Only sparse data on determination of E_a under conditions of microwave treatment can be found in the literature. The researchers' opinions concerning the coincidence of the activation energies of processes carried out with traditional and microwave types of heating are different. For example, the activation energy for sintering of alumina calculated for microwave heating [70] is several times lower than the E_a value for this process carried out with traditional heating. Apparently, this is due to the specific character of microwave heating, namely, high temperature and time gradients and a change in the ratio of contributions of various reactions to the overall process under these conditions. A refined mathematical model describing the temperature–time distribution in solid metal oxides heated by MW has been reported.[20]

ature. An important aspect in using the dynamic method is substantiation of the applicability of experimental results to the construction of the Arrhenius plot and determination of the thermodynamic characteristics of the processes.

Modern commercially produced laboratory microwave systems are equipped with fibre-optics sensors for direct measurement of the temperature of the reaction mixture, by monitoring systems of the pressure in the vessel and facilities for data recording in graphical and digital forms at 1 – 30 s intervals. Hence, this equipment can be used to study processes during which the pressure in the system varies together with the temperature, in particular, due to the formation of gaseous reaction products. This formed the basis of a mathematical model for the kinetics of a chemical reaction [4] proceeding in a closed vessel under the action of MW, which was developed in the simple approximation of homogeneous distribution of the temperature and pressure in the system. The above-considered dynamic method for determination of the activation energy for the oxidation of organic compounds by nitric acid from the experimental exponential dependence of the system pressure on the reciprocal temperature of the reaction mixture was substantiated.

Microwave oxidation of individual organic compounds (amino acids, stearic acid, monosaccharides) forming the basis for the most important natural products (proteins, fats and carbohydrates) has been studied.[73, 74] Figure 3 shows the temperature and pressure variation in the system *vs.* time during the oxidation of phenylalanine by nitric acid; Figure 4 presents the Arrhenius dependence of the total pressure in the system, which is proportional, in the chosen approximation,[4] to the rate constant

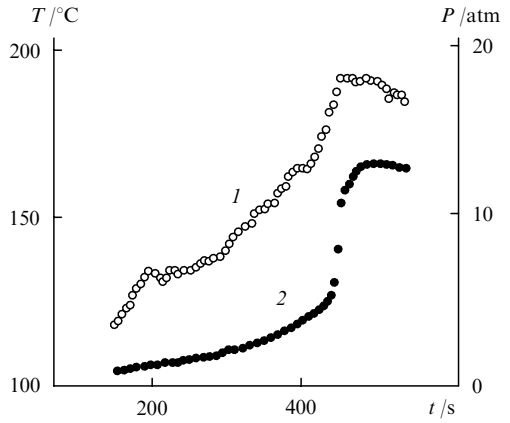


Figure 3. Effect of microwave radiation on the variation of temperature (*1*) and pressure (*2*) in a closed vessel during oxidation of phenylalanine by nitric acid.[74]

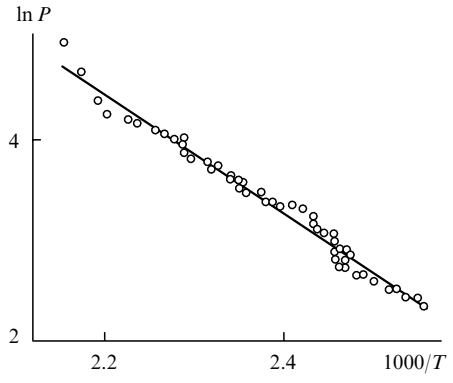


Figure 4. Arrhenius dependence of pressure on temperature during oxidation of phenylalanine by nitric acid under conditions of microwave heating (E_a = 50.1 kJ mol^{-1}).[74]

Table 3. Experimental values of the activation energy (E_a) for the oxidation of organic compounds determined under microwave heating conditions.[74]

Class	Compound	E_a /kJ mol^{-1}
Sugars	saccharose	73.3
	galactose	73.5
Amino acids	lysine	24.0
	phenylalanine	50.1 (50.0 [a])
	tryptophan	32.0 (29.8 [a])
Fatty acids	stearic acid	76.4

[a] The data were obtained with electrochemical detection of the products of decomposition of amino acids at constant temperatures (static method).[69]

for the oxidation, on the reciprocal temperature. The data for the calculation of the activation energies for the oxidation of some model compounds and natural products are listed in Table 3. These values fall in the normal range of the E_a values typical of reactions of this type carried out with traditional heating (40 – 120 kJ mol^{-1}) [75] and are correlated with the strengths of chemical bonds in the molecules of these compounds.

The approach to the determination of the activation energy of oxidation used in this work was implemented within the framework of formal kinetics and the views of the collision theory in which the pre-exponential factor $A = zN$ in the Arrhenius equation $k = A\exp[-E_a/(RT)]$ reflects the influence of the steric factors (N) and the number of collisions (z). In addition, this approach does not contradict interpretation of the results obtained in terms of the transition state theory. In this case, the activation energy correlates with the enthalpy of formation of the activated complex, and the pre-exponential factor is correlated with entropy. The former correlation leads tacitly to a fundamentally important conclusion stating that the reaction pathway remains invariant irrespective of whether it is induced by microwave or traditional thermal heating, and the latter correlation attests to an important role of the entropy factor, *i.e.*, the orienting influence of the electrical component of a microwave field on the reacting species. Thus, acceleration of chemical reactions by microwave radiation is due to kinetic factors. Hence, microwave heating can be used not only to affect physicochemical processes in solutions or heterogeneous systems but also for fast determination of the quantitative characteristics of reactions and modelling of kinetically hindered transformations.

4. Synthesis of organic compounds

Within the scope of this review, which is mainly devoted to the processes used in the chemical analysis and accelerated by microwaves, it is also pertinent to touch upon some aspects of organic synthesis. First, for many reactions involving organic compounds, the reaction mechanisms, the roles of the solvent and the composition of the reaction mixture and reaction conditions have been studied in sufficient detail. This makes easier the identification of the effects caused by the additional external treatment and promotes the understanding of the general mechanisms of the microwave influence on chemical transformations. Most of the results unexplainable in terms of thermal effects alone and most studies analysing the patterns of MW influence on the course of reactions refer to the processes of organic synthesis.[2, 3, 42] Second, diverse compounds of the organic nature (solvents, extractants, polymer-based sorbents, complexing reagents including macroheterocycles) play an enormous role in analytical research, and development of methods for preparing them remains a topical task.

The extensive use of MW for synthetic purposes started in 1986.[76, 77] Acceleration in a microwave field of many organic reactions such as elimination, esterification, cycloaddition, isomerisation, substitution, hydrolysis, dehydration, condensation, *etc.*, has been noted.[2, 3, 42] In some cases, the reaction time

determined on the basis of the product yield can be shortened by three orders of magnitude.[78] The reaction conditions are exceptionally diverse — at atmospheric or elevated pressure, in a flow, in aqueous or non-aqueous solutions, on a solid surface [2, 42, 79] and in the solid phase.[80] A laboratory setup has been elaborated for microwave organic synthesis [81] carried out at high pressures (up to 100 atm) and at a temperature of up to 260 °C.

The decrease in the solution viscosity, heating of the solution to a temperature higher than the boiling point, change in the electron density distribution in the molecules of organic compounds and in the contribution of the products of competing reactions are, apparently, the main factors inducing the effects observed when organic reactions are carried out under microwave radiation. It has been shown [82] that the kinetics and the order of reactions do not depend on the method of heating. However, some abnormal features may arise on exposure to MW.[83] In competing reversible reactions,[31] the rate of warming-up of the reaction mixture plays the most important role because the ratios of the products formed are different at different temperatures. Fast microwave heating allows one to perform the reaction at a strictly specified temperature and to minimise the duration of the temperature variation step and, hence, to avoid conditions that may bring about the formation of undesirable products. In some cases, the abnormally high selectivity and substantial yields of the reaction products for the reactions taking place in the presence of catalysts or on supports after the removal of a solvent, can be explained by the selective heating of separate sections of the surface on which the reaction takes place, due to the microwave irradiation. A sharp increase in the yield (from 2% to 92%) of the product of intramolecular rearrangement of unsaturated ketones has been noted [84] (the results were obtained from conventional and microwave heating, respectively, at the same temperature; the publication cited contains no kinetic data [84]). The synthesis of acetylene in a yield of >90% by microwave cracking of benzene has been reported [85] (the thermal cracking of benzene scarcely takes place). The reaction mode also has a certain influence on the product yields. For example, the increase in the yields of products in some organic reactions induced by microwave radiation was reported to be more pronounced in the flow mode than in closed vessels.[86] This fact was attributed [2] to the higher surface area of the reaction mixture in the case of flow systems, because the action of MW on the surface increases the contribution of the interfacial polarisation mechanism.

It has been suggested in a review [42] generalising the results of a large number of synthetic studies dealing with the use of MW that, if the radiation energy is absorbed only by the solvent, the acceleration of reactions with respect to those proceeding by conventional heating will not be significant. If the radiation interacts with either the reactants or intermediate compounds, the increase in the reaction rate can be appreciable. The absorption of the radiation energy by not only the solvent but also the reacting substances is observed, in particular, for polymerisation processes.[87–89] This makes it possible to control the conditions of synthesis with high accuracy and to reduce the energy expenditure by a factor of 10–20. The polymers produced in this way often possess better physical properties, for example, higher strengths,[3] than the polymers synthesised with conventional thermal heating,[42] although the structures of both types of polymer are similar.

The conditions used to conduct reactions are diverse, and the outcome depends appreciably on the type of the process, the nature of the solvent and the reactants, the radiation power and the way of irradiation,[42] because these factors determine the degree of action of MW on the reaction system. For example, variation of the conditions of emulsion polymerisation of acrylates allows, apart from shortening of the polymerisation time by a factor of 60,[90] the synthesis of poly(*p*-nitrophenyl acrylates) with molecular masses ranging from 40 000 to 180 000.

IV. Microwave-assisted sample preparation in chemical analysis

The preparation of samples for the measurement of the analytical signal from a particular component can include drying, ashing, mineralisation, decomposition (dissolution) and preconcentration (matrix separation). The sample pretreatment operations are based on various chemical reactions and physicochemical interactions involving components of the sample. Many of these reactions (hydrolysis, oxidation, complexation) have been considered above; their typical features observed under microwave heating also remain valid for sample pretreatment processes. Despite the obvious similarity of the occurrence of chemical reactions under thermal and microwave heating, significant additional effects can be attained in the latter case by using the specificity of warming-up induced by radiation. The development of microwave-assisted sample preparation techniques has been the subject of hundreds of papers, two monographs [2, 8] and several reviews.[11, 15, 18, 58, 63, 91–95]

1. Drying

Owing to the direct absorption of the MW energy by H_2O molecules, heating and vaporisation of water present in the pores of a material proceed much faster than under conventional conditions. Unlike the situation with traditional heating, warming-up of the material becomes less pronounced as water is removed, and by the end of the process, the sample temperature decreases.

It is expedient to carry out microwave-induced drying for individual substances, for example, in the preparation of inorganic specimens,[96] or in those cases where the accuracy of analysis is not subject to stringent requirements. This is due to the fact that it is difficult to select conditions for the microwave drying of materials with mixed or variable composition [97] because water molecules bound to the matrix in different manners absorb the MW energy to different extents. If a determination reproducibility equal to several percent is admissible, drying in microwave ovens has a substantial effect.[2, 12, 98] The results of early studies on the use of microwave drying are summarised in a monograph,[2] and the most recent achievements along this line have been reported.[99] An interesting way of using MW for drying of silicic acid gels in the preparation of modified xerogels has been proposed.[51]

2. Ashing and fusion

These operations involve no direct action of MW on the substance under analysis; as in the case of conventional heating, the material is warmed up by the muffle furnace walls, which are heated extremely rapidly (in several minutes) to 1200 °C due to the efficient absorption of the radiation energy by silicon carbide, which is the material of the internal walls.[8] As a consequence, the time required for the furnace to be heated is markedly shortened and the efficiency of the method increases. The duration of the ashing decreases several-fold because of the use of forced convection; fusion can also be carried out 1.5–2.0 times faster.

3. Digestion

One of the most important applications of microwave systems in analysis is to decompose samples having highly diverse compositions and origins. Since the first publication [100] dealing with the use of a microwave oven to accelerate the sample pretreatment appeared in 1975, numerous expedients and techniques of microwave decomposition suitable for virtually any type of object have been developed; they are covered in the above-mentioned monographs [2, 8] and reviews.[18, 58, 63, 91–95] We shall note only typical features of this method for sample digestion.

Decomposition of substances on treatment with inorganic acids is a heterogeneous reaction the rate of which can be determined by either diffusion processes or interactions at the solid–solution interface. In both cases, treatment with MW substantially accelerates the processes involved. The regularities

considered above established for individual reactions (shortening of the reaction time, decrease in the reactant ratio down to stoichiometric amounts, an increase in the completeness of reactions) are clearly manifested in decomposition processes.

Microwave digestion is carried out using the same reagents (most often, acids and their mixtures) as that induced by conventional heating.† Treatment can be carried out both in usual open vessels made of materials which slightly absorb MW (glass, quartz or fluoroplastic) and in closed systems at elevated temperatures and pressures. This allows the mixture under analysis to be heated to a temperature markedly exceeding the boiling point of the used acid under normal pressure; therefore, both the rate and the degree of transfer of the sample into a solution become much higher. An important advantage of microwave-assisted digestion in closed vessels is low pressure with a relatively high temperature (see Figs 1, 3), due to the fact that radiation causes heating of the liquid but not of the gas phase.

Since the temperature of decomposition dictates the range of applicable acids, an increase in this temperature often makes it possible to replace high-boiling perchloric, sulfuric or phosphoric acid by hydrochloric or nitric acid, which are more convenient for digestion. In some cases, the higher degree of sample dissolution at higher temperatures makes it possible to eliminate the stage of fusion of the residue after sample dissolution in acids.

It is fairly useful to apply microwave heating for decomposition of organic matrices (biological and clinical objects, pharmaceutical preparations, foodstuffs, forages, food raw materials and ecosystem components). In this case, the time of analysis can be appreciably reduced. Decomposition of organic matrices can be carried out in both closed and open systems. The use of open systems is recommended for working with large amounts (up to 10 g) of materials when considerable amounts of gaseous products of oxidation are evolved during the process. In combination with modern, highly sensitive methods of analysis (for example, atomic spectroscopy techniques such as ETAAS, ICP AES or ICP MS) in which determination of elements at a level of $10^{-6}\% - 10^{-5}\%$ can be accomplished using fractions of a gram of the material, closed or flow systems are used more frequently. Flow setups represent a step towards automation of the analysis, attained by connecting a flow system for sample digestion to the injecting device of a spectrometer. The samples are commonly introduced in the systems as suspensions in acids.[101, 102] The publications describing the use of microwave heating for decomposition of organic matrices are devoted, most of all, to determination of trace elements and identification of the species containing them in environmental and biological objects by instrumental methods.[18, 26, 65–67, 103–106]

Decomposition of inorganic matrices often requires drastic conditions; therefore, for this purpose, it is expedient to use closed vessels, which are applicable up to a temperature of ~ 350 °C and a pressure of 200 atm.[107–109] These conditions may ensure dissolution of the most complex geological specimens (for example, those containing noble metals), poorly soluble oxides (such as niobium and tantalum oxides), metals, alloys or catalysts.[18, 110, 111] The use of microwave setups including automated or robotised ones acquires special significance in the analysis of radioactive specimens.[112] Data on the time required for preparation of some substances for the analysis using traditional and microwave heating procedures are compared in Table 4.

The main causes for the intensification of sample digestion in the case of microwave treatment include high rate and uniformity of heating of the reaction mixture; exceeding of the boiling point corresponding to the given pressure; and local effects (warming-up of the solvent in the sample pores, *i.e.*, actually, in a confined space, and sample destruction under high pressure; selective heating of components of heterogeneous systems; reflection of the radiation to the near-surface layer of the solution in the case of digestion of metallic samples). Indeed, according to our data, the dissolution of gold alloys under microwave heating is twice as fast as that at the same temperature achieved by conventional heating.

The specific features of microwave digestion have a substantial influence on the metrological characteristics of the results. Due to good reproducibility of decomposition conditions, it is possible to obtain solutions of virtually identical compositions from identical samples, which is favourable for the reproducibility of the subsequent determination. The work with stoichiometric or nearly stoichiometric reactant ratios leads to a considerable decrease in the blank correction. A decrease in this value is also attained owing to use of closed or flow systems, which eliminates the loss of the analyte as volatile compounds and the ingress of contaminants from air; in combination with the use of high-purity chemicals, this brings the analysis closer to the 'clean room' conditions.[113] In addition, simplification of the composition of the reaction mixture allows some sample pretreatment operations to be avoided, which also improves the metrological characteristics of the analysis as a whole. Mention should be made of high productivity and economic efficiency of the microwave techniques, and their flexibility in combination with preconcentration and instrumental determination.[2, 4, 58]

The most promising approach to the substantiated selection of digestion conditions consists in modelling with the use of individual compounds of various classes. This approach was used, for example, to establish the conditions for the oxidation of model organic compounds by nitric acid. Kingston and Jassie [114] showed

† However, due to specific features of microwave heating and the change in the kinetics of chemical reactions, the conditions chosen for thermal digestion can be regarded only as the starting point in microwave procedures.

Table 4. Comparison of the times of digestion of various samples in the conventional and microwave heating modes.[4, 22]

Sample type	t_1 /h [a]	Microwave digestion conditions	t_2 /min [b]	t_1 / t_2
Biological objects (trace components)	8	HNO_3 or its mixtures with HF and HCl, closed systems	1.5–30	16–100
Geological objects (macrocomposition)	6	HNO_3, HCl, closed systems	4	90
Geological objects (trace components)	4–16	HF and HCl, HF and HNO_3, closed or open systems	10–20	24–32
Objects with an organic matrix (trace components)	8–16	HNO_3, closed systems	10–20	24–64
Biological objects, Kjeldahl determination of nitrogen	2–6	H_2SO_4, open systems	3–6	20
Alumina	24	H_2SO_4, H_3PO_4, closed systems	40	36
Steels	1	HCl, HF, HNO_3, closed systems	1–2	45
Soils, dust	8	HF, HNO_3, closed systems	20	24
High-purity compounds	8–24	HF, HNO_3, closed systems	12	40–120
Waste water	6	HNO_3, closed systems	10	60

[a] Time of traditional sample pretreatment. [b] Time of microwave pretreatment.

that carbohydrates, proteins and fats are oxidised on exposure to MW at 140, 150 and 160 °C, respectively. Later, the activation energies for the oxidation of a number of model organic compounds were determined; these data were shown to be suitable as the basis in choosing for conditions for decomposition of natural products.[74]

The principles of selection of the conditions for microwave decomposition depending on the sample weight, the rate of temperature rise, the volume of the reaction mixture and the total volume of the vessel have been considered in detail by Knapp.[115]

4. Preconcentration of traces of elements

Exposure to radiation permits fast preconcentration of trace amounts of metals by evaporation [99] or by using organic sorbents that react with metal ions according to complex-formation or ion-exchange mechanism. Preconcentration by sorption is carried out in either the static or dynamic mode. Preconcentration of platinum group metals and chromium on nitrogen-containing complexing sorbents has been reported.[104, 110]

5. Identification of the element forms (speciation)

Analysis with the use of MW, which provides simultaneously specific chemical treatment and fast heating of the system, permits selective isolation of analytical forms of elements without changing their chemical composition in the sample. The compounds are collected using organic solvents or mixtures based on inorganic acids.[116] This expedient was used for mass-spectrometric identification of chemical species containing mercury,[117] tin [118] and heavy metals.[119]

6. Extraction of organic impurities

Of special interest are recent studies dealing with the selective microwave-assisted extraction of toxic organic compounds into organic solvents.[11] These studies would undoubtedly serve as a significant stage in the development of organic analysis methods, first of all, chromatographic techniques. The advantages (considerable acceleration and an increase in the degree of extraction of the organic impurities to be determined) are caused in this case by the increase in the temperature of the extraction system by several tens of degrees. A highly important specific feature of microwave extraction is the fact that this method allows selective collection of components either through selective heating of the phase or a separate component of the system (for example, free water molecules in plant cells), depending on its dielectric properties, or through choosing an organic solvent that would selectively extract one or another component. In addition, the consumption of organic solvents and, hence, the amount of toxic wastes markedly decrease, which is beneficial from the environmental standpoint.[14, 15]

An interesting version of microwave-assisted extraction is the withdrawal of volatile organic compounds to the gas phase through microwave heating of a matrix containing a polar solvent (water). The gas phase which does not absorb MW does not warm up, and under certain conditions, it virtually does not contain solvent vapour due to the non-equilibrium character of the system. Determination of the impurities of relatively volatile organic compounds in solid matrices such as soils is also possible; the most polar substances are the first to be evaporated. Upon irradiation of solid materials containing moisture, the selectivity of determination is due to the separate transition to the gas phase of components characterised by different vapour pressures.[11, 14]

The principles of selection of the conditions for the extraction of organic impurities (biologically active nutritional compounds, antioxidants, UV stabilisers of plastics, pesticides, polyaromatic hydrocarbons, phenols, organometallic compounds and other contaminants) in microwave systems and comparison of the results with traditional methods have been reported.[11, 14, 15]

7. Determination of the contents of total nitrogen and phosphorus

Under conditions of traditional heating, sample digestion, which is the limiting step in determination of the total nitrogen, takes 2 to 6 h. Since sulfuric acid, used in the Kjeldahl method, efficiently absorbs microwave radiation, the time it takes for the reaction mixture to warm up to 400 °C can be shortened from 45 min to 3–6 min. The introduction of an additional oxidant (Caro's acid) and the use of special techniques make it possible to reduce both the duration of decomposition of the organic matrix and the time of cooling the mixture and also to simplify titration. The problems of the traditional Kjeldahl determination of nitrogen and the capabilities of the microwave modification of this analysis have been considered quite comprehensively in a publication.[120] The results of application of microwave methods for determination of nitrogen [121] and phosphorus [122] in the analysis of environmental objects have been generalised.

V. Conclusion

The significance of MW for analytical chemistry grows continuously and rapidly. In the 1970s, there were only seven publications devoted to analysis using MW; in the 1980s, the number of publications increased to 132, while over a period of only four years, from 1991 to 1995, according to the data of a review,[18] 166 more studies were published. About 1000 studies related to the application of MW in analysis have now been published. The main topics considered in these studies are related to sample digestion, drying and ashing under the action of MW. The microwave-assisted sample preparation has underlain new-generation analytical techniques — fast and highly efficient methods having good metrological characteristics; this reduces the gap between the existing power of instrumental determination of elements and the level of sample pretreatment techniques and extends the range of objects that can be analysed by routine methods. Due to the versatility of microwave methods, it is possible to design integrated analytical sequences consisting of inseparably connected operations and meant for the determination of a wide range of substances and materials, instead of separate procedures. This field of analytical chemistry is being vigorously developed.

The design of multipurpose analytical schemes on the basis of minimisation of the number of operations and integration of operations in space and in time [123] implies, first of all, improvement of the sample preparation step and convenient combination of this step with instrumental determination. The most promising lines of development of inorganic analysis with the use of MW were outlined by Matusiewicz and Sturgeon.[91] They believe that the goals of using MW should include the decrease in the number of analytical operations and the time required to perform them through intensification of chemical processes, integration of operations, development of on-line analysis and speciation methods and implementation of rational hybrid methods. Generally, these trends correspond to the general principles of the development of analysis discussed in a number of publications.[123–129]

Attempts to develop general approaches to the design of analytical schemes based on the microwave sample pretreatment, to improve individual stages and to implement integrated sequences of operations in a microwave field within a single system have been undertaken.[6, 130, 131] An approach proposed in our study [12] and developed further under the name 'total microwave sample preparation' (which implies sample pretreatment in which all operations are carried out under the action of MW, are interrelated and often combined with one another) [132] is regarded to be one of the major directions in the microwave-assisted sample preparation.[2] In the development of hybrid methods and analytical schemes for analysing unique samples by high-sensitivity instrumental methods, non-traditional combinations (in particular, those with the use of micromethods, *i.e.*, techniques and expedients for working with small amounts of the analyte) are

fairly promising. The methods of sample preparation with the use of MW are suitable for complex analytical objects, both for elements and matrices such as geological (ores, rocks), environmental (foodstuffs and raw materials, biological preparations, natural water, soil), industrial (high-purity substances, concentrates, metals, alloys, second-hand raw materials) containing heavy, rare and noble elements as macro- and micro- components. The use of MW substantially improves characteristics of analysis, not only that carried out by advanced instrumental methods but also of the analysis performed by well-known traditional methods, thus providing an increase in the potential of the existing analytical equipment. Owing to the microwave pretreatment, it is possible to reduce several-fold the duration of analysis, decrease the consumption of chemicals and energy expenditure, and to reduce the required man-hours.

In addition to ultra-trace analysis of components, which is associated with specific conditions (clean chemistry), one more important analytical problem that has appeared quite recently is elaboration of methods for determination of the forms in which elements exist. Microwave methods, which possess great potential due to the diversity of operations carried out in a microwave field and the flexibility of combinations with instrumental methods, are undoubtedly promising in this respect. Microwave systems are used to increase the efficiency of multistep procedures of successive selective acid extraction of various chemical forms of metals, sample digestion and extraction with organic solvents. Sample derivatisation, *i.e.*, preparation of a derivative convenient for the subsequent instrumental determination of the element, is also carried out directly in the microwave oven; this is done in open, closed or flow systems.[2, 116, 117] By combining microwave pretreatment with atomic and mass spectrometry or liquid and capillary gas chromatography, hybrid methods have been developed, which shorten the time of analysis by a factor of 20 – 100.[130, 131, 133, 134]

Yet another important feature of microwave methods is the possibility of preparing metals as convenient analytical forms and as complexes that are difficult to prepare by traditional methods due to kinetic restrictions. A simple procedure for preparation of the required analytical forms under the action of MW increases the efficiency of rather long-lasting classical spectrophotometric, fluorescence, luminescence, sorptional, electrochemical and other methods that are sensitive to the form of element existence in solution. The correlation between the specified conditions of reactions and the quantitative and qualitative composition of the products provides the possibility of targeted synthesis of both inorganic complexes and macrocyclic reagents [40, 41] or polymers.[4, 90]

The embodiment of the potential of microwave methods is determined by the development of instrumentation, increase in the efficiency of the control of process parameters, and the decrease in the cost of equipment. Thus an increase in the speed of analysis can be achieved by two methods: by increasing the number of samples treated simultaneously [in closed systems, this can be 52 (see Ref. 135)] and by using flow systems in which, according to the data of CEM company, 180 samples can be prepared over a period of 3 h. The metrological characteristics of analysis can be improved, for example, by using steel autoclaves in combination with microwave heating by focused radiation; in Matusiewicz's opinion,[108] this ensures faster heating, a higher pressure, and a better reproducibility of results. A promising technique is the use of microwave flow setups for digestion and preconcentration coupled with automated determination. The scopes of the two approaches are analysed in a publication.[66] Flow setups appear to be the optimal devices for the design of automated systems, although other facilities (for example, open and robotised devices [2, 136, 137]) can also serve as parts of these systems used to solve particular analytical problems. Undoubtedly, with the advent of new technologies and materials, novel engineering solutions for the implementation of microwave heating will also arise (the ways of radiation supply; the design of the vessels, flow systems, automated injection units and types of coupling with instrumental determination) and new ways of controlling the parameters (temperature, pressure) and of the 'parameter – process' feedback will appear. This will give rise to a new generation of laboratory microwave systems.

The possibility of conversion of microwave devices from a fairly advanced facility used for routine sample pretreatment into a tool for investigation of the regularities of chemical transformations appears to be of fundamental importance.[69, 71, 73, 80] The change in the kinetic parameters of reactions on exposure to radiation with maintenance of invariable thermodynamic properties of the system allows quantitative investigations of the slow physicochemical processes, simulation of various reactions in model systems and, thus, provides a way for predicting the results of processes taking place under real conditions. This is of interest from both theoretical and practical standpoints, for example, for the perfection of complex technological processes involving a series of reactions with participation of many components.

The development of the theoretical basis of microwave sample pretreatment is a topical subject. Further studies along this line should probably be related to in-depth investigations of the interaction of MW with substances of different chemical nature (solvents, analytes, structural components of microwave systems); research into the influence of physical parameters of MW (frequency and intensity) on the course of physicochemical processes in solutions or heterogeneous systems. This would enable researchers to ensure selective transfer of energy to the reaction system components and, thus, to propose new in kind routes to the solution of analytical problems. In addition, extension of the range of chemical processes taking place under the action of MW, in particular, study of the influence of MW on catalytic and enzymic processes, organic synthesis, preparation of coordination compounds and polymerisation is also important for modern analytical methods.

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