ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

3 (63)

ИЮЛЬ – СЕНТЯБРЬ 2018 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2018

UDC 547.673

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CHARACTERISTICS OF MICROWAVES, SOME ASPECTS THEORY OF MICROWAVE HEATING AND THE FIELD OF APPLICATION OF MICROWAVES IN ORGANIC CHEMISTRY AND CHEMISTRY OF NATURAL COMPOUNDS

Abstract. The review considers the characteristics of microwaves, the theory of microwave heating in a comparative analysis with the features of thermal heating. The presented material shows the areas of use of the microwave radiation in organic chemistry and chemistry of natural compounds.

Key words: microwave radiation, microwave heating.

The problem of complex processing of plant raw materials and the creation of new highly effective methods for obtaining biologically active substances (BAS) are among the priority directions in the development of chemical science. At the same time, an important aspect in the development and use of new chemical, physico-chemical, physical and biological approaches is the following principles of «green chemistry» [1, 2].

Currently, studies are underway to modify and improve these processes, which include such areas as: improvements in the technical equipment of the process, replacement of the conditions for carrying out the reaction and extraction, including the solvents used, the use of various factors of physical impact, including ultrasonic and microwave treatment [3-7].

Microwave radiation and its characteristics. Microwaves are electromagnetic waves, consisting of two oscillating perpendicular fields: electric and magnetic (figure 1).

The microwave radiation is electromagnetic radiation, which includes a decimeter, centimeter and millimeter wave ranges. Quantum energy, frequency (ν) and wavelength of their waves (λ) are joined by rigid dependencies (figure 2). In accordance with them, the electromagnetic spectrum is conventionally divided into partially overlapping bands, depending in part on the source of the radiation. Microwave is usually called the spectral region in the frequency range 300 GHz – 300 MHz (wavelength from 1 mm to 1 m). It is located in the interval between the infrared and radio frequency ranges [8-10].

Microwaves are used as information carriers or as energy vectors. Microwave radiation of low intensity is used in communications, mostly portable, and microwave radiation of high intensity is used for contactless heating of bodies. The second direction is related to the direct action of waves on a material that is

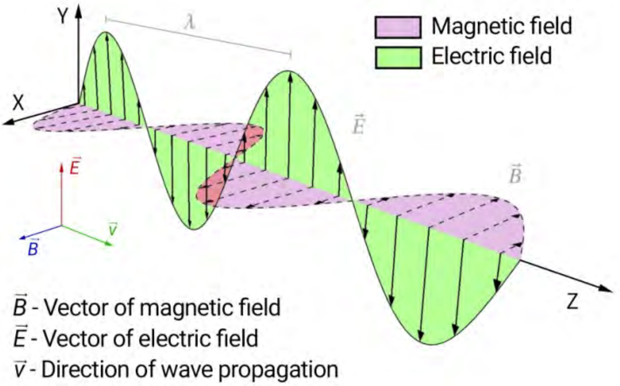

Figure 1 – Schematic description of the electromagnetic wave

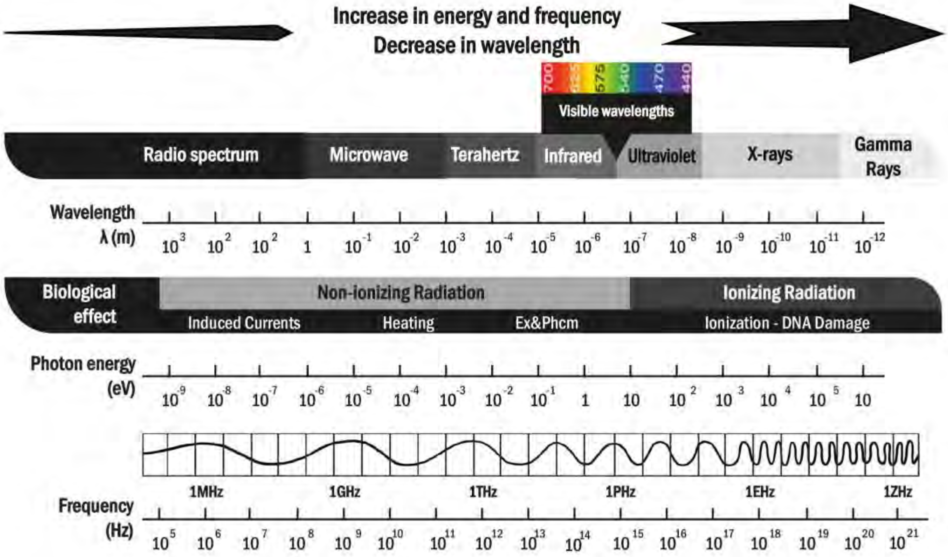

Figure 2 – The scale of electromagnetic radiation

capable of absorbing some of the electromagnetic energy and turning it into heat and used for heating [8, 9].

In most microwave installations, including household microwave ovens, a frequency of 2,450 MHz is used, which can only cause the rotation of molecules. This frequency was chosen to avoid interference with radar and telecommunications systems. The wavelength and frequency are related by the relation: $\lambda = c/\nu$, where λ - wavelength, c - wave propagation velocity, ν – frequency. Knowing that electromagnetic waves propagate at a speed of light equal to 300,000 km/s, it is not difficult to calculate what the wavelength of the microwave radiation of a given frequency is equal to: $\lambda = c/\nu = 12.25$ cm.

Features of thermal and microwave heating. An important factor affecting the extraction process and the reaction in solutions and heterogeneous systems is the increase in temperature. The traditional (thermal) method of heating is characterized by the transfer of heat from the surface to the volume of matter by means of thermal conductivity and convection (figure 3). However, with a slow transfer of thermal energy from the source to the sample and inside it, obstacles are created that do not allow significantly accelerating the course of the processes. In the case of the low thermal conductivity of the object, heating proceeds slowly and is complicated by local overheating on the surface [10].

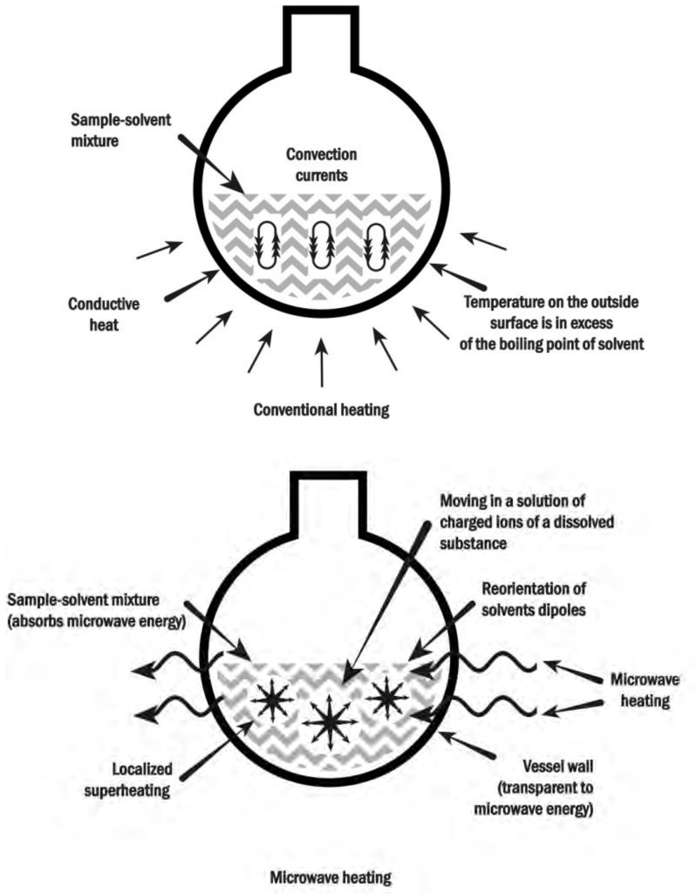

Figure 3 – Schematic representation of specificity thermal and microwave heating [12]

Microwave heating is an alternative way to increase the temperature. When microwave radiation is used, the mechanism of interaction with matter consists in absorbing the energy of electromagnetic radiation and scattering it in the form of heat. In this case, heating occurs from within the entire volume of the sample due to the creation of the effect of dielectric losses. Microwave heating differs from the traditional method by a high volume and time gradient, and also by the unequal ability of solutions and components of a heterogeneous system that differ in composition to absorb radiation energy [11].

There are two main mechanisms for the interaction of microwave radiation with matter. The transformation of electromagnetic energy into thermal energy is due to two mechanisms: ionic conductivity and dipole rotation. Ionic conductivity generates heat due to resistance. Migration of dissolved ions causes collisions between molecules because the direction of ions varies as many times as the field changes sign. Dipole rotation is associated with an alternative motion of polar molecules which is caused by the continuously changing direction of the vector of the electrical component of the radiation. Multiple collisions associated with such a movement of molecules generate energy and, consequently, an increase in temperature. The frequency of microwave radiation corresponds to the rotational motion of molecules (figure 4), and in the condensed state, in which there is no free rotation, the absorption of energy leads to its redistribution between molecules and homogeneous heating.

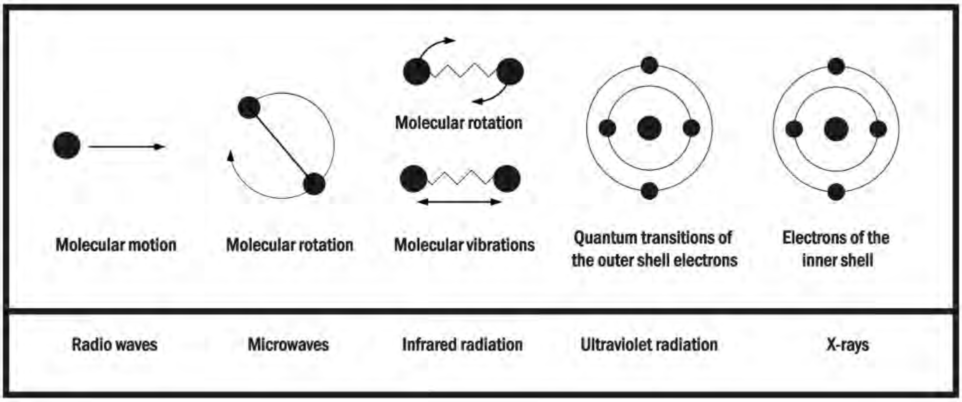

Figure 4 – Motion of molecules at different frequencies electromagnetic radiation [13]

Since the frequency of microwaves used is 2,450 MHz, and one hertz is one oscillation per second, the megahertz is one million oscillations per second. During one period of the wave, the field changes its direction twice, hence, the field in which the molecules are located changes the polarity 4,900,000,000 times per second. The change in the electrical component of the wave 4.9×10^9 times per second contributes to the generation of unorganized motion of polar molecules, which when irradiated by microwaves and produce heat [4, 5]. This heating is a consequence of the interaction of the electrical component of the electromagnetic wave with charged or polar particles. In the absence of an external electric field effect, such particles have random chaotic motion or oscillate with respect to the equilibrium state (figure 5A). When an external electric field is imposed, such

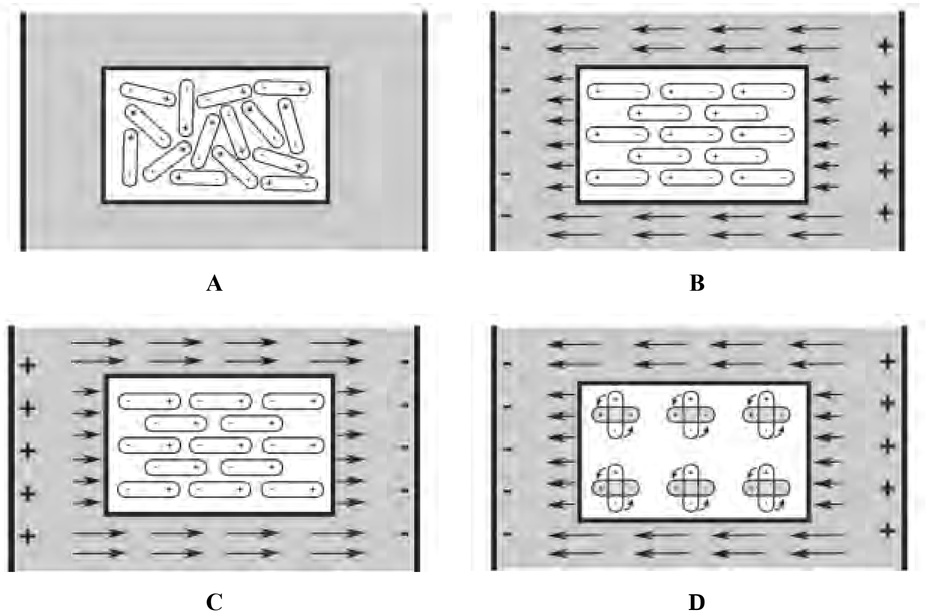

Figure 5 – Schematic representation of interaction microwave radiation with polar particles

particles are ordered, electrostatic forces will tend to orient the dipole moments of the molecules along the field lines (figures 5B and 5C), and if the field is ascending, their orientation will change with each oscillation (figure 5D). Thus, the reorientation of particles, which is activated by an alternating electric field, and causes intense internal heating.

Thus, the effect of the electromagnetic wave on the substance of the microwave band leads to a continuous reorientation of the polar molecules, due to the continuously changing direction of the vector of the electric component of the radiation, which, as a result of intermolecular interactions, leads to the release of heat.

In the case of a condensed phase in which free charged particles exist, these particles will move in accordance with a change in the electric field and generate an electric current. This situation is typical for metals, where electrons act as mobile charged particles, and for solutions of electrolytes in which charge carriers are ions. If microwave radiation is used for a phase containing polar molecules, then these molecules will orientate themselves in the applied electric field and reorient themselves with its oscillations. Such a motion and collisions of molecules in the condensed phase will cause heating, thus conditioning «from within». Another property of the microwave heating is that it does not affect nonpolar molecules and materials such as quartz, ceramics and glass that do not contain water, Teflon, polyethylene, alkanes. This allows them to be used (quartz, ceramics, glass, teflon) as dishes for chemical reactions, as well as (non-polar solvents) as a specific reaction medium. As a rule, in the microwave treatment the polar solvents are used, because they effectively absorbing microwave radiation.

Some aspects of the theory of the microwave heating and effects of microwaves on solutions. Discussing the feature of microwave heating it should be noted that in contrast to thermal heating when it is used there is a so-called dielectric heating. In this case, the total heating is made up of the electrical conductivity losses that occur when in a dielectric or a reaction mixture there are free ions capable of moving in an electric field and which, when moving and colliding with the molecules of the substance, transform some of the electrical energy into thermal energy, as well as to relaxation losses, which are due to the orientation of the dipole molecules in the direction of the lines of force of the electric field [10]. At the frequency that is used at 2450 MHz, the electric field strength vector changes its direction $4.9 \cdot 10^9$ times/s. Because of it the vibrational vibrations of the dipole moments of the molecules occur, which contributes to the transfer of some of the energy of the electromagnetic field, and accordingly to the temperature increase which occurs uniformly throughout volume, taking into account the depth of penetration of microwave radiation (table 1).

Table 1 – Data on penetration depth microwave radiation (20-25 °C) [10 (p.16), 14]

Substance	Depth of penetration (cm) microwave radiation at different frequencies		
	433 MHz	915 MHz	2450 MHz
Water	70,5	23,4	3,5
Methanol	33,0	7,8	1,4
Glass	4600	2180	840

In the superposition of a high-frequency electromagnetic field, in addition to dielectric polarization, atomic, electronic, and structural polarization are also observed. The first is due to the displacement of the atoms relative to each other because of the nonuniformity of the charge distribution, the second is due to the displacement of electrons relative to the atomic nucleus. The contribution of structural polarization, which is observed at the interface of inhomogeneous media, is relatively small [9, 10].

The release of heat is observed merely when the materials have dielectric losses during microwave irradiation. The ability of a substance to store potential energy under the action of an electric field is characterized by a dielectric constant, denoted by ε'. The coefficient of dielectric loss ε'' determines the efficiency of conversion of electromagnetic energy into heat. The absorbed energy depends on the defined coefficient as the tangent of the dielectric loss angle:

$$\tan \delta = \varepsilon'' / \varepsilon' \qquad (1)$$

where ε'' is the coefficient of dielectric losses, which characterizes the efficiency with which the energy of the electromagnetic field is converted into heat, and ε' is the dielectric constant.

Thus, the value of the tangent of the dielectric loss angle characterizes the ability of a given material at a fixed temperature to absorb MB radiation of a certain frequency and convert this energy into energy of thermal motion. The values of ε 'and ε" depend on the nature and state of the substance, the frequency of electromagnetic radiation and temperature. Compounds that have high dielec-tric losses are mainly polar compounds. The dielectric constants of some solvents are given in table 2.

Table 2 – Values of the dielectric constant and coefficient
the dielectric losses of some solvents [9]

Solvent	Frequency					
	$3 \cdot 10^8$ Hz		$3 \cdot 10^9$ Hz		$1 \cdot 10^{10}$ Hz	
	ε'	ε"	ε'	ε"	ε'	ε"
Water (t=25 ºC)	77,5	1,2	76,7	12,0	55,0	29,7
Aquatic NaCl (0,1 M)	76,0	59,0	75,5	18,1	54,0	30,0
Heptane	1,97		1,97	$2 \cdot 10^{-4}$	1,97	$3 \cdot 10^{-3}$
Methanol	30,9	2,5	23,9	15,3	8,9	7,2
Ethanol	22,3	6,0	6,5	1,6	1,7	0,11
n-Propanol	16,0	6,7	3,7	2,5	2,3	0,20
n-Butanol	11,5	6,3	3,5	1,6	0,2	
Ethylene glycol	39,0	6,2	12,0	12,0	7,0	5,5
Carbon tetrachloride	2,2		2,2	$9 \cdot 10^{-4}$	2,2	$3 \cdot 10^{-3}$

The rate of temperature rise due to the electric field of microwave radiation is determined by the following equation:

$$\frac{dT}{dt} = \frac{const \cdot \varepsilon' \cdot f \cdot E^2}{\rho \cdot C_\rho}$$

where f is the frequency of the radiation (Hz); E is the field strength (V/cm); ρ – density of the substance (kg/cm^3); C_p is the heat capacity of the substance (kJ/kg·K).

It follows from the equation that at a constant radiation frequency, the heating rate depends on the electro-physical properties of the substance and the power of the electromagnetic radiation.

The value of the thermal energy (Q, W/cm^3), which is released per unit of time per unit volume, can be determined from the equation (2) below, from which it follows the amount of energy released depends on the dielectric properties of the object, the frequency and the electric field strength [10]:

$$Q = 0{,}055 \cdot 10^{-14} \cdot \varepsilon' \cdot f \cdot E^2 \cdot \mathrm{tg}\,\delta = 0{,}555 \cdot 10^{-14} \cdot \varepsilon'' \cdot f \cdot E^2 \qquad (2)$$

where f is the radiation frequency, Hz; E is the intensity of the electrical component of the electromagnetic field, V/cm, ε ' is the dielectric constant, tg δ is the tangent of the dielectric loss angle, ε '' is the coefficient of dielectric losses.

The last expression shows that the amount of thermal energy released in the material depends only on the electrical characteristics of the material and the field parameters and does not depend on the thermal conductivity of the material. This feature obtain the primary advantage of microwave heating, which allows to significantly intensify the process of material heating in comparison with any other traditional type of heating, where the main role in the heating speed is played by thermal conductivity.

As a result of the interaction of radiation with matter, its intensity decreases exponentially as it passes through matter. The distance from the material surface at which the energy flux density decreases by "e" times (where, e is the basis of natural logarithms) in comparison with its value on the surface is called the depth of penetration. The depth of penetration of the electromagnetic field into matter decreases with increasing ε ', tg *δ*, f, and the released thermal energy increases.

Because of the decrease in the radiation intensity, the thermal power released per unit volume of the material falls off exponentially. It is therefore natural to expect a decrease in temperature from the surface to the center of the volume of the material. This occurs when the depth of penetration is much less than the thickness of the heated object. In the opposite case, when the depth of penetration is comparable or exceeds the dimensions of the object, there is a reverse, or inversion, temperature profile, i.e. the temperature inside the material is higher than on the surface. This is explained by thermal radiation from the surface and by convection cooling of the outer layers of the material with ambient air. The volume, and not only the surface nature of the heating of the irradiated samples, in the case of the usual thermal action, is an important feature of the action of microwaves.

From the foregoing it follows that microwave heating has a completely different nature than convection heating. In the case of convection heating, diffusive heat transfer from the coolant to the heated substance occurs. In the microwave heating, the increase in the internal energy of a substance occurs as a result of the dissipation in the substance itself of some part of the absorbed electromagnetic energy. From this follows the following significant advantages and peculiarities of microwave heating: heating occurs throughout the volume of the material, and the thermal conductivity of the material does not play a role; the temperature change of the heated material occurs without inertia in accordance with the change in the input power; the possibility of dynamic temperature control during the experiment; possibility of rapid temperature rise of the material up to the set values; the absence of heat transfer agent eliminates the possibility of burning the material.

An important factor to consider when using microwave heating is the thermal and electrical strength of the object, which is the limit for increasing the strength of the electric field. In this case, it is necessary to take into account that as the frequency increases, the depth of penetration of microwave radiation into the dielectric decreases (table 1).

In the case of microwave heating of solutions, the conversion of electromagnetic energy into thermal energy takes place due to two mechanisms: due to the reorientation of the dipoles of the solvent in an alternating electric field and as a result of directed migration of the dissolved ions present in the solution under the action of an external field, that is, due to dipole polarization and ionic conductivity [10-12].

The second factor is especially important for the release of heat during microwave exposure to solutions. Its mechanism of microwave heating is associated with conductivity effects, which can be caused by electrophoretic migration of ions in a solution when an electromagnetic field is applied. Such migration of ions is actually an electric current flowing through the solution. The passage of current I through a conductor with resistance R leads to the release of heat. Moreover, the higher the concentration and mobility of ions, the more intense the heating. Ionic conductivity is the conductive migration of dissolved ions that occurs when an electromagnetic field is applied, which leads to a loss of I2R (where I denotes the current intensity and R is the resistance) through the resistance to ion flow. Since the resistance R increases with increasing temperature, and the strength of the current carried by the ions I with increasing their concentration, both these factors significantly affect the tangent of the losses of microwave radiation in solutions. The contribution of the mechanism of ionic conductivity in solutions is determined by the dimensions, charges and specific electric conductivity of ions, and also by the interaction of ions with solvent molecules. Ionic conductivity depends on the concentration, mobility of ions and temperature of the solution [11].

In the case of microwave heating of water and other solvents, in which the degree of dissociation is low, the mechanism of dipole polarization will be the main one. The rate of heating will depend on the initial temperature, the frequency of the radiation and on the properties of the solvent, in particular its dielectric constant. The contribution of dipole polarization or ionic conductivity is largely determined by the temperature. For water molecules and other solvents, the dielectric losses due to the contribution of dipole rotation decrease with increasing temperature, and the dielectric loss due to ionic conductivity, on the contrary, increases with increasing sample temperature [11, 15].

With thermal heating, the number of boiling points in the solution volume is much less than that of the surface. In microwave treatment, heating is carried out from within throughout the entire volume, as a result of which the temperature of the solution is higher than the temperature of its environment (the walls of the vessel and the gas phase above the surface of the solution, etc.). In addition to the bulk thermal effect, the advantage of microwave heating is the rate at which such heating takes place. When using microwaves, the effect of overheating is possible, since the temperature, which is reached, can be higher than their theoretical boiling point. Thus, the rate of heating of the sample using microwaves depends on the dielectric characteristics, heat capacity, volume and power of the radiator.

Table 3 – Boiling temperatures (T_b, ºC) and temperatures under microwave heating of some organic solvents of 50 ml volume after microwave for 1 minute at 560 W, 2450 MHz [9]

Solvent	Conventional heating	Microwave heating
	Boiling temperature T_b, ºC	Heating temperature T_h, ºC
Water	100	81
Methanol	65	65
Ethanol	78	78
n-Propanol	97	97
n-Butanol	117	109
1-Pentanol	137	106
1-Hexanol	158	92
Dimethylformamide	153	131
Hexane	68	25
Heptane	98	26
Ethyl acetate	77	73
Chloroform	61	49
Acetone	56	56
Diethyl ether	35	32
CCl_4	77	28
Acetic acid	119	110

Thus, table 3 gives data on the temperature values that are reached by microwave heating of some solvents.

The variety of factors influencing the microwave heating makes it difficult to model this process, although the literature suggests a physical model that allows calculations of the temperature change in an open system, analysis of the mechanisms for obtaining and energy losses in solution, and theoretical aspects of microwave heating of solids [16, 12]. The review [17] discusses the theories underlying microwave dielectric heating and presents dielectric data for various organic solvents used in microwave synthesis.

Areas of use of microwave treatment in organic chemistry and chemistry of natural compounds. Microwaves have found application in various fields of science, as shown in figure 6. As can be seen from the presented data, microwave radiation has found the greatest application in chemistry (42.4%), chemical engineering (14.5%) and materials science (9.3%).

The first use of microwave treatment in chemistry was described in 1975 by Adu-Samra et al. [19] who used a microwave oven for laboratory analysis of trace amounts of metals in biological media. Since that time, the number of scientific publications devoted to the effects of microwaves and their use in chemistry has

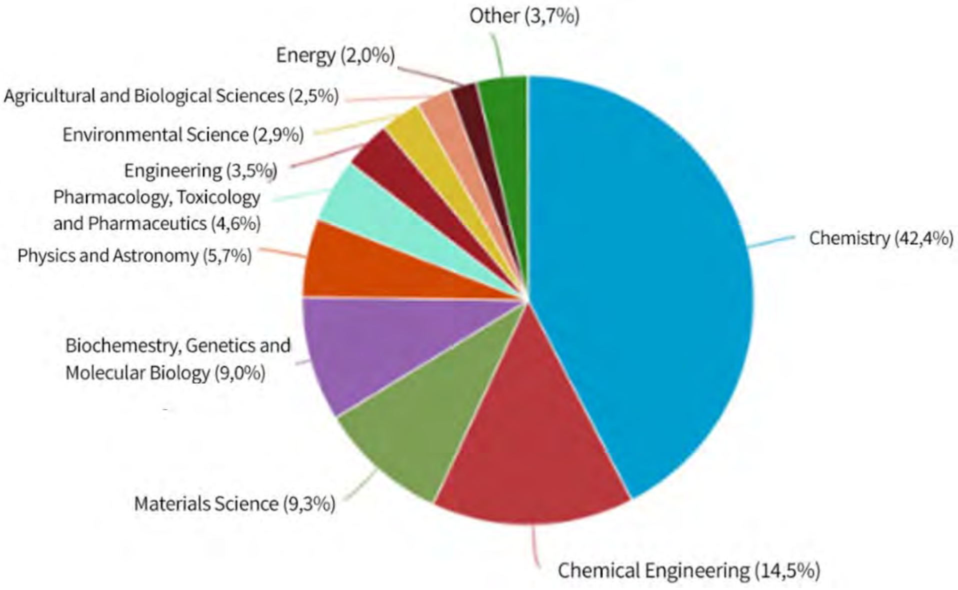

Figure 6 – Application of microwaves in various fields of science [18]

been increasing every year. Thus, according to the data of [18], there is a steady interest of researchers in the use of microwave radiation, which is confirmed by the number of publications presented on the histogram (figure 6).

At present, microwave radiation has found practical application in sample preparation [11, 20], for extraction [21-34], drying of plant objects [35], thermal

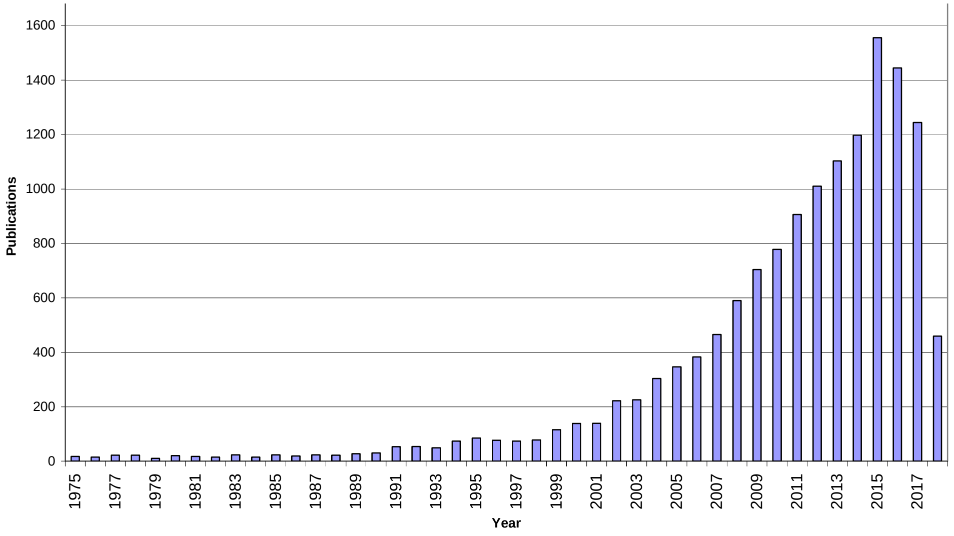

Figure 7 – Number of publications on use microwave radiation in chemistry [18]

decomposition of plant biomass [36], in particular hydrolysis of plant biomass for biofuel production (bioethanol), as well as for enzymatic [37] and acid hydrolysis [38,39], pyrolysis of wood [40], delignification, for example rice hull [41] and beech wood [42], and after the appearance of the first works on the use of microwave radiation in organic synthesis, which by appeared in 1986 [43,44], intensive studies of the influence of microwave treatment on the course of chemical reactions and chemical modification of plant raw materials began. Thus, the accumulated experimental material indicates the acceleration of many chemical reactions under the action of microwave treatment: elimination, esterification, cycloaddition, isomerization, condensation, substitution, hydrolysis, oxidation, etc. [10, 45-51]. The reaction conditions are extremely diverse, and the final effect depends on the nature of the process, the nature of the reacting particles, the type of solvent and the power of the microwave radiation.

Microwave radiation is used to dry food materials, as well as plant objects. Overview of the latest microwave technologies, including microwave drying, heating and sterilizing fruits (bananas, apples, olives, blueberries, kiwi, strawberries, etc.), vegetables (potatoes, onions, beans, pumpkin, eggplant, garlic, cabbage, tomato, cassava, lentils, chickpeas, broccoli, brussels sprouts, cauliflower, etc.), fish (sardine, carp, salmon, cod, etc.) and meat products (beef, etc.) are discussed in detail in [52, 53]. Data on the use of microwaves for drying grain of wheat after its treatment with aqueous solutions of disinfectants, protective equipment, etc. are described in [54], and the application of microwave radiation for wood drying is presented in [55].

Hydrolysis under the influence of microwave radiation was used to synthesize a number of organic derivatives [56, 57], was used for the cleavage of proteins in order to establish their amino acid composition [58, 59] and in the analysis of the composition of some natural compounds [59, 60]. Thus, the authors of the study [39] used acid hydrolysis to convert carbohydrates derived from biomass into sugars such as glucose, mannose and fructose, which are important universal products that are easily processed into biofuel. The highest yield of mannose (92.11%) was achieved under optimal conditions: 148 °C, 0.75 N H_2SO_4, time 10 min and substrate to solvent ratio (w/v) 1: 49.69.

Hydrolysis should take into account the fact that under severe conditions with the use of concentrated acids and increasing the temperature, the process will promote the cleavage of most of the hydrolysable bonds in organic compounds, which may affect the course of side processes and the destruction of the starting compounds.

The results of studies on the microwave oxidation of individual organic substances, such as amino acids, monosaccharides and stearic acid, whose structures are the basis of such natural compounds as proteins, carbohydrates and fats, are reported in Refs [61, 62].

As an example of chemical modification of plant raw materials, reviews [63, 64], which describe methods for modifying polysaccharides under the action of microwave irradiation, are given. In [65] the process of cellulose treatment with crosslinking reagents is presented, and the authors of the study [66] indicated the possibility of esterification of cellulose from marine herbaceous plants *Posidonia oceanica* with succinic, maleic and phthalic anhydride. The results of studies on carboxymethylation of cellulose under the influence of microwave treatment are summarized in the reviews [67, 68], the results on carboxymethylation of cotton stems are presented in [69], and in the article [70] - cassava starch.

Of particular interest are papers aimed at investigating the selective extraction of organic compounds by solvents under the action of microwave radiation [21-34]. To date, the microwave-assisted extraction (MAE) technique has been developed to extract soluble components from plant, ecological, biological, geological and metallic matrices. Simultaneously, technology and technology were developed with the creation of commercial reactors for laboratory microwave extraction technology both in closed reactors and in systems communicating with the atmosphere [30, 31, 71]. Thus, in [27], methods for extracting organic toxic substances are described, and the review [72] presents a material on the use of microwave radiation for the separation of polychlorinated biphenyls, pesticides, phenols, organometallic compounds and dioxins. Great prospects are associated with the use of microwave extraction in the chemistry of natural compounds to extract components of plant raw materials [29-34].

Acknowledgements. The work was supported by the Ministry of Education and Science of the Republic of Kazakhstan (№ BR05234667/PCF «Physico-chemical bases of creation of inorganic, organic, polymer compounds, systems and materials with the pre-set properties» and on the project «The search for new medicinal substances on the basis of available synthetic analogues of natural derivatives of anthraquinone» (IRN: AP05131788)).

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Резюме

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МИКРОТОЛҚЫНДАР СИПАТТАМАСЫ, СОНЫМЕН БІРГЕ МИКРОТОЛҚЫНДЫҚ ҚЫЗДЫРУ ТЕОРИЯЛАРЫНЫҢ КЕЙБІР АСПЕКТІЛЕРІ МЕН ОРГАНИКАЛЫҚ ХИМИЯДА ЖӘНЕ ТАБИҒИ ҚОСЫЛЫСТАР ХИМИЯСЫНДА МИКРОТОЛҚЫНДЫҚ СӘУЛЕЛЕНУДІҢ ҚОЛДАНЫЛУЫ

Өсімдік материалдарын кешенді өңдеу мәселесі мен биологиялық активті заттарды алудың жоғары эффективті әдістерін жасау химия ғылымын дамытудың басым бағыттарының ішіне кіреді. Осы процестерді жақсарту үшін маңызды жағдайы «жасыл химия» принциптерін сақтау болып табылады. Шолуда микротолқындар сипаттамалары, сонымен бірге микротолқындық қыздыру жылулық қыздыру ерекшеліктерімен салыстырмалы сараптамасы және еріткіштерге микротолқындардың кейбір әсер ету мәселелері қарастырылған. Микротолқындық сәулелендірудің органикалық химияда және табиғи қосылыстар химиясында микротолқындық сәулеленудің қолданылу аймақтары қарастырылған.

Түйін сөздер: микротолқындық сәулелендіру, микротолқындар.

Резюме

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ХАРАКТЕРИСТИКИ МИКРОВОЛН, А ТАКЖЕ НЕКОТОРЫЕ АСПЕКТЫ ТЕОРИИ МИКРОВОЛНОВОГО НАГРЕВА И ПРИМЕНЕНИЕ МИКРОВОЛНОВОГО ИЗЛУЧЕНИЯ В ОРГАНИЧЕСКОЙ ХИМИИ И ХИМИИ ПРИРОДНЫХ СОЕДИНЕНИЙ

Проблема комплексной переработки растительных материалов и создание высокоэффективных методов получения биологически активных веществ входят в число приоритетных направлений развития химической науки. Важным условием для улучшения этих процессов является соблюдение принципов «зеленой химии». В обзоре рассматриваются характеристики микроволн, а также теория микроволнового нагрева в сравнительном анализе с особенностями теплового нагрева и некоторые вопросы влияния микроволн на растворы. Рассмотрены области использования микроволнового излучения в органической химии и химии природных соединений.

Ключевые слова: микроволновое излучение, микроволны.