1 General Introduction to Microwave Chemistry

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1.1 Electromagnetic Waves and Dielectric Materials

The common characteristics of electromagnetic waves (light and radio waves) are that they (i) have no mass, (ii) are free to move at the speed of light, (iii) cannot collide with each other, (iv) possess significant energy, and (v) are reflected on a metal surface. By contrast, when microwaves (MWs) are used to irradiate dielectric materials, various phenomena occur according to the nature of the electromagnetic waves. The influence of electromagnetic waves on dielectric materials in various ranges of the electromagnetic spectrum is summarized in Figure 1.1 [1], which also shows the various analytical instruments and their usefulness in the ranges indicated.

Atomic species: If a dielectric is placed in an alternating electric field of the electromagnetic waves, the positions of the atomic nucleus (protons) and of the electrons that constitute the dielectric tend to follow the course of the electric field. The spatial relationship of a proton and an electron in an atom becomes distorted when subjected to the electric field (referred to as electronic polarization). Since the electric dipole that reflects the electric deviation (a proton and an electron) inside an atom is very small, a resonance phenomenon will occur with light of short wavelengths such as X-rays and ultraviolet rays.

Molecular species: The distortion of the electric charge by electromagnetic waves also occurs in a molecule with an electric dipole moment and in a salt. For example, in the structure of NaCl salt, composed of Na\(^+\) and Cl\(^-\) ions, distortion of the structure arises when subjected to an alternating electric field (referred to as ionic polarization). An electric dipole moment of a molecule is large compared with that of an atom, so that resonance occurs in the infrared domain, that is, at the longer wavelengths. The magnitude of ionic polarization is dictated by the interionic distance and the types of ions involved. Moreover, changes in bond lengths in an organic molecule occur through stretching and bending vibrations. These
The resonance phenomenon of a dielectric

<table>
<thead>
<tr>
<th>Wave length (m)</th>
<th>Frequency (Hz)</th>
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<td>$3 \times 10^{18}$</td>
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</tr>
<tr>
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<td>$3 \times 10^{12}$</td>
</tr>
<tr>
<td>$3 \times 10^{10}$</td>
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<tr>
<td>$10^{-10}$</td>
<td>$10^{-12}$</td>
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**Figure 1.1** Resonance of dielectric to electromagnetic waves and positioning of the analytical equipment. Reproduced from Ref. [1] Copyright 2013 by Wiley-VCH Verlag GmbH.

phenomena occur at various wavelength regions absorbed, depending on the chemical structure; they can be observed by means of an infrared absorption spectrophotometer.

**Molecular assemblies:** Orientation polarization of a dielectric possessing an electric dipole takes place on interaction with the electromagnetic waves in the microwave range. Moreover, as for the case of ions in a solution, Joule heating takes place by space-charge polarization. For example, when microwave heating an electrolyte/water solution, dielectric heating and Joule heating occur simultaneously compared with pure water; and thus the exothermic efficiency becomes remarkably high. Accordingly, dielectric heating by orientation polarization of water and resistance heating by the Joule process are enhanced in electrolyte/water media.

### 1.2 Microwave Heating

Microwave radiation is electromagnetic radiation spanning the frequency range 30 GHz – 300 MHz (i.e., from a wavelength of 1 m to 1 cm). It is used widely in communications and in heating processes, especially in the heating of foodstuff. Historically, the powerful interaction of microwaves with materials was discovered in 1946 from the melting of chocolate, a process attributed to
microwave heating, whereas the first commercial microwave oven was developed in 1952 by the Raytheon Company [2]. This discovery is frequently taken up as an example of serendipity. Before the discovery of microwaves, high-frequency induction heating was commonly used. The patent of dielectric heating by means of high-frequency induction was issued in 1933 [3]. In the 1970s, the microwave generator was re-engineered by Japanese scientists into a domestic microwave oven (using a simple, reliable, and inexpensive magnetron), which allowed for simple food and mass processing [4]. Domestic and industrial microwave ovens generally operate at a frequency of 2.45 GHz corresponding to a wavelength of 12.24 cm and an energy of $1.02 \times 10^{-5}$ eV, or around 900 MHz with a longer wavelength of 37.2 cm, which can provide up to 100 kW in larger process heating applications [5]. Since then, microwave chemistry has become a rapidly developing branch in numerous fields of research, in industry, and in its applications.

A molecule is formed when atoms combine to share one or more of their electrons. This rearrangement of electrons may cause an imbalance in charge distribution, thereby creating a permanent electric dipole moment. These moments are oriented in a random manner in the absence of an electric field so that no polarization exists. Electric dipole moments in a polar molecule undergo group movement so that a mutual electric dipole may be left without. When a microwave is applied to this state, an electric field has an influence on the electric dipole (Figure 1.2). The microwaves’ electric field ($E$ field) will exercise a torque ($N$) on the electric dipole, and the dipole will consequently rotate to align itself with the electric field thus causing orientation polarization to occur [6]. If the field changes direction, the torque will also change. The orientation polarization changes by a vibration in a microwave electric field. A time difference is caused between the frequency of the microwave electric field and the electric dipole of molecules. At the general frequency of 2.45 GHz, the microwaves vibrate 2 450 000 000 times/s; a molecular cluster cannot follow this vibration through the power chain with the surrounding molecules. This delay changes to heat energy (kinetic energy) as loss of the electromagnetic wave energy. The friction accompanying the orientation of the dipole will contribute to dielectric losses. The dipole rotation causes a variation in both $\varepsilon_r'$ (the relative dielectric constant) and $\varepsilon_r''$ (the relative dielectric loss) at the relaxation frequency, which usually occurs in the microwave region. Water is an example of a substance that exhibits a strong orientation polarization.

![Figure 1.2 Image of dipole rotation for polar molecule in an electric field ($E$ field).](image-url)
By contrast, a solid substance with a partial electric charge (a dielectric material) is also an insulator. The slight distortion of the atomic position (lattice point) in a structure lattice, and the lattice strain of a crystal of solid substances cannot follow the changing time of the microwave electric field. Microwave heating of a solid substance progresses by these phenomena [7]. On the other hand, the heating of solid substances with a magnetic dipole moment occurs by the microwaves’ magnetic field component. The heating process is the same phenomenon as by the microwaves’ electric field [8]. Generation of heat by magnetic loss heating is expected only in magnetic (solid) materials. Joule heating progresses by the interaction of an electric or a magnetic field with solid particles of activated carbon and with solids possessing conductivity-like metallic properties [9].

1.3 The Various Types of Microwave Heating Phenomena

Polarization phenomena are generated regardless of the polar or nonpolar nature of the molecules. On the other hand, alignment polarization (molecular alignment) occurs only when the polarity of molecules is affected by the electric field because of their permanent dipoles. Thus, the role of microwaves (and radio waves) is not simply as a heating source. With regard to the latter, we must recognize three types of heating phenomena caused by microwaves: (i) conduction loss heating, (ii) dielectric heating, and (iii) magnetic loss heating. In this regard, the thermal energy $P$ produced per unit volume originating from microwave radiation is given by Eq. (1.1) [10]:

$$P = \frac{1}{2} \sigma |E|^2 + \pi f \varepsilon_0 \varepsilon_r'' |E|^2 + \pi f \mu_0 \mu_r'' |H|^2$$

(1.1)

where $|E|$ and $|H|$ denote the strength of the microwaves’ electric and magnetic fields, respectively; $\sigma$ is the electrical conductivity; $f$ is the frequency of the microwaves; $\varepsilon_0$ is the permittivity in vacuum; $\varepsilon_r''$ is the relative dielectric loss factor; $\mu_0$ is the magnetic permeability in vacuum; and $\mu_r''$ is the relative magnetic loss.

The first term in Eq. (1.1) expresses conduction loss heating; the second term denotes dielectric loss heating, whereas magnetic loss heating is given by the third term. Microwave heating of solutions is governed mostly by dielectric loss heating, whereas conduction loss heating involves mostly, but not exclusively (see later), solid materials. Therefore, microwave heating of materials is dictated by the electrical, dielectric, and magnetic properties. Moreover, when a change of frequency occurs, their behavior also changes. It is possible to design catalyzed reactions based on these properties and build innovative microwave chemistry processes. A catalyzed reaction occurring on a solid catalyst is expected to show characteristic differences relative to the solution bulk because the reacting substrates in the liquid medium may be adsorbed onto the solid’s surface. Temperature rise in
systems involving solely gaseous molecules is negligible because the molecular density is rather small.

1.3.1 Conduction Loss Heating (Eddy Current Loss and Joule Loss)

The hydroxide ion is a typical ionic species with both ionic and dipolar characteristics. The conductive loss effect can become larger than dipolar relaxation in solutions that contain large quantities of ionic salts. Conduction losses tend to be less at ambient temperatures in the case of solids but can change substantially with an increase in temperature. A typical example is alumina (Al₂O₃) whose dielectric losses are negligibly small (≈10⁻³) at ambient temperature, but can reach fusion levels in very short times (minutes) in a microwave cavity. This effect originates from a strong increase in conduction losses associated with the thermal activation of electrons, which migrate from the oxygen’s 2p valence band to the aluminum’s 3s, 3p conduction band. Moreover, conduction losses in solids are usually enhanced by defects in materials. These sharply reduce the energy needed to generate electrons and holes in the conduction and valence bands, respectively. In the particular case of carbon black powder, conduction losses are rather high, so much so that this material is often used as an impurity additive to induce losses within solids whose dielectric losses are too small.

1.3.2 Dielectric Heating

Nonconductive materials can be heated by the microwaves’ electric field through molecular rotation of the molecules’ electric dipoles, with the latter aligning themselves with the field. As the field alternates, the molecular dipoles reverse direction (vectorially) and accelerate the motion of individual molecules or atoms, thereby generating heat through friction of the molecules as they rotate against each other. Dielectric heating can therefore be applied to the heating of solutions. By contrast, heating of electroconductive solids, such as metals, implicates ohmic losses in the material in virtue of the current flow induced by the oscillating electric field.

The dipolar polarization mechanism only concerns polar compounds, for example, water, methanol, ethanol, which possess a permanent dipole moment [4]. With regard to the frequency of the applied electric field, the dipoles can behave threefold: (i) at low frequencies, the dipoles keep in phase with the electric field and the temperature of the irradiated medium hardly rises; (ii) at high frequencies, the response time of the dipoles is too long to follow very rapid oscillations of the electric field and no energy is absorbed; and (iii) at the microwave frequencies, the dipole rotation lags behind the changes of the electric field and results in the heating of the irradiated material.

Dipolar polarization, \( P_d \), occurs on a timescale of the order of those associated with microwaves. Hence, when a dielectric is subjected to an external electric field
of strength $E$, the polarization is related to the intrinsic properties of the material through the relation expressed by Eq. (1.2) [11]:

$$ P_d = \varepsilon_0 (\varepsilon_r - 1) E $$

(1.2)

where $\varepsilon_0$ is the permittivity in free space and $\varepsilon_r$ is the relative permittivity of the material. Given that in reality the permittivity is a complex quantity, $\varepsilon^* \text{ (equal to the product } \varepsilon \cdot \varepsilon_r \text{ and expressed as } \varepsilon^* = \varepsilon' + i\varepsilon'')$ [12], then the loss tangent ($\tan \delta$) is commonly used to describe the interaction of a dielectric with the microwaves. The ability of a material to convert microwave energy to thermal energy ($\tan \delta$) depends on the dielectric properties of the material and is defined by Eq. (1.3):

$$ \tan \delta = \frac{\varepsilon_r''}{\varepsilon_r'} $$

(1.3)

Dielectric parameters of common organic substances typically used in industry have been determined at various temperatures at 10°C intervals using a conventional plate heater. The temperatures of the solutions were measured with an optical fiber thermometer. The temperature-dependent $\tan \delta$ of these substrates at 20, 50, and 90°C are summarized in Table 1.1.

1.3.3 Magnetic Loss Heating (Eddy Current Loss and Hysteresis Loss Heating)

In metal oxides such as ferrites and other magnetic materials, magnetic losses occur in the microwave region. These losses are different from hysteresis or Eddy current losses because they are induced by domain wall and electron spin resonance (ESR). Such materials are typically placed at positions of magnetic field maxima for optimal absorption of the microwave energy. Transition metal oxides (e.g., iron, nickel, and cobalt oxides) possess high magnetic losses and can thus be used as added loss impurities or additives to induce losses within those solids for which dielectric loss is too small. For instance, induction heating by the microwaves’ magnetic field is expected to occur in catalyzed reactions involving solids, an example being the rapid induction heating of magnetite ($\text{Fe}_3\text{O}_4$) but not hematite ($\text{Fe}_2\text{O}_3$) as the latter is not a magnetic material [13].

1.3.4 Penetration Depth of Microwaves

Even though the dielectric loss of a solvent may be high, the heating efficiency is sometimes low. This may be caused by the shallow penetration depth of the microwaves. For example, though solar light is absorbed by sea water, it is nonetheless dark at greater depths. A similar phenomenon occurs with microwaves in that as the microwave energy is changed into heat it decreases. Therefore, if a large size reactor is used, the microwaves may not heat the center of the solution. The penetration depth $D_p$ (in cgs units) is the depth at which microwaves pervade into the material and the power flux has fallen to
### Table 1.1 Temperature-dependent dielectric loss factor ($\tan \delta$) of common organic substances at temperatures of 20, 50, and 80 °C.

<table>
<thead>
<tr>
<th>Organic substance</th>
<th>$\tan \delta$ at 20 °C</th>
<th>Organic substance</th>
<th>$\tan \delta$ at 50 °C</th>
<th>Organic substance</th>
<th>$\tan \delta$ at 80 °C</th>
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<tbody>
<tr>
<td>Ethylene glycol</td>
<td>1.0137</td>
<td>1-Propanol</td>
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<td>1-Butanol</td>
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<td>0.8130</td>
<td>1-Pentanol</td>
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<td>0.7089</td>
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<td>$\alpha$-Methyl phenol</td>
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<td>Tetrahydroxyfururyl alcohol</td>
<td>0.3350</td>
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<td>$p$-Methyl phenol</td>
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(continued overleaf)
Table 1.1  (Continued)

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<th>Organic substance</th>
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<th>Organic substance</th>
<th>tan δ at 50 °C</th>
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<td>0</td>
<td>Dichloromethane</td>
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<tr>
<td>Triethylamine</td>
<td>0</td>
<td>Monopropylamine</td>
<td>Over b.p.</td>
<td>n-Hexane</td>
<td>Over b.p.</td>
</tr>
</tbody>
</table>
1.4 Fields of Applications with Microwave Heating

$1/e (=36.8\%)$ of its surface value. That is, it denotes the depth at which the power density of the microwaves is reduced to $1/e$ of its initial value; $D_p$ can be estimated by Eq. (1.4) [7]:

$$D_p = \frac{\lambda}{4\pi} \left[ \frac{2}{\varepsilon' \left( \sqrt{1 + \left( \varepsilon''/\varepsilon' \right)^2} - 1 \right)} \right]^{1/2}$$

where $\lambda$ is the wavelength of the radiation, $\lambda_{(2.45\text{GHz})} = 12.24\text{ cm}$. Since the dielectric constant and the dielectric loss are components of this equation, we can expect that the penetration depth will change with an increase in temperature. For example, since the penetration depth at $25\,^\circ\text{C}$ is about $1.8\text{ cm}$ for water, even if we used a reactor $10\text{ cm}$ in diameter, the microwaves will not reach the center of the reactor. However, at $50\,^\circ\text{C}$, the penetration depth is $3.1\text{ cm}$, and at $90\,^\circ\text{C}$ it is $5.4\text{ cm}$ so that now the microwaves do reach the center of the water sample [14]. The penetration depth of the microwaves into almost all nonpolar solvents is very deep compared with polar solvents. On the other hand, if ions are added to water, the penetration depth then becomes remarkably shallow. For example, when NaCl ($0.25\text{ M}$) is added to pure water, the penetration depth into this saline solution changes from $1.8\text{ cm}$ (pure water) to $0.5\text{ cm}$ at ambient temperature [15]. Moreover, even if this electrolyte/water system was to be heated, the penetration depth would hardly change ($0.4\text{ cm}$ at $90\,^\circ\text{C}$). Therefore, in the case of solutions containing ions, since microwave heating does not occur, temperature hot spots will occur only at the surface of the reactor and it will be necessary to carry out vigorous stirring to control these. Hence, it is necessary to examine the heating efficiency and the penetration depth of microwaves into a substance to achieve optimal microwave heating.

1.4 Fields of Applications with Microwave Heating

To the extent that microwaves are electromagnetic waves, they move at the speed of light. Since a sample is directly heated by microwaves, the time of heat conduction is shortened considerably relative to conventional heating, and this regardless of however complex the reactor design might be because reactor design has no influence on reaction times. Accordingly, microwaves have become an important heat source in a wide set of applications superseding the more traditional thermal methods. Microwave energy has been widely developed and applied to almost every field of chemistry. Figure 1.3 summarizes some of the applications where microwaves have become a common source of thermal energy, for example, in such fields as attenuation of environmental pollution, in the medical field, in printing, in paints, in foodstuff, in the fabrication of thin films, in agriculture, and in the drying of wood [16].
Microwave heating in application

Environmental
- Sintering of asbestos
- Decomposition of dioxin and PCB
- Oil recovery from plastics
- Process treatment of waste oil
- Processing of medical wastes
- Processing of radioactive contaminated substances
- Degradation of chlorofluorocarbons
- Decomposition of VOCs
- Exhaust gas treatment
- Incineration of garbage
- Electrodeless lamps
- Biomass
  - Oxidization of soot
  - Enhancement of activity of photocatalysts
  - Recycling of scrap tires
  - Solidification of waste plastics

Medical uses
- Hyperthermia
- Sterilization
- Muscular warming
- Cutting of blood vessels

Usage for foodstuffs
- Sterilization
- Processing
- Defrosting
- High-speed cooking
- Reduced-pressure drying
- Activation of enzyme and yeast

Ink and paint
- Drying of printing ink
- Drying of paints

Films and paper
- Dryness of book cover
- Selective heating of pastes
- Sintering of electronic wiring
- Film curating

Agriculture
- Sterilization of soil
- Drying of wood
- Extermination of noxious insects in wood
- Extraction and degradation of contaminants

Usage in Wood treatments
- Adhesion processing
- Bending
- Drying of wood

Figure 1.3 Fields of applications with microwave heating. Reproduced from Ref. [16]. Copyright 2013 by Wiley-VCH Verlag GmbH.
Not least, microwaves have also been used for other purposes such as when used as a plasma source in the treatment of semiconductor surfaces or in the fabrication of industrial diamonds. Moreover, ESR spectroscopy used in chemistry makes use of 9 GHz microwaves. Also, the microwave radiation used in military communications has found a domestic niche in the widely used microwave ovens. The technology has developed into various other fields, one of which that is relevant here is in microwave chemistry, an area that has witnessed unparalleled growth in the last decade. The applications of microwaves in the chemical field are also summarized in Figure 1.3, the major ones being organic chemistry, analytical chemistry, biochemistry, polymer chemistry, catalysis, photochemistry, and inorganic chemistry of materials.

1.5 Microwaves in Solid Material Processing

A study carried out on the calcination and sintering of ceramics by microwaves was reported as early as 1972 [17]. Fundamental and application studies soon followed around 1980. The early industrial use of microwaves as a heat source was to remove water from inorganic materials. It was soon discovered [18], however, that ceramics could also be heated with microwaves (latter half of the 1970s), which led to the effective sintering of ceramic powders. The conventional heating methods for such tasks are heat conduction and radiation heating. With regard to microwave irradiation, the sample itself generates heat. Therefore, a sintered compact product is obtained at low temperature for a short time.

A symposium held at a conference on materials science by the Materials Research Society (MRS) revealed that materials processing by microwaves was a topic that drew a great deal of interest [19]. Indications from the conference also showed that microwaves could be used not only to determine the quantity of water in ceramics but also as a technique to detect and analyze formation of fissures in ceramics and metals [19]. The basic interactions between the microwaves and materials were also widely discussed. Various kinds of ceramics have been treated by the microwave method [20]. In recent years, the calcination of special ceramics with a specific microwave method has also been reported [21].

Since the 1990s, several reactions have been carried out in the presence of solid catalysts for a potential application of microwave radiation in materials synthesis: for example, the synthesis of acetylene by oxidization of methane using particulate metal catalysts [22]. In contrast to microwave heating, when a conventional heating method was used, catalyst activity stopped when the reaction was only about 25% complete, whereas with microwave heating the reaction proceeded to about 90% completion. Research into the dechlorination of chlorinated substrates with heterogeneous metal catalysts was also examined in the initial stages (1990s) of utilization of microwave radiation. The influence of both the microwave frequency and pulsed microwave irradiation was considered; optimal reaction conditions were determined in the presence of a solid catalyst [23]. Of particular
interest were catalysts that absorbed microwave radiation, and not least was the notion of differential heating in the quality of a reaction group that involved formation of hot spots on the catalyst surface. Accordingly, the next section examines selective heating of a heterogeneous catalyst (metallic or organic catalyst) by the microwaves.

1.6 Microwaves in Organic Syntheses

Two pioneering papers that made use of microwaves in organic synthesis were published nearly three decades ago in 1986. Gedye and coworkers [24] carried out organic syntheses using a Teflon reactor and a commercial/domestic microwave oven; this resulted in a remarkable decrease in reaction time compared to conventional heating methods. Giguere and coworkers [25] pointed out that reactor, solvent, and temperature management were important factors in microwave-assisted organic syntheses. Research into such application of microwaves increased but slowly and gradually. By contrast, the number of publications in microwave chemistry has increased dramatically since 2000 [26], due in large part to the availability of commercial microwave devices intended for organic synthesis that led many chemists to convert from the traditional microwave oven to these newly fabricated devices. Safety, reproducibility, control of microwave output power, temperature, and pressure were some of the important and attractive features of such devices. Currently, microwave organic synthesis systems have become fully automated by combining with robot technology. Such systems are playing an active part in such fields as combinatorial chemistry. This has also led research of microwave chemistry from the academic laboratory level to the industrial level where microwaves are being used as a heating tool in organic syntheses.

The biggest attraction of microwaves in this field is the dramatic enhancement of reaction rates. An example is the Suzuki–Miyaura crossing coupling reaction, which when performed with microwaves occurs in a reaction time of about 50 s, whereas when using the traditional heating methods the reaction times are of several hours [27]. Similar findings have been reported in various other organic reactions. Several synthetic examples of solvent-free and noncatalytic reactions have also been reported. Not surprisingly then, the use of microwaves in chemical syntheses is particularly attractive in the field of Green Chemistry. Many excellent books are now available that describe some of the details of microwave-assisted organic syntheses [28].

1.7 Microwave Chemical Equipment

The inner intricacies in commercial microwave chemical equipment cannot be judged by looking at the steel case. The equipment consists of various parts to apply microwave radiation to a sample. The various parts included in microwave
chemical equipment are explained below. An applicator is needed to apply microwaves to a sample either in single-mode (mono-mode) operation or in multi-mode operation. In single-mode operation, the sample is placed at the maximum location of the standing wave. The resonance of the microwaves in the single-mode applicator can be adjusted with the iris and the plunger. Heating of the sample solution in a reactor can be achieved in the single-mode microwave apparatus of Figure 1.4a either at positions of maximal electric field ($E$ field; position (i)) density or at the maximal magnetic field ($H$ field; position (ii)) density within the waveguide. It is not possible to change the strength of the electric field and the magnetic field under multi-mode operation. On the other hand, the sample size is subject to restrictions. One of the advantageous features of the multi-mode applicator is that it can irradiate large samples. To apply microwaves uniformly, a stirrer and/or a turntable are used. Therefore, the heating efficiency of a sample is lower than under single-mode operation. The multi-mode applicator is used in a domestic microwave oven.

The composition of a simple microwave chemical equipment consists of an applicator connected to the microwave generator (magnetron, power source, and control unit) by a waveguide. Low-cost microwave commercial ovens consist of the same components. On the other hand, when performing highly precise experiments, it is possible to add additional parts to the equipment. For example, the parts used in a microwave chemical reactor of a single-mode system are displayed in the schematic of Figure 1.4a, whereas the actual system is pictured in Figure 1.4b. An iris, a three-stub tuner, a power monitor, and an isolator are connected between the microwave generator and the single-mode applicator. A short plunger is also connected to the single-mode applicator. The impedance between the equipment and the sample can be adjusted with the short plunger and the three-stub tuner. The higher efficient microwave radiation can be applied to a sample with impedance matching. On the other hand, an isolator is used to

![Figure 1.4](image.png)

**Figure 1.4** (a) Details of the experimental setup and positioning of the samples in the single-mode microwave resonator; (i) maximal position of the electric field ($E$ field) density and (ii) maximal position of the magnetic field ($H$ field) density. (b) Photograph of the single-mode microwave resonator and the 2.45 GHz semiconductor microwave generator.
General Introduction to Microwave Chemistry

protect the equipment from absorbing the reflection wave. The power monitor is used to monitor the incident wave and the reflection wave.

A waveguide is a tube made of metal. An optical fiber is a useful tool currently used to transmit light to its destination. On the other hand, in the domain of microwaves, the waveguide consisting of a metal tube is used to transmit the microwaves. The cross-sectional size of the waveguide tube (Figure 1.5) changes according to the frequency (wavelength) of the microwave radiation generated by the magnetron or by the semiconductor generator [14].

A magnetron generator is generally used in commercial microwave organic synthesis apparatuses, regardless of whether it operates in the single-mode or the multi-mode method. Since high reproducibility has been achieved in recent years in single-mode apparatuses, organic syntheses carried out using single-mode equipment have attracted much attention. As a follow-up on this, a semiconductor generator began to be used in order to obtain high resonance inside the single-mode applicator. However, a disadvantage of the semiconductor generator has been the price and the maximum power available. Nonetheless, semiconductor generators with maximum power of 500 W and with highly accurate microwave frequencies have recently become available at a price similar to the costs of magnetrons. A further spread in the use of semiconductor microwave generators should reduce the price even further. The performance of the electrical appliance was improved remarkably by switching to a transistor semiconductor from a vacuum tube. The spread of small cellular phones depends on the development of a microwave semiconductor oscillator. This course is also having an influence on microwave chemical equipment. The features of the semiconductor and magnetron generators are described later.

The frequency distribution of the microwave radiation from the magnetron generator in microwave cooking ovens is reported in Figure 1.6a, which shows that the frequency of the microwaves is distributed over a large frequency range from 2.25 GHz to 2.45 GHz.
Figure 1.6 Frequency spectral distribution of the 2.45 GHz microwave radiation emitted from the (a) magnetron generator and (b) the semiconductor generator. Reproduced from Ref. [29]. Copyright 2011 by the American Chemical Society.

to 2.60 GHz [29]. The distribution of the microwave frequency changes depending on the characteristics of the microwave generator equipment. Note that narrower frequency waves can be generated with a magnetron of high accuracy. By contrast, the semiconductor generator produces microwaves only within a very narrow frequency range of 2.4500 ± 0.0025 GHz (Figure 1.6b). In the case of the magnetron generator, the microwave input power distribution reflects the widely dispersed frequency distribution. Therefore, the output of the actual 2.45 GHz microwaves is smaller than the input power. On the other hand, when using a semiconductor microwave generator, the heating can progress efficiently because the microwave input power is concentrated at the 2.45000 GHz frequency. The microwaves can resonate better in a single-mode apparatus.

More importantly, a different advantage of a semiconductor microwave generator is the compact size of the equipment. For example, the power supply of the magnetron necessary for a 1-kW input power weighs 6 Kg, whereas the
power supply of the semiconductor generator necessary for a 1-kW input power weighs only 0.5 Kg. A photograph of a magnetron generator and a semiconductor generator is displayed in Figure 1.7. Clearly, the semiconductor transmitter is smaller. Microwaves from a semiconductor generator are distributed through a coaxial cable, not a waveguide. Therefore, a flexible coaxial cable can be used for connecting a chemical reactor to a semiconductor generator. It is also possible to install a semiconductor generator in a small available space. Also important, the lifetime of a semiconductor generator is very long (20 years) compared to a magnetron generator (about 500–1000 hrs). For the input, microwave radiation of hundreds of watts is generally sufficient in many organic syntheses carried out at the laboratory scale.

The semiconductor generator can reproduce similar temperature rise conditions in a liquid sample compared with the magnetron generator using remarkably lower microwave input power. Moreover, the semiconductor generator is an optimal microwave emitter in frequency-dependent reactions (processes) because the frequency can easily be set in the semiconductor generator. A demonstration model using these advantages is displayed in Figure 1.8 that shows the inner chamber of a commercial microwave cooking oven equipped with two GaN semiconductor generators (maximum power, 250 W). Each semiconductor generator is connected to directional antennas inside the oven (top and bottom positions). The microwave radiation from the semiconductor transmitter consists of a wave of regular frequency, and so it is possible to synthesize by the phase control of the microwaves emitted from the two antennas depicted in the oven. Accordingly, selective heating of food can easily be achieved in such microwave cooking ovens. For instance, if two different foodstuffs are placed on a dish (meat and potatoes), it is possible to selectively heat only the desired foodstuff (e.g., meat). Moreover, even though the two foodstuffs may have different dielectric

![Figure 1.8](image-url)
1.8 Chemical Reactions Using the Characteristics of Microwave Heating

Materials synthesis possessing nanoscale mesoscopic structures, for example, SnO$_2$/TiO$_2$, using SnO$_2$ (high microwave heating efficiency) and TiO$_2$ (low microwave heating efficiency) has been reported by Takizawa and coworkers [30] using microwave selective heating (Figure 1.9). Such heating by the microwaves produces a supersaturated solid solution, after which the nanoscale mesoscopic structures are generated in the microphase.

When titanium metal is heated under an air atmosphere, TiO$_2$ is formed by oxidation, whereas titanium nitride (TiN) is generally prepared by a sputtering method, which is expensive and requires equipment of a complicated organization and not least coating of an uneven sample presents some difficulties. On the other hand, when microwave heating is used, it is possible to synthesize TiN easily from a titanium metal substrate under air conditions at 800°C for 10 min (Figure 1.10) [31]. TiN possesses excellent wear resistance, corrosion resistance, and thermal conductivities. Mechanistic details of the preparation of TiN have not been elucidated.

Microwave calcination equipment for the fabrication of nanometallic inks is displayed in Figure 1.11a. The lower melting point of the metal nanoparticles compared with bulk metal makes the former useful in new electronic wiring, among other applications. Since differential heating can be carried out in the atmosphere...
under microwave irradiation, such plastics as polyethylene terephthalate (PET) can form the base of the electronic wiring. When the pattern on the plate is written with a paste of either silver or gold, sparks will result if microwave irradiation was to be carried out in a regular microwave oven. However, a significant advantage of the microwaves’ magnetic field heating is that no sparks occur when heating the metal nanoparticles. Low-temperature calcination of an indium tin oxide (ITO) film or a ZnO film, and recovery of a rare earth (among others) are possible with such a methodology.

An additional advantage of the microwaves’ magnetic field heating method is on the coating of a PET plastic base to form Ag, Cu, and CuO nanoparticle ink (Figure 1.11b). Generally, oxidation of the surface of copper occurs when heated by a conventional heating method in an open atmosphere. However, with microwave magnetic field heating, even if heating was carried out in the presence of air, the copper surface is not oxidized because oxidation would drastically change the electrical properties of the ink. Clearly the microwave method that avoids formation of an oxide film is an effective methodology in such materials processing.

A relation between oxygen and the microwaves also seems appropriate in solution chemistry. To the extent that some reactions are oxygen sensitive, degassing of dissolved oxygen in water and in 2-propanol solvent was examined by microwave heating [32]. Degassing dissolved oxygen from a water sample is more efficient when the solution is exposed to microwave irradiation (heating) than when heated by conventional means (oil bath) under otherwise identical temperature conditions. The efficacy of the microwaves was greater at the lower frequency of 915 MHz than with the more commonly used frequency of 2.45 GHz as a result of the greater penetration depth of the 915 MHz microwaves into the reactor. Degassing was carried out by exposing the water sample to 2.45 GHz microwaves with the sample located within the waveguide at positions rich in either the electric field or magnetic field densities ($T = 80^\circ$C). Microwaves
were again more effective than conventional heating (38% vs. 30%) in degassing dissolved oxygen in 2-propanol solvent. Figure 1.12 illustrates a photograph of the reaction solutions degassed with argon purging the solution with a Pasteur pipette after heating for a 10-min period [32]. The initial light yellow solution (Figure 1.12a) changed to a brownish color after this time period with the color intensity differing according to the heating method used. The intensity of the brownish color increased in the order: 915 MHz (Figure 1.12b) < 2.45 GHz (Figure 1.12c) ≪ oil bath (Figure 1.12d). The solution heated with the oil bath displayed the most intense color change (Figure 1.12d), suggesting some oxidative decomposition of Wilkinson’s catalyst present in the synthesis of cyclohexanol from cyclohexanone in 2-propanol solvent. Similar observations of color change were made when the initial solution that had been purged with oxygen gas was heated. Evidently, degassing the oxygen-rich 2-propanol solution was slow compared to the inactivation of Wilkinson’s catalyst. With regard to the effects of microwave irradiation versus conventional heating on product yields in the conversion of cyclohexanone to cyclohexanol in 2-propanol media and in the presence of Wilkinson’s catalyst, ClRh(PH₃)₃, little difference was found in product yields irrespective of whether the reaction was activated by microwave irradiation or by conventional heating from an oil bath (81–86% after 10 min). However, argon purging the solution with a Pasteur pipette did reveal some changes in product yields: about 13% by conventional heating, 37% by 2.45 GHz microwaves, and 41% with 915 MHz microwaves also after 10 min. Wilkinson’s catalyst appeared more stable under microwave irradiation than under conventional heating.

Organic syntheses have been carried out using some of the features of microwave heating. The efficiency of microwave heating changes according to the dielectric loss of a substance. Organic syntheses that use this characteristic have been reported by Raner [33]. After commencement of microwave heating a two-phase water/chloroform system (1:1 by volume; 100 ml) for 40 s, the temperatures of the aqueous and organic phases were 105 and 48 °C, respectively, owing to differences in the dielectric properties of the solvents. A sizable
differential could be maintained for several minutes before cooling. Comparable
conditions would be difficult to obtain by traditional heating methods. Differential
heating is particularly advantageous in carrying out Hofmann elimination
reactions (Figure 1.13) [33]. A mixture of $N$-[2-(4′-ethoxybenzoyl)ethyl]-$N,N,N$-
trimethylammonium iodide, water, and chloroform was heated with stirring for
1 min at 110 °C (temperature of the aqueous phase). During the reaction, the
product 4′-ethoxyphenylvinyl ketone was extracted and diluted into the poorly
microwave-absorbing but cooler organic phase. The mixture was then subjected
to rapid post-reaction cooling; the ketonic monomer was obtained in 97% yield.
Selective heating can occur in a heterogeneous catalyzed reaction.

A study that considered microwave frequency effect has also been reported.
For example, the usefulness of the 5.8 GHz microwaves was demonstrated by car-
yrying out the organic solvent-free synthesis of 2-allylphenol through the Claisen
rearrangement process, as well as the synthesis of the $C_{12}$–$C_2$–$C_{12}$ Gemini surfa-
tant in ethanol solvent to demonstrate the usefulness of the 915 MHz microwave
frequency [15].

Microwave chemistry has been a subject that has generated much excitement
of late. Prompt and high-quality syntheses can be achieved using the microwave
technique. Some of the fundamental research in microwave radiation has been
developed by industry. The next stage will involve the improvement of efficient
chemical syntheses as might be required for possible industrial applications in the
preparation of significant quantities of high-value chemicals. For this to occur,
however, it will necessitate a combination of microwave chemistry with highly
coherent microwaves as established in the communication field. In this regard,
such coherence of electromagnetic waves is typically found in lasers. The ampli-
fication by interference of a highly coherent wave promises to enhance the effi-
ciency of microwave chemistry accompanied with high energy saving. However, it
is very difficult for a chemist to understand, let alone master microwave radiation.

![Figure 1.13](image)

Figure 1.13 Hofmann elimination reaction taking place by selective heating. Reproduced from Ref. [33]. Copyright 1995 by the American Chemical Society.
Properties of the sample (i), heating the sample (ii), and the electromagnetic waves (iii) must always be controlled. Various factors impact microwave chemistry. The interconnections between these factors are summarized in Figure 1.14 [34].

1.9 Microwave Frequency Effect in Chemical Syntheses

Microwaves are electromagnetic waves that span the frequency range 0.3–300 GHz so that there is no need to adhere to the commonly used 2.45 GHz frequency. When examining frequency effects, two barriers have obstructed the researcher’s curiosity. In the first, the microwave device that can generate different microwave frequencies have tended to be very expensive compared to devices that operate at the common frequency of 2.45 GHz. Recently, however, chemical reaction equipment that can generate different frequencies has become available at costs otherwise similar to those available at the 2.45 GHz frequency. The second barrier has been with the industrial, scientific, and medical (ISM) bands.
that have been reserved internationally for the use of radio frequencies employed for ISM purposes other than communications [35]. Examples of applications in these bands include radio frequency process heating, microwave heating source, and medical diathermy machines. The powerful emissions of these devices can create electromagnetic interference and disrupt radio communications that use the same frequency. Accordingly, these devices have been limited only to certain frequency bands. The ISM bands are defined by the International Telecommunication Union – radio communications sector (ITU-R). The globally used frequencies are 2.45, 5.8, and 24 GHz; other frequencies are established by each country (Table 1.2) [14].

For several years, the microwave (MW) frequency response and impact on chemical reactions have been examined in only but a few cases. Research reports regarding frequency effects in microwave-assisted organic syntheses have tended to be rather scarce. In the field of inorganic chemistry, Möller and Linn [36] used 5.8 GHz microwaves to calcine ceramics, and Takizawa and coworkers [37] utilized 28 GHz microwaves for the rapid synthesis of \((\text{In}_{0.67}\text{Fe}_{0.33})_2\text{O}_3\), whereas 5.5 GHz microwaves were used [38] in the rapid syntheses of cryptomelane-type manganese oxides for catalysis. In the field of organic chemistry, Gedye and Wei [39] used a variable-frequency microwave oven to effect the Knoevenagel reaction of acetophenone with ethyl cyanoacetate in the presence of piperidine (no solvent; microwave frequency, 8.1 GHz); with anisole as the solvent, the reaction was carried out at 12.2 GHz. Séguin and coworkers [40] reported a new IR reactor cell built with a microwave cavity operating at a frequency of 5.8 GHz; this equipment allowed efficient and time-resolved heating of the catalyst. The authors also showed that the 5.8 GHz microwave frequency is the optimal frequency for catalyst heating. Microwave-induced oligomerization of methane

<table>
<thead>
<tr>
<th>Frequency (GHz)</th>
<th>Tolerance level (GHz)</th>
<th>Area permitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.43392</td>
<td>0.43305–0.43479</td>
<td>Austria, Netherlands, Portugal, West Germany, Switzerland, Africa</td>
</tr>
<tr>
<td>0.896</td>
<td>0.886–0.906</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>0.915</td>
<td>0.902–0.928</td>
<td>North and South America</td>
</tr>
<tr>
<td>2.375</td>
<td>2.325–2.425</td>
<td>Albania, Bulgaria, Hungary, Romania</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Czechoslovakia, USSR</td>
</tr>
<tr>
<td>2.450</td>
<td>2.400–2.500</td>
<td>Worldwide except where 2375 MHz is used</td>
</tr>
<tr>
<td>3.390</td>
<td>3.1866–3.5934</td>
<td>The Netherlands</td>
</tr>
<tr>
<td>5.800</td>
<td>5.725–5.875</td>
<td>Worldwide</td>
</tr>
<tr>
<td>6.780</td>
<td>6.765–6.795</td>
<td>The Netherlands</td>
</tr>
<tr>
<td>24.125</td>
<td>24.000–24.250</td>
<td>Worldwide</td>
</tr>
</tbody>
</table>

a) Reproduced from Ref. [14]. Copyright 2012 by Wiley-VCH Verlag GmbH.
1.9 Microwave Frequency Effect in Chemical Syntheses

with nickel, iron, and activated carbon catalysts has been examined relative to microwave frequency and other parameters by Conde and Suib [41]. When frequency was increased, the activity of the catalysts was enhanced. Watanabe and coworkers have proposed microwave solvolysis as a pretreatment of wood biomass using 5.8 GHz microwaves [42].

Both the chemical structure of the substrates and the frequency of the microwave radiation have been shown to be important parameters in the synthesis of 3,6-diphenyl-4-n-butylpyridazine through a Diels–Alder process [43], in the syntheses of [bmim]BF₄ ionic liquid [44], in the synthesis of cyclohexanol with Wilkinson’s catalyst [32], in the synthesis of C₁₂–C₂–C₁₂ Gemini surfactant [15], in preparing 4-methylbiphenyl using the Suzuki–Miyaura coupling reaction [14], in nanoparticle synthesis [45], in photocatalytic wastewater treatments [46], and in the enzymatic proteolysis of a peptide [47]. Despite the preponderance of worldwide microwave ovens (including commercial systems used by research chemists) that operate at 2.45 GHz, the use of other microwave frequencies should not and must not be disregarded in furthering the development of microwave chemistry and the possible scale-up of microwave-assisted organic syntheses. For instance, using a single-mode applicator, microwaves at the 915 MHz frequency (wavelength: 32.79 cm) can permit irradiation of a reactor of larger size because of the inherent larger size of the waveguide (sectional area of the waveguides: 24.77 × 12.38 cm²) compared to the 2.45 GHz (wavelength: 12.24 cm) waveguide (sectional area of the waveguides: 10.92 × 5.46 cm²) [15]. Furthermore, heating large quantities of alcohols is remarkably effective at the lower frequency compared to the higher microwave frequencies, namely 915 MHz and 2.45 GHz.

At the industrial scale, it is well known that the extent of energy conversion (more than 80%) and the lifetime (more than 10,000 h) of a 915 MHz magnetron are two attractive features of this frequency than those of the 2.45 GHz magnetron (70% and 8000 h). Conditions for which 915 MHz was more suitable for making large-sized equipment have been met. On the other hand, heating a nonpolar solvent with 5.8 GHz microwaves is particularly effective owing to the higher densities of the electric and magnetic fields. The wavelength (sectional areas of the waveguides: 4.0 × 2.0 cm²) of the 5.8 GHz (wavelength: 7.46 cm) is most suitable for heating a small sample because it is short compared with 2.45 GHz (Figure 1.5). It is difficult from the point of view of controlling the temperature to heat a small quantity with microwaves [48]. The domestic multi-mode technique provides a field pattern with areas of high and low field strengths, such that the temperature of small samples (e.g., biological materials) can vary drastically between different positions of the samples, which could lead to formation of localized hot spots and cold spots. For example, the microwave apparatus proposed for enzymatic reactions at the microliter scale can achieve strict temperature control when using a 5.8 GHz microwave system [47] that incorporates a semiconductor generator. Therefore, power-saved microwaves (microwatt level) can stably irradiate small-scale biomaterial samples (Figure 1.15) [47].
Figure 1.15  (a) Details of the experimental setup and positioning of the samples in the single-mode 5.8 GHz microwave resonator; (i) maximal position of the electric field (E field) density and (ii) maximal position of the magnetic field (H field) density. (b) Photograph of the single-mode microwave resonator and the 5.8 GHz semiconductor microwave generator; the photograph also shows the actual position of the sample at the H field maximum. Reproduced from Ref. [47]. Copyright 2015 by Elsevier B.V.
1.10 Summary

The fields of microwave chemistry and material processing have grown immensely since the 1990s, and considerations from a physicochemical point of view are advancing the microwave effect. Studies of chemical processes using the features of microwave heating have also become popular. Choosing the optimal frequency of the microwaves for each situation can promote microwave chemistry further. Moreover, the use of several microwave frequencies could also prove beneficial to the chemical industry in microwave organic chemistry, as it may open up new applications of microwave-assisted organic syntheses, such as solvent-free reactions and supported reactions, as well as the preparation and reactions of inorganic solids, particularly where solvents cannot be heated by the most commonly used 2.45 GHz microwaves.

References


