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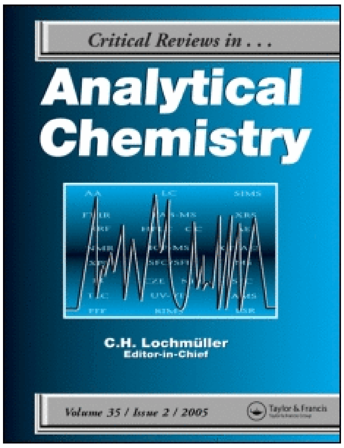

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

The Application of Microwave Radiation to Analytical and Environmental Chemistry

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To cite this Article Zlotorzynski, Andrzej(1995) 'The Application of Microwave Radiation to Analytical and Environmental Chemistry', Critical Reviews in Analytical Chemistry, 25: 1, 43 — 76

To link to this Article: DOI: 10.1080/10408349508050557

URL: http://dx.doi.org/10.1080/10408349508050557

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Critical Reviews in Analytical Chemistry, 25(1):43–76 (1995)

The Application of Microwave Radiation to Analytical and Environmental Chemistry

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ABSTRACT: This review presents the latest advances in the application of microwave energy to analytical chemistry. The fundamental principles of microwave field interaction with the matter are presented and their significance for the chemist is discussed, followed by the basic principles of microwave equipment construction and operation. Examples of the techniques that utilized microwave energy for digestion, extraction, chemical reaction, preconcentration, and desorption of the analytical sample are presented. A separate section describes the examples of usage of microwave technology in catalysis, environmental, and nuclear chemistry and engineering.

KEY WORDS: microwave energy, microwave chemistry, digestion, extraction, preconcentration, desorption, microwave catalysis, soil decontamination.

I. INTRODUCTION

In the past few years there has been a growing interest in the use of microwave heating in analytical and environmental chemistry. Microwave sample dissolution has been established as a standard method for preparation of samples for elemental analysis. Since the first article published by Samra et al.[1] in 1975, it has taken 10 years to spark the wider interest of the analytical chemistry community in the application of electromagnetic energy to sample preparation. The data presented in Figure 1 illustrate the remarkable growth of research on the application of microwave radiation as an energy source for sample digestion.

The heating effect of high-frequency fields on some materials was recognized even in the 19th century. Large-scale facilities using dielectric heating (up to 10^8 Hz) were in operation in the first decades of the twentieth century.[3] However, the first compact and simple microwave ovens were only available in the 1950s;[4] in view of its long history, the late acceptance of this technique in the chemical laboratory is surprising. The main reason for this is that the mechanism of energy transfer using a microwave field is very different from that of the three well-established modes of heat transfer, that is, conduction, radiation, and convection. The average prospective user of microwave equipment has little knowledge of microwave fundamentals and the properties of processed materials. The designers of the microwave equipment, electrical and telecommunication engineers, lack the understanding of the processes taking place in the course of chemical reactions or in analytical sample preparation. Improved communication between users and designers of microwave equipment should lead to big advances in the utilization of this electromagnetic energy in chemistry. The renowned Soviet physicist Kapitsa[5] wrote:

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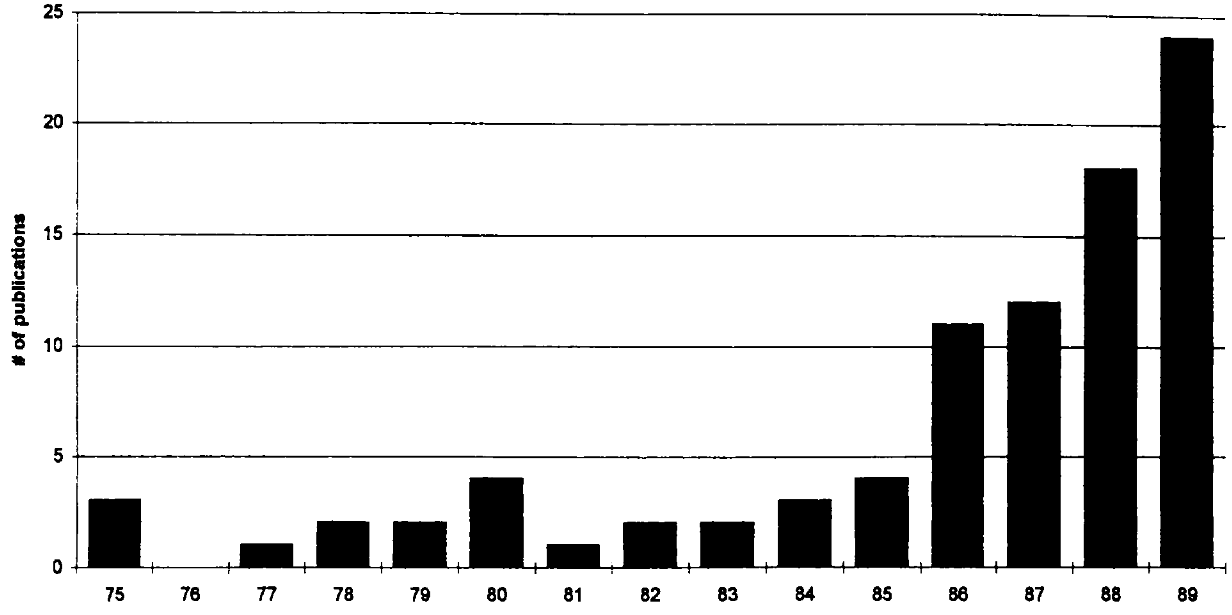


FIGURE 1. Annual literature citation (excluding conference abstracts) on microwave sample digestion. (From Reference 2. With permission.)

> It is worth noting that, before electrical engineering was pressed into service by power engineering, it was almost exclusively occupied with electrical communication problems (telegraphy, signaling, and so on). It is very probable that history will repeat itself. At present, electronics are used mainly in radio communication, but its future lies in solving major problems in power engineering.

The following sections deal with the interaction of microwaves with matter and with microwave equipment requirements for chemical laboratories. A review then follows of current publications dealing with the application of microwave energy to environmental and analytical chemistry.

II. MACROSCOPIC AND MOLECULAR PROPERTIES OF DIELECTRICS

In discussing electromagnetic waves and their interaction with matter we will suppose that a dielectric can be exposed to an electromagnetic field of any frequency by filling a capacitor or a coil with the matter in question and connecting it to an alternating voltage source. This Münchausen device requires a variety of equipment for its practical realization in order to cover the whole frequency range. The electromagnetic spectrum is shown in Figure 2.

A condenser or a coil is used for frequencies from 0 to 10^8 Hz (radio frequencies [RF]). In the microwave region from 10^8 to 10^{12} Hz (wavelength 1 m to 1 mm) the dimensions of the dielectric become comparable to those of the wavelength, and standing wave patterns can be measured in the materials. In the higher frequencies (infrared, visible, or UV light) we can measure- dielectric properties of materials by the measurement of light transmission and reflection. Finally, in the X-ray region the size of the atoms becomes comparable to the incident wavelength, and so the interference technique can be used to measure dielectric properties of the materials in this frequency range.

A. Complex Permittivity

A capacitor *in vacuo* connected to a sinusoidal voltage source acquires a charge Q, given by

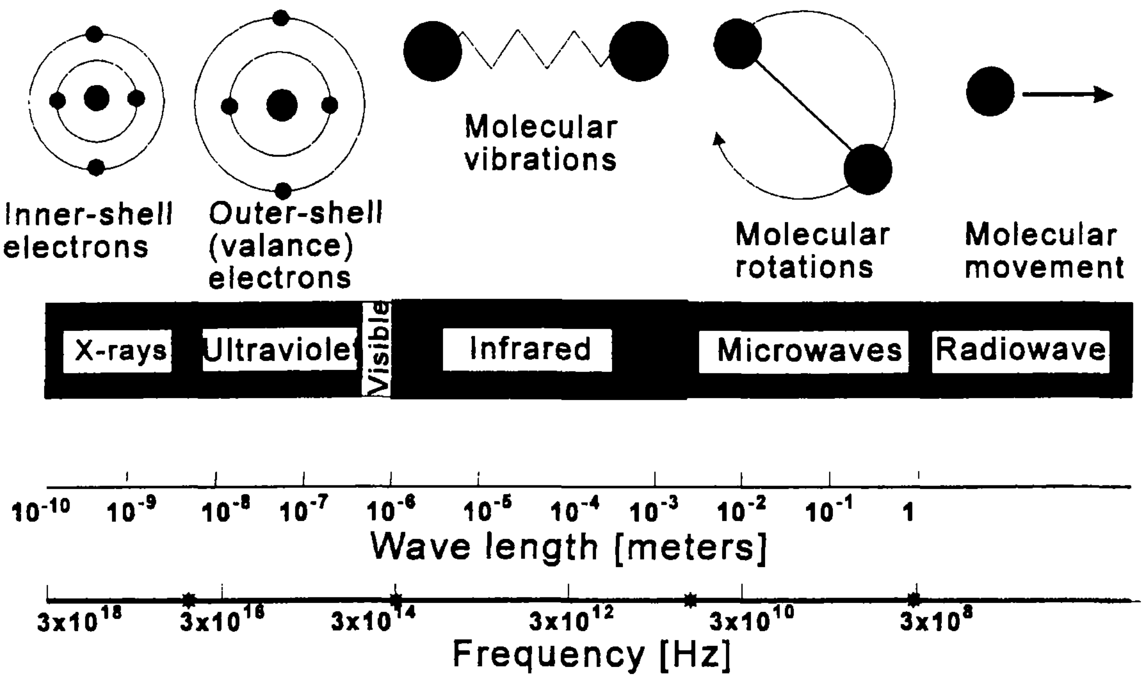


FIGURE 2. Electromagnetic spectrum.

$$Q = C_0V = C_0V_0 \sin \omega t$$

where C_0 is the capacitance of the condenser with a vacuum between the plates, V_0, V are a maximum and at a given time t potential differences between the plates, and ω is a radial frequency 2πf.

This condenser draws a charging current I_c, given by

$$I_c = \frac{dQ}{dt} = I_0 \cos \omega t$$

The current is out of phase with the voltage by 90°. C_0 is the vacuum capacitance of the condenser. When filled with some substance, the condenser increases its capacitance to $C = C_0\, \varepsilon'/\varepsilon_0$ where ε' is called the *real permittivity* (often called dielectric con-

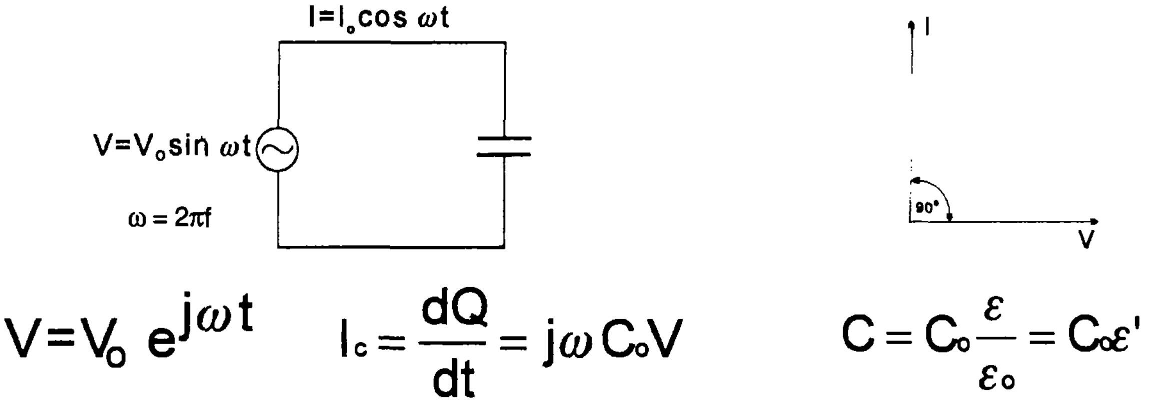


FIGURE 3. Electric model of ideal capacitor.

stant, but note that this "constant" is a function of frequency and temperature) and ε_0 is a free space permittivity $\varepsilon_0 = 8.85$ pF/m.

The dielectric material can conduct an electric current and so in addition to the charging current there is a loss current in phase with the applied alternating voltage. The total current traversing the capacitor will be out of phase with the voltage by the angle $\Theta < 90°$, that is, by the loss angle δ against the charging current. Tan $\delta = I_c/I_l$ is called the *dissipation factor* or *loss tangent* and expresses the ability of a material to convert electromagnetic energy into other forms of energy. Theoretical and observed values of tan δ as a function of the frequency are presented in Figure 4.

The calculated frequency response of this circuit does not agree with that observed, because the conductance term need not stem from a migration of charges, but can represent any other energy-consuming processes. To numerically express this phenomena, *complex permittivity* was introduced

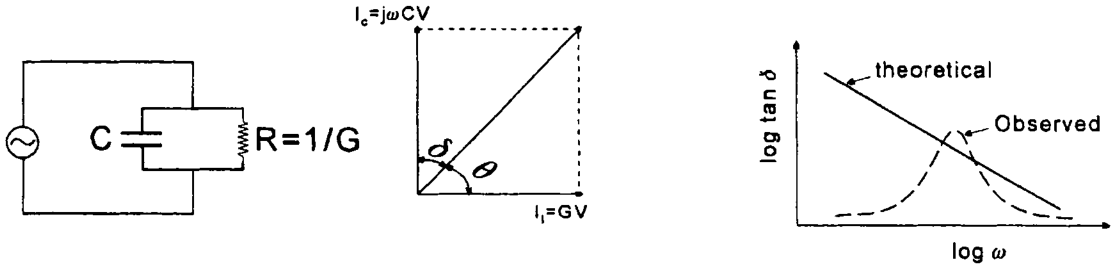
$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

where ε' is a *real permittivity*, $j = \sqrt{-1}$, and ε'' is called the dielectric loss factor and expresses the efficiency of the material in converting electromagnetic energy into heat. The product of ε'' and the angular frequency are equivalent to a dielectric conductivity $\sigma = \varepsilon''\omega$ and numerically express all dissipative effects; the conductivity is caused by migrating charges and the other energy-consuming processes associated with electromagnetic field interactions with the matter. Tan δ can be derived directly from the *dielectric loss factor* and *real permittivity*.

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

A similar model of the interaction of the magnetic material with the electromagnetic field can be made by replacing the capacitor with a coil. Because most of the materials in the chemical laboratory do not exhibit any macroscopic magnetic activity this problem will not be discussed. A detailed description of *magnetic permeability* (the magnetic version of electrical permittivity) can be found in von Hippel's *Dielectric and Waves*.[7]

Examples of materials having different dielectric loss factors and different permittivity are shown in Table 1. From data presented in Table 1 it is evident that there is no visible relationship between dielectric permittivity (dielectric constant) and dielectric loss factor at a given frequency. Contrary to popular beliefs, not all materials with high dielectric permittivity exhibit a high loss factor, high absorption of microwave en-



$$C = C_0 \frac{\varepsilon}{\varepsilon_0} = C_0\varepsilon'$$

$$\tan\delta = \frac{I_l}{I_c} = \frac{1}{\omega RC} = \frac{\varepsilon''}{\varepsilon'} \equiv D \text{ - Dissipation Factor}$$

FIGURE 4. Electric model of a capacitor with loss.

TABLE 1
Dielectric Permittivity and Dissipation Factors of Different Materials at Frequency 3 GHz and Temperature 25°C

Material	ε'	ε''	Tan $\delta \times 10^4$
Ice	3.2	0.00288	9
Water temperature = 25°C	76.7	12.0419	1570
Aqueous NaCl 0.1 mol/l	75.5	18.12	2400
Aqueous NaCl 0.5 mol/l	67.0	41.875	6250
Methanol	23.9	15.296	6400
Ethanol	6.5	1.625	2500
n-Propanol	3.7	2.479	6700
Ethylene glycol	12.0	12	10,000
CCl_4	2.2	0.00088	4
Heptane	1.9	0.00019	1
Monochlorobiphenyl	2.75	0.28325	1030
Trichlorobiphenyl	2.72	0.1088	400
Pentachlorobiphenyl	2.70	0.01188	44
Calcium titanate	163.0	0.3749	23
Selenium (policrystaline)	10.4	1.6016	1540
Ivory soap	2.9	0.51185	1765

From Reference 7. With Permission.

ergy. The dielectric loss factor can be calculated from "dielectric constants" only when the values of dielectric permittivity are known in the whole frequency spectrum.

B. Molecular Approach

The theory of interaction of an electromagnetic field with matter has been developed by many authors, among them Debye,[8] Fröhlich,[9] Cole and Cole,[10] Hill[11] et al., and Hasted.[12] Whereas a full comprehensive account of all aspects of dielectric theory will not be attempted here, the following outline will describe the basic ideas that help the understanding of electromagnetic field interactions with matter. Also, although atoms and molecules can be satisfactorily represented only by quantum mechanics, no quantum mechanical description of dielectric theory will be presented. We shall mainly concern ourselves with dielectric effects associated with molecular movement, for which classic theories are quite adequate.

The common feature of dielectric materials is their ability to store electrical energy. This is accomplished by the displacement of positive and negative charges under the effect of an applied electric field and against the forces of atomic and molecular attraction. There are four main types of dielectric polarization:

- Electronic polarization, by realignment of electrons around specific nuclei.
- Atomic polarization, by the relative displacement of nuclei due to the unequal distribution of charge within the molecule.
- Orientation polarization results from the reorientation of permanent dipoles by the electric field.
- Space charge polarization occurs when the material contains free electrons whose

displacement is restricted by grain boundaries. Entire macroscopic regions of the material become either positive or negative. This mechanism is often called the Maxwell-Wagner effect. It takes place in low frequency fields.

A graphic exhibition of the different forms of polarization is shown in Figure 5. Numerically, polarizability is represented by real permittivity. The bigger the ε' value the more electromagnetic field energy can be stored in the material. In an alternating field the orientation of a polarization varies cyclically with the field. At low frequency, all types of polarization synchronize their orientation with the field, but as the frequency increases, the inertia of the molecules causes certain modes of polarization to lag behind the field. In RF and microwave frequencies, electron and atomic polarization are much faster than the field and so these effects do not contribute to the dielectric heating. Dipole and space charge polarization are in the same time scale and so there is an interaction producing energy transfer from the electromagnetic field. The phase lag between the polarization and the applied field leads to an absorption of energy and Joule heating. The rate of conversion of electrical energy to heat in the material is represented by the imaginary part of ε^*, and ε'' is in this way referred to as the dielectric loss factor. When the frequency rises further only extremely fast electronic polarization can take place. Other modes become too slow to respond to field changes. These phenomena take place at optical and UV frequencies, so ε' for these frequencies is called the optical dielectric constant.

C. Dielectric Relaxation

Dielectric relaxation occurs when the electric field that induces the polarization is removed. The material takes a certain time to return to its original molecular disorder. Debye[13] used a simple model of a spherical dipole to calculate the relaxation time τ (time required to reduce the order to 1/e of its original value). He was able to calculate this time statistically by deriving the space orientation under the counteracting influences of Brownian motion and of a time-dependent electric field. He found that

$$\tau = \frac{\xi}{2\ kT}$$

where ξ is a coefficient depending on the size of the molecule and its intermolecular attraction forces. For a spherical molecule of

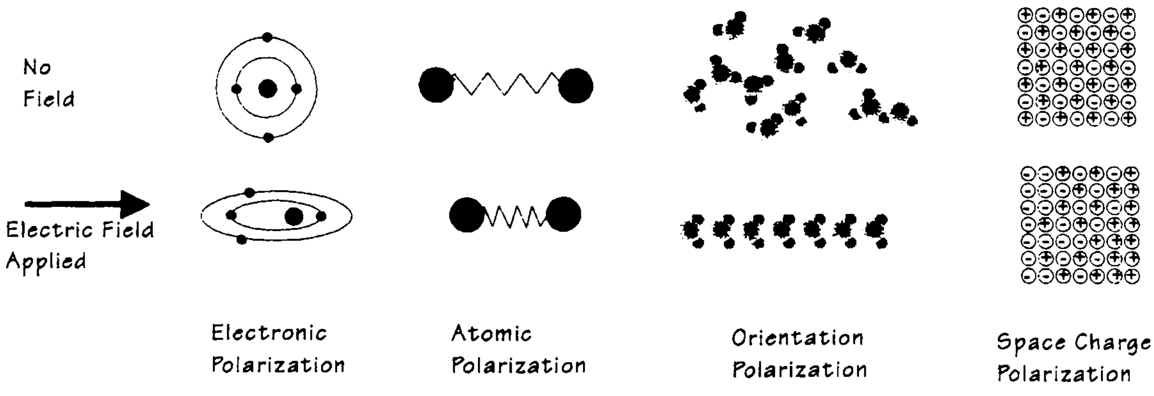


FIGURE 5. Mechanisms of polarization.

radius r, rotating in a liquid of viscosity η, Stokes' law gives

$$\xi = 8\pi\eta r^3$$

Combining these equations, Debye obtained the relaxation time for a spherical rotating ball in a viscous liquid.

$$\tau = \frac{1}{\omega} = \frac{4\pi r^3\eta}{kT} = V\frac{3\eta}{kT}$$

The relaxation time is proportional to the volume of the sphere and the macroscopic viscosity of the liquid. The complex permittivity ε^* can be calculated from values of the relaxation time and the real permittivity.

$$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + j\omega\tau}$$

By separating the real and imaginary parts we obtain the Debye equations for the loss factor and real permittivity.

$$\varepsilon' = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + \omega^2\tau^2}$$

$$\varepsilon'' = \frac{(\varepsilon'_s - \varepsilon'_\infty)\omega\tau}{1 + \omega^2\tau^2}$$

Where ε'_s is a specific permittivity for a static electric field and ε'_∞ is a specific permittivity for a frequency $\omega >> 2\pi/\tau$. These values, ε'_s and ε'_∞, are often called the static dielectric constant and optical dielectric constant, respectively. The loss factor ε'' has a maximum when $\omega = 1/\pi$. A classic Debye plot is presented in Figure 6.

In practice the relaxation spectra of liquids and solids are often flatter and more extended than predicted by the Debye equations, because of the interaction of the molecules with their neighbors. In the condensed state, dipoles can have a number of equilibrium states separated by potential barriers over which the dipole must pass in turning from one direction to another. Fröhlich[9] suggested that the relaxation time, τ, is dependent not only on the size of the molecule but also on the height of the potential barrier that the molecule has to cross in the process of reorientation.

$$\tau = \tau_0 e^{U/kT}$$

where τ_0 is a relaxation time calculated from a Debye equation and U is a value of the potential barrier that a molecule has to cross in the course of the rotation.

Moreover, there could be many different interactions between molecules, and many different potential wells in the course of molecular rotation. As a simple example, the internal rotation of 1,2 dichloroethane is shown in Figure 7.

Even in so simple a system as 1,2 dichloroethane three potential wells and three potential barriers can be seen in the course of rotation of the carbon-carbon bond. Mathematically this situation is expressed by the introduction of a distribution factor α in the Debye equations. This new equation is known as the Cole-Cole equation[10] expressed as:

$$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + (j\omega\tau)^{1-\alpha}}$$

The empirical constant α, which may vary between 0 and 1, describes the broadening of the relaxation region. It is worth noting that not only short range interactions between molecules can broaden the relaxation spectrum. Long-range phenomena, such as interaction within a crystal lattice or interactions between long-chain molecules, can also have a big impact on the relaxation time (the frequency with maximum efficiency of conversion of electromagnetically energy into heat energy). Other complications can arise for macromolecular or conducting systems as a result of the Maxwell-Wagner effect.

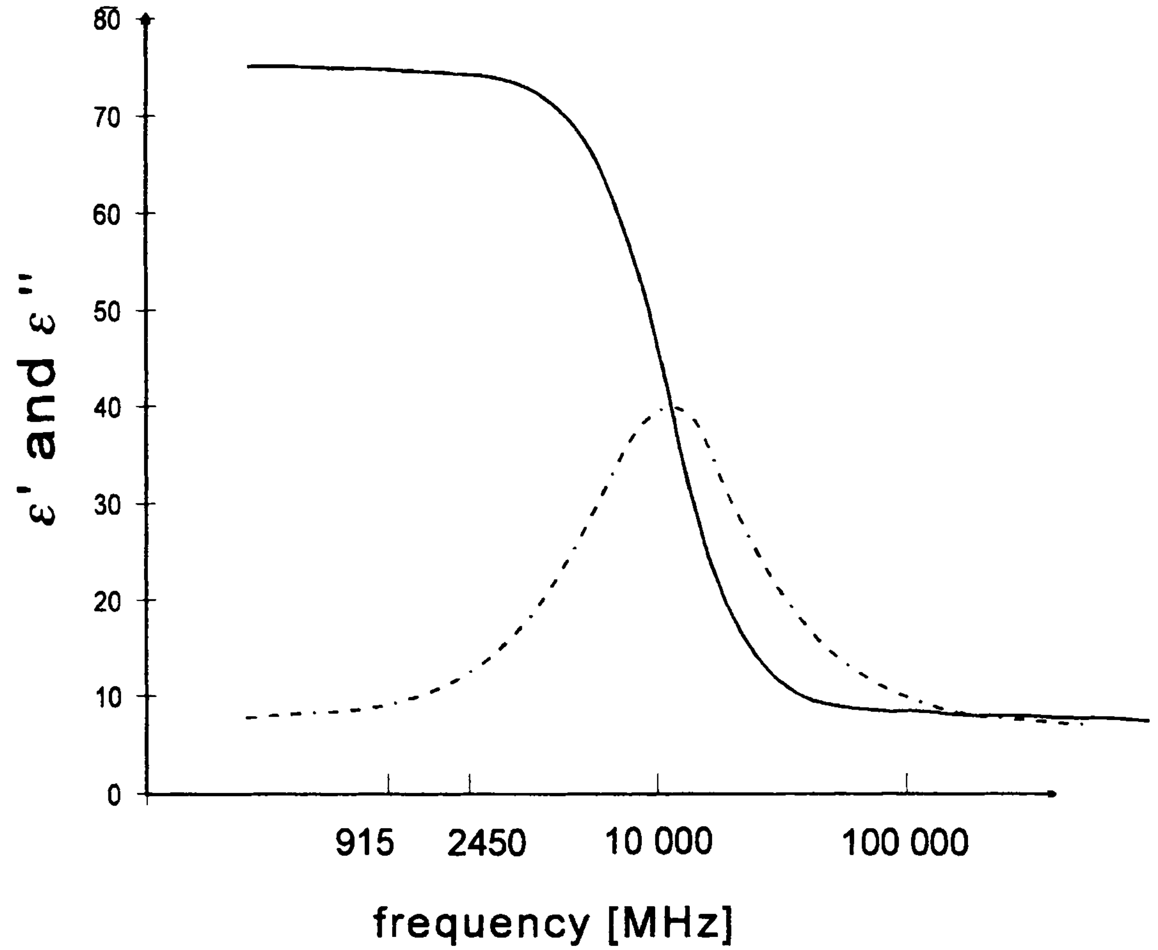


FIGURE 6. Real and imaginary components of dielectric permittivity as a function of frequency (Debye plot).

The simple mechanical model derived by Debye can no longer explain, by the introduction of a simple microscopic relaxation time, all processes occurring during electromagnetically induced molecular rotation. The value of the relaxation time is no longer singular, but is distributed around the central value τ. Figure 8 shows a Debye plot for vulcanized rubber plus the theoretical function of dielectric permittivity and dielectric loss calculated from the Debye equations.

D. Penetration Depth

From values of ε′ and ε″ as a function of the frequency it is obvious that every compound or mixture has its own characteristic frequency at which it will absorb energy most efficiently. For example, water will absorb energy most efficiently at around 20 GHz. One other important parameter of electromagnetic heating is the penetration depth. An approximate relationship for penetration depth, D^p (the depth into the material where the power falls to 1/e of the value on the surface), is given by:

$$D_p \approx \lambda_0 \varepsilon' / 2\pi\varepsilon''$$

where λ_0 is the wavelength of the electromagnetic radiation. The penetration depth of an electromagnetic field into water as a function of the radiation frequency is shown in Figure 9.

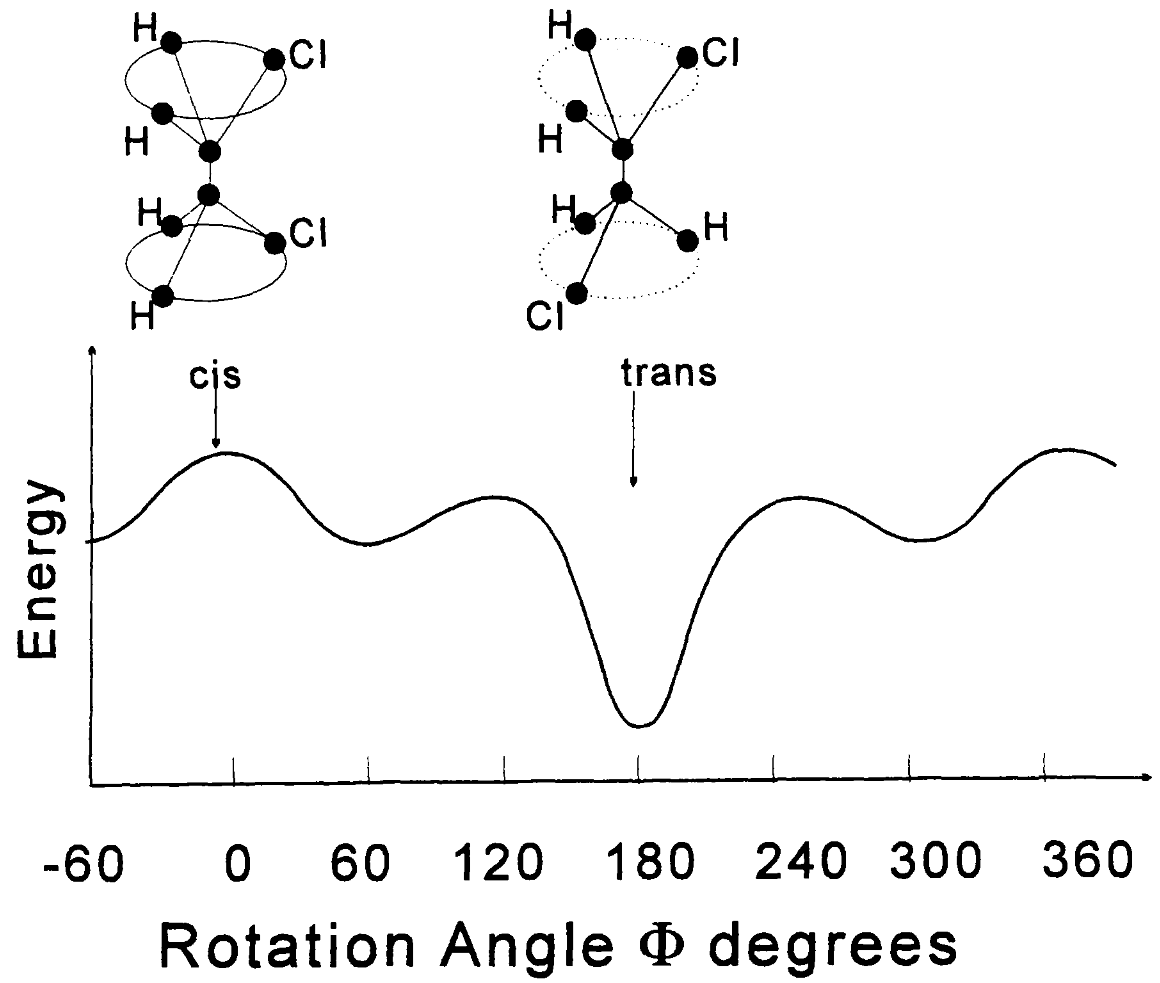


FIGURE 7. Orientation of dipoles in the molecule of 1,2-dichloroethane.

It is clear that the frequency of maximum energy conversion (ca. 20 GHz) is not good for volumetric heating. Only very thin outer layers will be heated and so the interior will get energy only by "classical" means, namely, thermal conductance and convection. Because ε″ does not change so sharply with frequency, the irradiation of matter with an electromagnetic field with frequencies away from $\omega = 1/\tau$ will facilitate penetration of energy into the bulk of the material. Entire bulk regions of the material can then be heated simultaneously, without any major temperature gradient. The rate at which the temperature will rise due to the electromagnetic radiation is determined by the following equation:[15]

$$\frac{\delta T}{\delta t} = \frac{\text{constant} \cdot \varepsilon'' \cdot f \cdot E^2}{\rho \cdot C_p}$$

where E is the electric field intensity, ρ density of the material, C_p the specific heat capacity, and f frequency of electromagnetic field in hertz.

This type of heating can be realized only by electromagnetic heating in the microwave and RF; other forms of electromagnetic radiation have too small a penetration depth and thermal conductivity is the limiting factor in heating by infra-red or shorter wavelengths of electromagnetic energy. In the microwave and RF region the rate of heating is dependent only on the material's dielec-

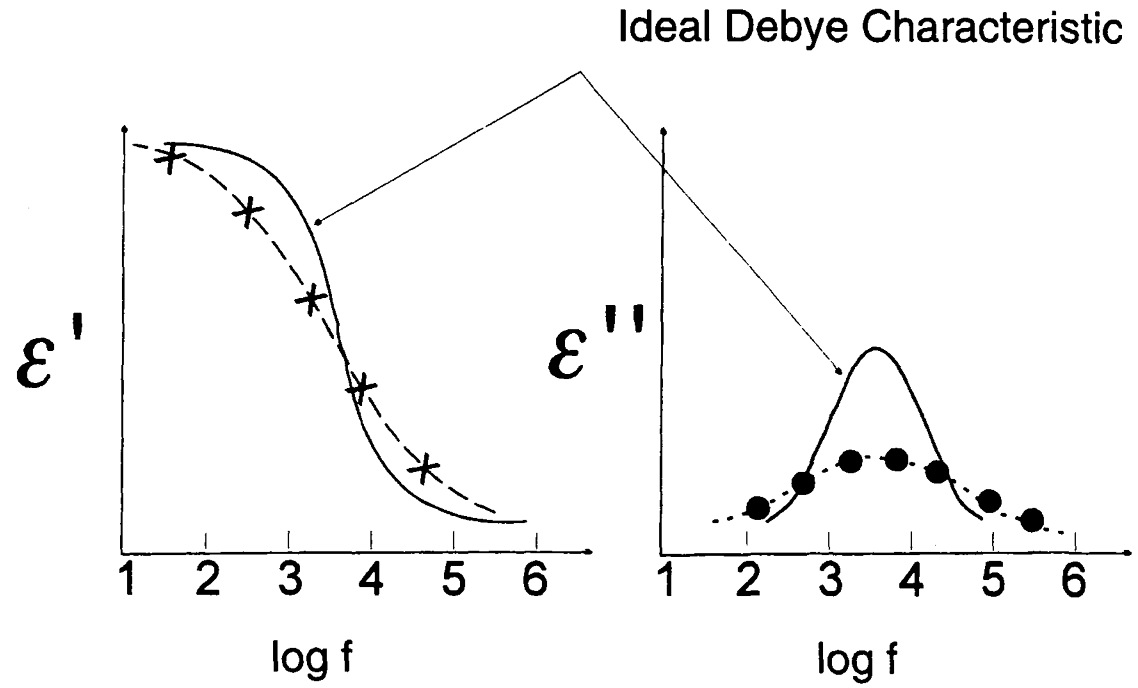


FIGURE 8. Dielectric permittivity and dielectric loss of vulcanized rubber as a function of frequency.

tric properties at the specific frequency and the intensity of the electromagnetic field at a given point in space. The interior region of the mass may be as much as hundreds of degrees warmer than the exterior. Even liquids exhibit a higher than normal boiling temperature under microwave irradiation,[16] because the walls of the container, where nucleate boiling takes place, are cooler than the interior of the liquid. Only microwave and RF fields can achieve such heating.

E. Temperature Effect on the Dissipation Factor

Water exhibits a reduction of the dissipation factor with increase in temperature. Most organic liquids behave differently, the dissipation factor rises with temperature. The dissipation factors of solids also rise with temperature. Many solids have very low dielectric loss at room temperature, but their absorption of electromagnetic energy rises very rapidly with temperature, and that phenomenon assumes an avalanche character. Temperature stabilization is possible only if heat can be removed at a sufficiently high rate, or by limiting the microwave power. There are reports of melting in a microwave field of "microwave transparent" materials such as fused quartz or polyetheretherketone (PEEK).[17] Detailed analysis of thermal runaway can be found in a paper by Roussy et al.[18]

F. Influences of Sample Shape on Microwave Absorption

The shape and the size of objects heated by microwave irradiation have much greater and completely different impacts on temperature distribution than classical means of heating. Microwave energy is deposited directly in the heated material, so the interior of the object can be heated without the mediation of conductive heating and usually temperatures inside heated materials are much higher than near the surface, especially for solids with low thermal conductiv-

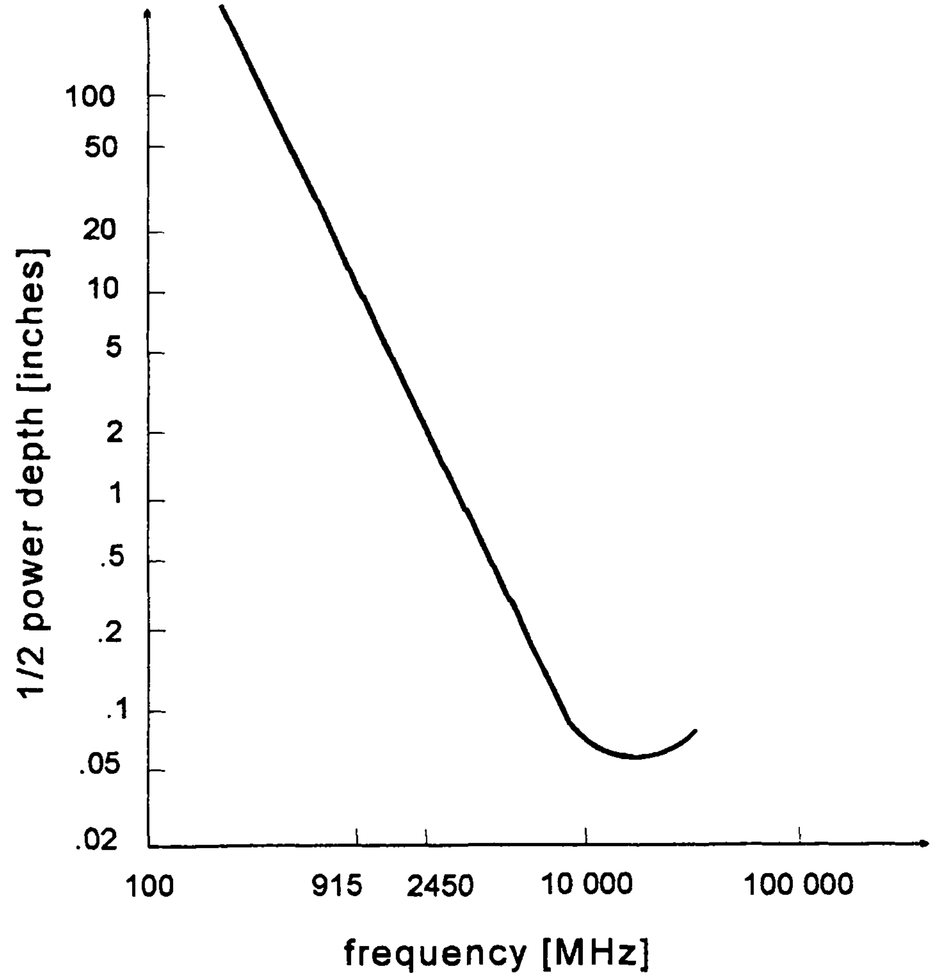


FIGURE 9. Variation of the penetration depth with frequency for water at 25°C. (From Reference 14. With permission.)

ity. Even in liquids, the temperature can be stratified, because convection cannot move the less viscous, lower density hot regions into the colder regions of the fluid more quickly than the power can accumulate the heat in the hotter region.

For most microwave heating applications, the electric field enters the processed material from another medium and so boundary conditions and object shape can significantly affect the distribution of electromagnetic energy inside the heated object. The normal (perpendicular) component of the electric field will be smaller in the material because of the differences in dielectric properties. The tangential (parallel) component of the electric field must be the same on the two sides of the interface. The net result is that the electric field will be bent (changed in direction) at the boundary between the material and surroundings. At microwave frequencies (where the dimensions of the heated objects are in the range of the wavelength) the field bending can give rise to a much higher concentration of the microwave field in certain regions of the processed material. Graphic presentation of this aspect of microwave heating is presented in Figure 10.

From observation of the bending of a microwave frequency field, it is expected

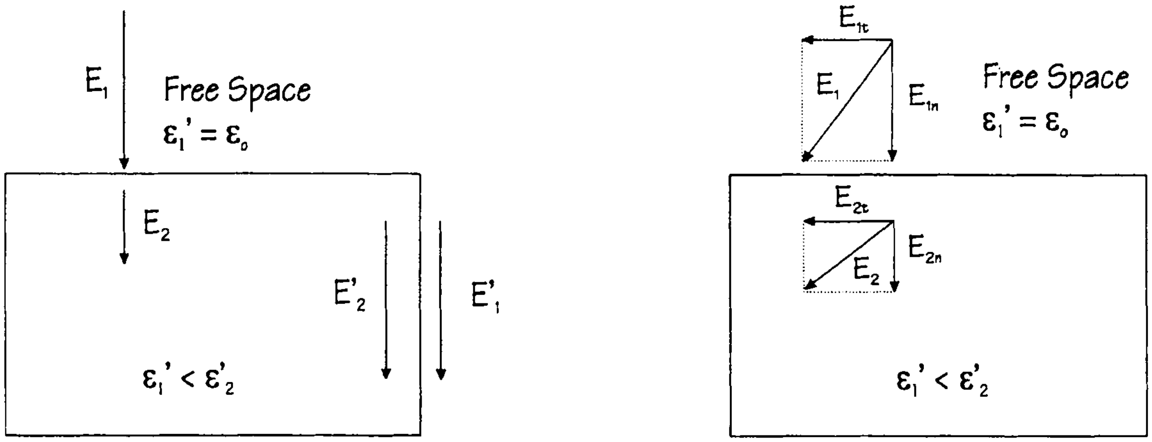


FIGURE 10. Bending of microwave field at a phase boundary.

that corners of material might be heated more in an electromagnetic field. This indeed happens. Materials of spherical appearance will concentrate an electromagnetic field at their center. For more complicated shapes the distribution of the electromagnetic field inside the processed object can be very complex, some places receiving much more energy than others.

In addition, the distribution of electromagnetic energy inside a processed material can be influenced by reflection of the electromagnetic wave from the phase boundary. If the heated object's dimensions are integral multiples of a half wavelength, resonance can occur leading to localized very hot spots inside the material. This was observed during microwave drying of carrots by Ponne et al.[19] Standing waves produced carbonized spots about 4 cm apart.

The wavelength of microwave radiation is related to dielectric properties of the medium by the equation

$$\lambda = \frac{2\pi}{\omega\sqrt{\varepsilon'}} = \frac{\lambda_0}{\sqrt{\varepsilon'}}$$

where λ_0 is a wavelength in free space (for most used 2450 MHz band wavelength in free space is 12.2 cm).

The correct electromagnetic power dissipation inside a processed material is very difficult to predict and calculate. Moreover, the boundary condition can change during microwave processing. Dielectric properties also change with temperature. Selective heating can lead to localized structure changes and so the shape and size of sample can be altered by microwave processing.

Most microwave processed materials are not homogeneous. This leads to further complications for predicting the distribution of microwave energy inside materials. Nonhomogeneous materials that have the same composition with phases consisting of species with different shapes will behave differently in a microwave field. When a component i is uniformly dispersed as spherical particles in a continuum c, the permittivity ε_m of the mixture is given by the Bruggeman equation:[20]

$$1 - \upsilon_i = \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i - \varepsilon_c}\left(\frac{\varepsilon_c}{\varepsilon_m}\right)^{1/3}$$

where υ_i is the volume fraction of the component i ($\upsilon_i + \upsilon_c = 1$).For discoidal particles

$$1 - \upsilon_i = \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i - \varepsilon_c}\frac{2\varepsilon_i + \varepsilon_c}{2\varepsilon_i + \varepsilon_m}$$

And for needle-like particles

$$1-\upsilon_i = \frac{\varepsilon_i-\varepsilon_m}{\varepsilon_i-\varepsilon_c}\left(\frac{\varepsilon_i+5\varepsilon_c}{\varepsilon_i+5\varepsilon_m}\right)^{2/3}$$

These examples show how complicated the prediction of the distribution of electromagnetic energy inside a processed material can be, and how different microwave heating is from classical means.

III. EQUIPMENT FOR ELECTROMAGNETIC HEATING

A. Frequencies Used for Electromagnetic Heating

Microwave frequencies and RF are very intensively used for telecommunication, radio broadcasting, and RADAR. In order not to interfere with these uses, the International Telecommunication Union (ITU) has allocated several frequency bands for exclusive use by industrial, scientific, medical, domestic, and all analogous applications other than telecommunication. Some of the frequencies allocated for these purposes (ISM bands) are given in Table 2.

Frequencies in excess of 10 GHz are not used in practice due to their low penetration range. Most domestic microwave ovens operate in the 2450-MHz band. The 915-MHz band and 27.12-kHz RF are most often used for industrial (large-scale) electromagnetic heating. Applications that use frequencies from outside the band allocated for nontelecommunication or RADAR have to be properly shielded in order for the radiation not to leak outside the applicator.

B. Generators and Applicators

All microwave appliances have two main components: a microwave generator with its electric power supply and an applicator. The latter may be an antenna for direct irradiation or a resonant or multimode cavity in which microwave treatment takes place. The connection between the two components is provided by a waveguide or a coaxial cable for lower (<400 W) power transmission. When the applicator is a cavity, it is coupled to the transmission line by an antenna-type junction. The two main types of generators of microwave energy are solid-state amplifiers and vacuum tubes.

At present, the production of the high power required for most scientific, industrial, medical, or domestic applications requires the use of vacuum tubes. Nevertheless, the recent advances in production of solid-state devices for cellular telephones have led to the construction of compact and very reliable power amplifiers generating 400 W of microwave energy in the frequency range of 900 to 915 MHz.[22]

TABLE 2
ISM Bands

Band	Central frequency	ITU article
433.05–434.79 MHz	433.92 MHz	661
902–928 MHz	915 MHz	707
2400–2500 MHz	2450 MHz	752
5725–5875 MHz	5800 MHz	806
24–24.25 GHz	24.125 GHz	881
61–61.5 GHz	61.25 GHz	911

From Reference 21. With permission.

There are two types of vacuum tube, that is, linear beam tubes (klystrons or traveling wave tubes [TWT]) and cross field tubes (magnetrons).

Klystrons are mainly used for the generation of TV signals and their utilization in ISM applications is rather limited. Details of klystron design can be found in the literature.[23]

TWT can generate very wide microwave bands. They are used mainly in RADAR jammers or for medical diathermy equipment. A TWT as a source of microwave energy was recently constructed by the Oak Ridge National Laboratory; it was a variable frequency microwave oven[24] operating at frequencies from 2.4 to 7.5 GHz. Unfortunately, the main disadvantage of TWT is its very high price and rather limited power generation (up to 400 W).

The magnetron was developed in the U.K. during the Second World War. Applications originally were only for military RADAR but this has spread to include uses in medical linear accelerators and all types of microwave ovens. Magnetrons are simple, reliable, and relatively inexpensive. They can generate up to 8 kW of continuous power at 2.45 GHz and up to 100 kW at a frequency of 900 MHz.

1. Principles of Magnetron Operation

A magnetron is a vacuum device that converts DC electrical energy into microwaves. It is a circular symmetric tube containing a hollow cylindrical anode with a directly or indirectly heated cathode along its axis. A constant potential is applied between the anode and cathode and an axial magnetic field is produced by a permanent magnet or an electromagnet. Electrons are emitted from the cathode and are accelerated towards the anode by the DC voltage between them. The presence of a strong magnetic field causes the electrons to follow curved paths spiraling away from the cathode.

The energy of the electrons is converted into RF energy in a series of resonant cavities. The resonant frequency of the cavity is determined by its physical dimensions. As an electron spirals away from the cathode and approaches the anode, it falls under the influence of the instantaneous RF field at the vane tips. At this point one of two situations occurs. Either (1) electrons are accelerated by the RF field, experiencing a greater "curling force" and are accelerated back to the cathode or (2) the electron is decelerated by the RF field and hence experiences less curling force and drifts toward the anode. The loss of potential energy by the electron in slowing down is matched by an equivalent increase of the energy in the RF field and, by this mechanism, the energy transferred to the anode structure is emitted by the antenna (see Figure 11).

The actual process of converting the energy of the moving electrons is somewhat analogous to generating sound by blowing air across an open bottle neck. The efficiency of the magnetron is of the order of 60 to 65%. The remaining power contributes to the heating of the cathode or is eliminated through Joule power dissipation in the anode where it is removed by means of radiator fins or a circulating water jacket.

In appliance-grade microwave ovens, the power output of the magnetron is constant and the power output of the oven is controlled by cycling the magnetron off and on to obtain an average power level. The duty cycle of the magnetron is the time the magnetron is on divided by the time base. Domestic microwave ovens typically have a time base of 10 to 30 s. Thus, to obtain one half of the rated output, the magnetron will be on only for half of the time base (e.g., for duty cycle of 20 s the magnetron will be emitting maximum power for 10 s and zero power for the next 10 s).

Prior to operation, the cathode must be given time to warm up or insufficient emission will be available for normal operation. This takes about 1 min. In order to overcome

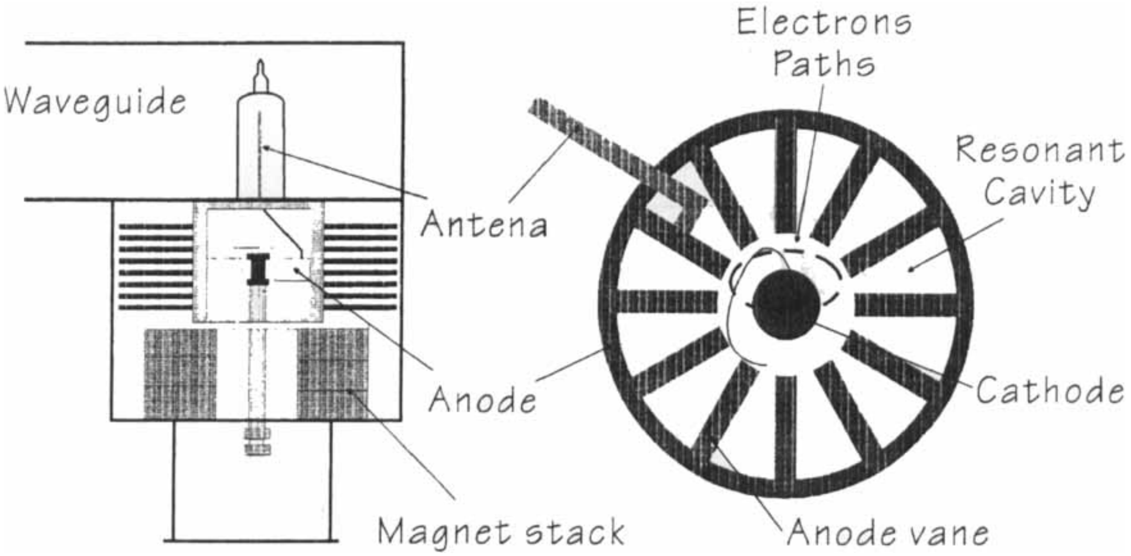


FIGURE 11. Schematic diagram of the magnetron.

this, short pulsed systems have a continuously heated cathode.

C. Applicators

The energy generated by the microwave tube must be transmitted to an applicator. Coaxial cables are used for power transmission up to a few hundred watts, and matched wave guides beyond that. A microwave applicator is a device designed to ensure the transfer of electromagnetic energy from the transmission line to the material to be treated. Its design depends on the nature, shape, and dimensions of the material to be heated. It also depends on the frequency, RF power, and the nature of the process (continuous or batch).

For high-volume materials, the applicator is usually a multimode cavity whose linear dimensions are large compared with those of the material and the wavelength. The electric field pattern produced by standing waves inside the cavity can be very complex. Some areas may receive a large amount of the energy, whereas others may be almost completely neglected. To ensure an even distribution of incoming energy, a mode stirrer (a reflective fan-shaped mixer) is sometimes used. This device simply moves the maxima of electromagnetic power around the cavity. Most microwave ovens are supplied with a turntable, which moves the processed material instead of moving the electromagnetic field. Such devices ensure that the average electromagnetic field experienced by the sample is approximately the same. A schematic illustration of the multimode cavity oven is shown in Figure 12.

Microwaves interact with all substances inside a microwave cavity. The metal walls of a domestic oven absorb microwave energy to a small degree, most of the energy being reflected. Because this energy absorption is small relative to the large load, this effect is generally not noticeable. When the load placed in the appliance-grade microwave oven is small (less than 25 ml of H_2O for example) the contribution of the walls becomes relatively large. A small load also means that more of the energy is returned to the magnetron, lowering its efficiency and its life. At higher powers, the reflecting energy may result in damage of the magnetron. To prevent this, a circulator (a three-way

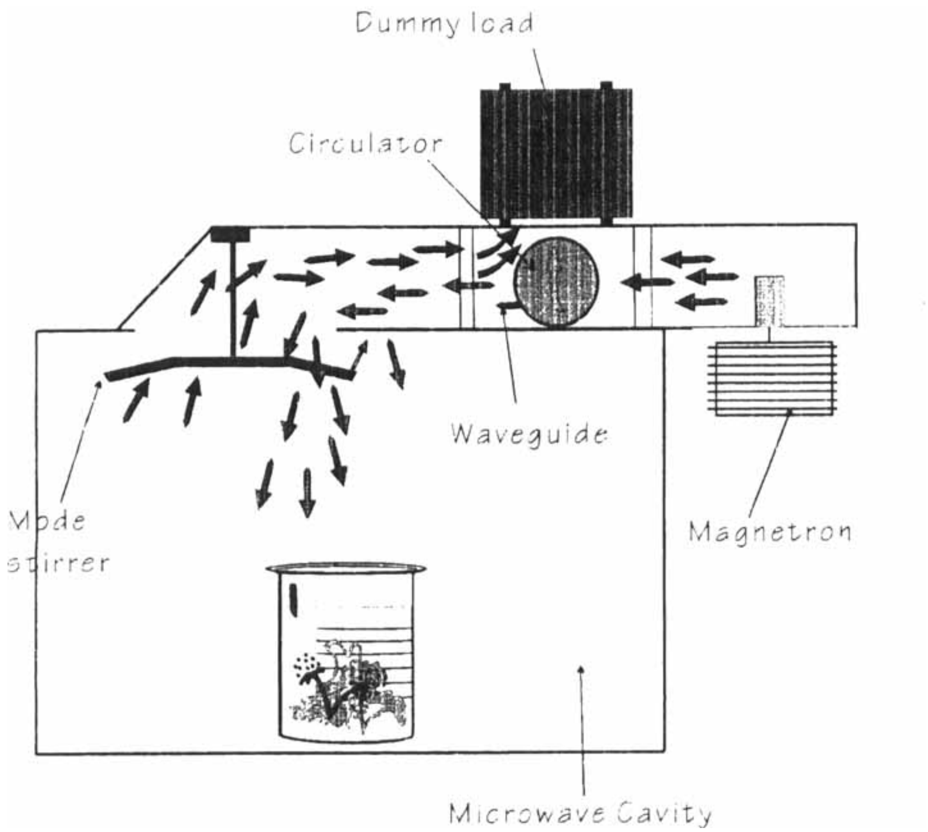


FIGURE 12. Schematic view of the microwave oven.

ferromagnetic "check valve"), which will redirect any reflected power away from the magnetron, is used in some microwave ovens. As the load becomes smaller, the heating efficiency becomes so poor that heating them in a multimode cavity is impractical. Figure 13 illustrates the decrease in the amount of absorbed microwave energy with a decrease in the water sample size.

A detailed review of the factors that affect the power delivered to materials placed in multimode cavity microwave ovens has been presented by Gerling.[26] Other reports concerning the utilization of appliance-grade microwave ovens in a chemical laboratory can be found in the literature.[27–33]

1. Applicators with a Single Mode Cavity

When the materials that are being processed by a microwave field are poor absorbers of microwave energy or are only available in small amounts, the multimode microwave oven is no longer the most efficient system. A single-mode resonant cavity, tuned to the characteristics of the heated material, has to be used. A schematic illustration of such a system is presented in Figure 14.

A single-mode microwave oven allows a sample to be placed in a much higher electric field than can be obtained in a multimode oven. Because insertion of the sample into the cavity changes the resonant frequency, a variety of microwave components are used for impedance matching, including:

- Mobile piston short circuits (Evanson cavity).[34]
- Capacitive or inductive waveguide impedance elements, in the form of thin obstacles inserted into the waveguide (apertures, irises, posts, or tuning screws).

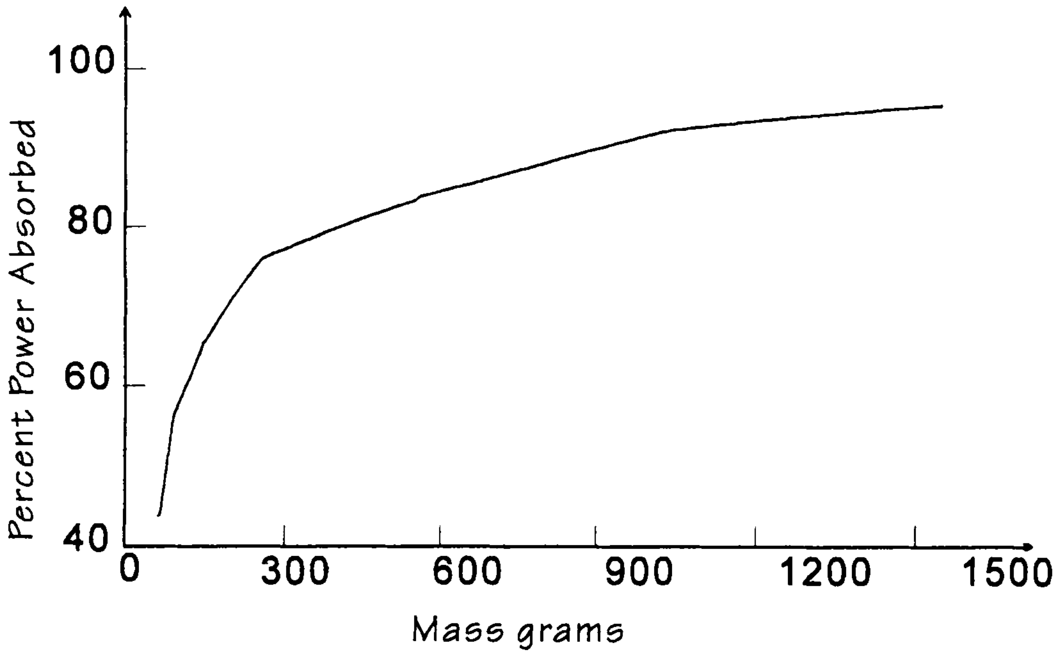


FIGURE 13. Percentage of microwave power absorbed by water in an appliance-grade microwave oven. (From Reference 25. With permission.)

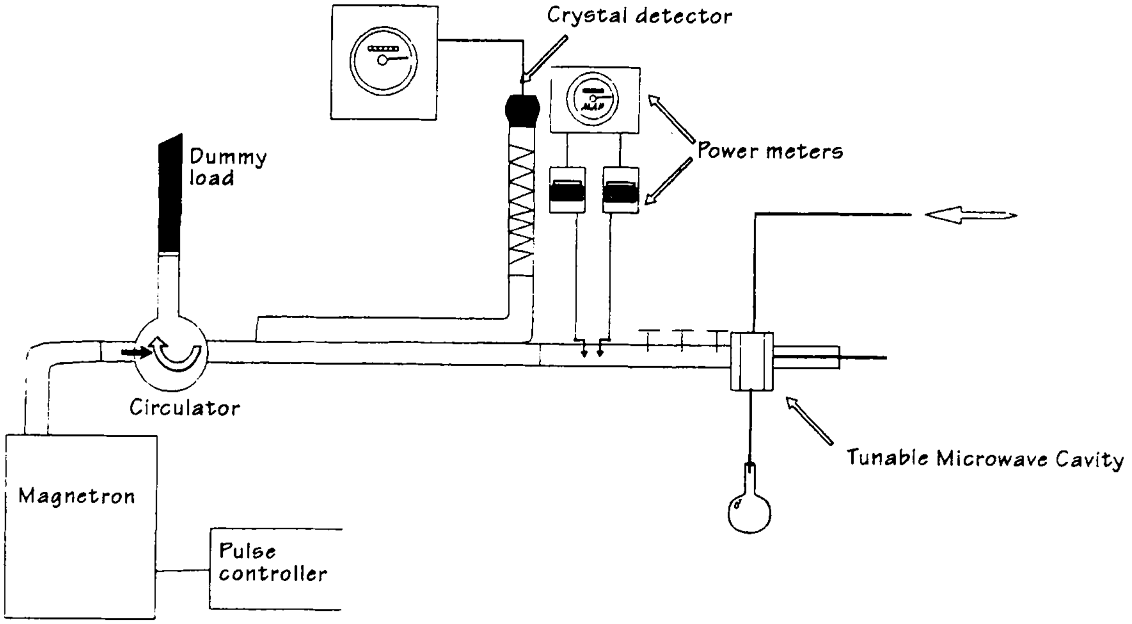


FIGURE 14. Single-mode, resonant heating system.

The efficiency of matching can be controlled by measurement of the forward and reflected power by a network analyzer. Because the dielectric properties of the material depend on temperature, the matching requirements of the cavity are continually changing and are usually controlled by computer. Use of a resonant cavity increases the effective cavity power by three orders of magnitude, allowing the microwave heating of relatively low-loss materials like glasses or polymers using low power. Further information about utilization of microwave resonant cavities in chemistry can be found in the literature.[35–38]

IV. THE APPLICATION OF DIELECTRIC HEATING IN ANALYTICAL CHEMISTRY

Microwave dielectric heating uses the ability of some liquids and solids to transform electromagnetic energy into heat. This *in situ* mode of energy conversion has many attractions for the chemist, because its magnitude depends only on the dielectric properties of the processed material. This allows the selection of target-specific molecules and deposition of the energy in the whole volume of the sample, without the usual limitations of heat conduction or convection. Microwave heating is the first fundamentally new heating technique since the discovery of fire. Microwaves are currently used for drying, polymerizing, melting, sintering, cooking, pasteurizing, and in many other processes.

Before reviewing the application of microwave energy in analytical chemistry it is worth noting that electromagnetic energy has been used in the synthesis of chemical compounds. The application of microwave ovens to organic synthesis was initiated by Gedey et al.[39] in 1986 and another early report was published by Giguere et al.[40] Since then a wide range of organic reactions have been successfully conducted with microwave irradiation. Literature reviews can be found in References 41 to 43. The time necessary to complete most synthetic reactions is significantly shorter than that required when using conventional heating.

In spite of the fact that a quantum of microwave energy ($W = h*f$ where h is Planck constant $6.626*10^{-34}$Js) has an energy less than $2*10^{-22}$ J (1-J.mol^{-1}), less than Van der Waals binding energies, one of the central issues in this field is the question of the presence or absence of a so-called "microwave effect." For some time now organic researchers have been attempting to determine if the reduction in time necessary to complete most organic reactions is due to the expected kinetic consequences resulting from the higher reaction temperature or if microwave interaction gives rise to specific localized effects (such as have been determined, for example, during sonication of organic reactions where cavitational collapses of microbubbles produce a localized extremely high temperature and pressure). Recently, it has been determined that many of the observed results in microwave-assisted reactions are due to superheating of the reaction solutions.[16] With several significant papers[44–46] having appeared in the literature in the past year, this debate is becoming better resolved. According to their authors, reports about a "microwave effect" often originated from the imprecise monitoring of the temperature of the reaction medium under microwave irradiation. New methods will have to be found to make instantaneous system-wide temperature measurements without invading the microwave system itself. The microwave-induced acoustic phenomenon, first described in July 1993 by Wan and Ioffe,[47] has the potential to be able to more precisely monitor microwave-irradiated systems.

The following sections will cover recent applications of microwave radiation relevant to the analytical chemist, such as mineralization, preconcentration, and extraction of the analytical sample. Other emerging new techniques that use microwave heating in environmental chemistry will also be discussed.

A. Microwave Digestion for Elemental Analysis

Microwave-assisted mineralization of samples for elemental analysis is now established as a routine, well-developed technique. Since the first experiments carried out by Samra et al. in 1975,[1] the application of microwave energy for digestion of a wide range of matrices has been investigated. A recent literature review[48] has 163 citations involving microwave digestion of biological, geological, metallic, and environmental materials. Other reported applications deal with mineralization of coal, fly ashes, oil, sewage sludge, and glass. Other reviews of methods of microwave dissolution are provided by Matusiewicz and Sturgeon[2] and Sinquin et al.[49] All published reports show a substantial speed-up of the microwave digestion compared with classic conductive heating. The precision of the determination is also improved, especially by utilizing closed vessel mineralization.

The speed of microwave Kjeldahl digestion for the determination of nitrogen is shown in Figure 15. One reason for such a remarkable development of microwave sample dissolution is the availability of specialized microwave ovens designed for such applications. Both types of microwave ovens, multimode and resonant cavity, are on the market. The book edited by Kingston and Jassie[50] has had a significant impact on the attitude of analytical chemists toward microwaves as an alternative source of energy.

B. Microwave-Assisted Extraction

The applicability of microwave irradiation to the extraction of various types of compounds from plant materials, food, and soil was investigated by Ganzler et al.[52–54] Samples were ground and mixed with an appropriate solvent, and the resulting suspensions were irradiated with 2450 MHz microwaves for 30 s in an appliance-grade microwave oven. The irradiation was repeated several times with cooling breaks in order not to boil the suspension. The yields of the compounds obtained by microwave-assisted extraction were comparable with those obtained by the traditional Soxhlet or shaking extraction, but microwave-assisted extraction was much faster than conventional methods. A comparison of the recoveries obtained and the time required in the traditional and microwave-assisted extraction methods is shown in Table 3.

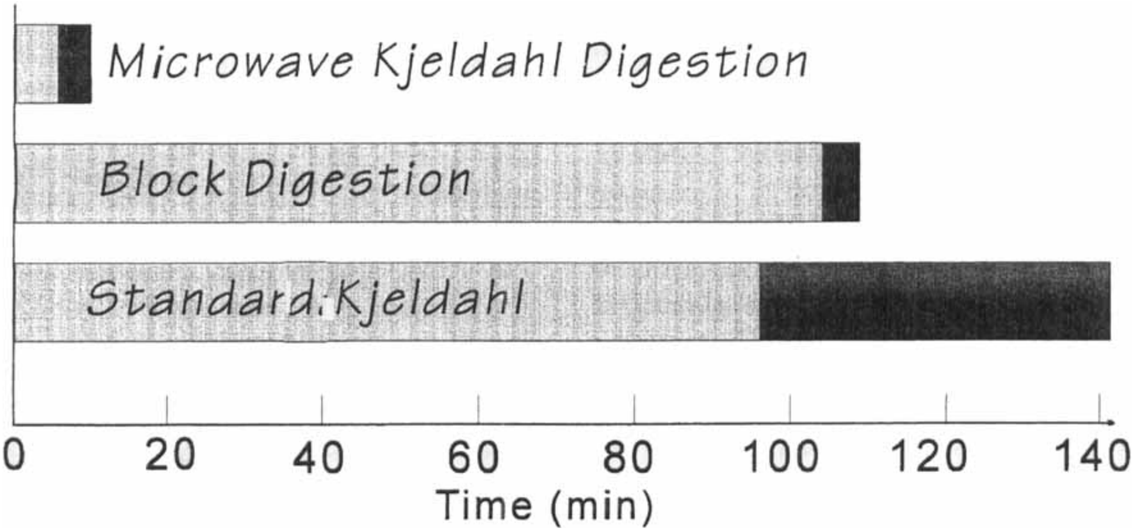


FIGURE 15. Comparison of digestion times for the microwave and standard Kjeldahl digestion methods. (From Reference 51. With permission.)

TABLE 3
Comparison of the Recovery Obtained and Time Required in (a) the Traditional and (b) Microwave Assisted Extraction Methods

	Recovery (%)		Time needed	
Compound	**a**	**b**	**a (h)**	**b (min)**
Crude fat from food	100	98	>3	<5
Antinutritives from fava beans	40	100	>3	<5
Pesticides from soil	90	100	>1.5	<1

From Reference 53. With permission.

Due to the considerable saving in time for the extraction, this method is particularly suitable for the extraction of thermally labile compounds. Extracts obtained by microwave-assisted extraction had none of the artifacts that could be found in the corresponding Soxhlet extracts. This method could also be suitable for the fast extraction of a large series of samples.

A novel method for the extraction of essential oils from fresh plant material using a modified kitchen microwave oven was developed by Craveiro et al.[55] The fresh plant material was irradiated in a microwave oven in a stream of pumped air. The flow of air, after passing through the processed sample, was directed to a condenser outside the microwave cavity. The condensed mixture of water and oils after 5 min of microwave irradiation had no qualitative differences compared with the mixture obtained by 1.5 h of steam distillation. The major advantages of the microwave oven extraction are the relatively small amount of the plant material required, the time of the complete extraction is shortened, and no water is added to the extract.

Meier et al.[56] have carried out the elution of antibodies from sensitized red blood cells using a conventional, appliance-grade microwave oven. The antibodies are extracted from the surface of the red blood cells using a relatively short exposure time (10 to 20 s) to 2450 MHz irradiation. The microwave technique is rapid and requires only 10 min for the final eluate preparation after the sensitized red blood cells are washed. Conventional methods take from 1 to 1.5 h to obtain comparable results. The microwave-assisted extraction of antibodies from the surface of red blood cells was also investigated by Torloni et al.[57]

In 1991 a US Patent on Microwave Assisted Natural Product Extraction was issued to Paré et al.[58] The patented process involved the microwave irradiation of material of biological origin in a solvent relatively transparent to microwaves. The microwave energy is deposited directly in the extracted material without mediation of the solvent. The cellular structure of the extracted material is disrupted by forces generated inside the structure of the material. Extraction using 30-s microwave irradiation is claimed to be comparable to 1 to 2 h of steam distillation and the quality of the extracts has been reported to be superior to that obtained by traditional methods. Further discussion of this sample preparation technique was published in 1994.[59] The authors claim that their patented microwave-assisted process (MAP™) can be used for such matrices as plant and animal tissues, soils, water, consumers' products, cosmetics, and others.

Rapid separation of stabilizers from plastics was studied by Freitag and John.[60] The polymer samples together with microwave-absorbing solvent were kept in sealed vessels and irradiated in a laboratory microwave oven. Fairly quantitative (>90% of the expected content) extraction of the stabilizers from a powdered polymer was achieved within 3 to 6 min. The traditionally used Soxhlet extraction requires up to 16 h to achieve the same recovery. The same approach was used by Jassie et al.[61] for extraction of polyaromatic hydrocarbons (PAH) from soil samples. The time of the microwave-assisted extraction in a pressurized container was significantly shorter than that of the traditional Soxhlet extraction. Lopez-Avila et al.[62] evaluated closed-vessel microwave-assisted extraction (MAE™) using a sample preparation system equipped with pressure and fluoroptic temperature control systems produced by CEM Corporation. Polynuclear aromatic hydrocarbons, phenols, and organochlorine pesticides were extracted from standard reference soils and sediments with hexane/acetone mixtures at temperatures from 80 to 145°C. Average recoveries were in the range 65 to 85% compared with 50% for the same procedure performed at room temperature. Lopez-Avila et al.[62] concluded that microwave-assisted extraction of stable organic compounds from soil was a viable alternative to conventional techniques employing Soxhlet or sonication extraction. Reduced extraction time and reduced solvent use are the main advantages of microwave-assisted extraction. However, they pointed out that some of the compounds investigated (2,4-dinitrophenol and 2-methyl-4,6-dinitrophenol) were degraded in the presence of the microwave field and the soil. A catalytic reaction in the presence of the soil was suggested to explain these low recoveries. There was no degradation of the above compounds when solutions were irradiated in the absence of soil.

In light of all these facts, the very low popularity of microwave-assisted extraction methods appears surprising. One reason for this is the lack of dedicated microwave equipment designed specially for small analytical samples. Also, the mechanism of microwave-assisted extraction seems to be very matrix dependent. Understanding the role of parameters, such as physical shape and dimensions, free and bound water content, or the spiking method, on the extraction efficiency still needs to be investigated. As an example of the overoptimistic prospects for the role of microwaves in the extraction of organic contaminants from soil, a paper by Zhu et al.[63] can be used. They reported that the microwave treatment of a soil contaminated by 9,10-anthraquinone (a model compound for dioxins) rendered the chemical compound nonextractable from the soil. Another report[64] showed that the simple addition of water lost by the soil in the course of microwave processing gave 9,10-anthraquinone, which could be rapidly recovered by the simple shaking method of solvent extraction.

Similarly, Onuszka and Terry[65] reported that 5 × 30 s microwave-assisted extraction of pesticides from sediments provided better recoveries than 8 h of Soxhlet extraction, but they compared the Soxhlet extraction of dry sediment with the microwave extraction of a sample fortified with water. They did not present a comparison of the extraction of exactly the same matrices with exactly the same solvents.

The microwave-assisted extraction of organic contaminants from an environmental sample (unlike microwave digestion procedures) is still in its infancy. More studies have to be done in order to validate this approach for the improvement of the extraction step in analytical sample preparation. From the papers referred to above it is obvious that microwave-assisted extraction shows potential for substantial improvement.

C. Speed-Up of Preconcentration of an Analytical Sample Under a Microwave Field

Kuz'min et al.[66] investigated the use of microwave radiation in the determination of noble metals in natural samples. They used a microwave oven to dry the sample and to wet-digest the matrix. As a novel approach they also used the microwave field to speed up the sorption of the metal traces onto a chelating sorbent. The authors suggested that the limiting steps in an adsorption process are diffusion of the analyte through the double layer at the solvent-sorbent border and the diffusion of analyte complexes in the solvent bulk. The microwave field, by fast cyclic reorientation of the water dipoles, can change the structure of the solution and destroy a double layer. Bulky complexes of the hydrated ions can be reduced to smaller, much more mobile species. As a proof they presented the visible light absorption spectrum of rhodium complexes in 1 *M* HCl and glycol in the presence and absence of a microwave field. This is shown in Figure 16.

As can be seen, there is a significant difference between the visible light absorption spectrum of rhodium complexes under the microwave field and without it. Moreover, the differences between the spectra obtained in different solvents disappear under the influence of the microwave field. This implied that complexed molecules were changed by the microwave field. The similarity of rhodium spectra in different solvents during microwaving suggests that the irradiation destroyed the solvation spheres of the rhodium ions by dipole rotation, that is, there is a different interaction between solvent and solute when the microwave field is in place.

The percentage of rhodium adsorbed on a chelating sorbent as a function of time for different conditions is shown in Figure 17. A substantial speed-up of adsorption of rhodium onto the chelating sorbent was achieved by microwave irradiation relative to conven-

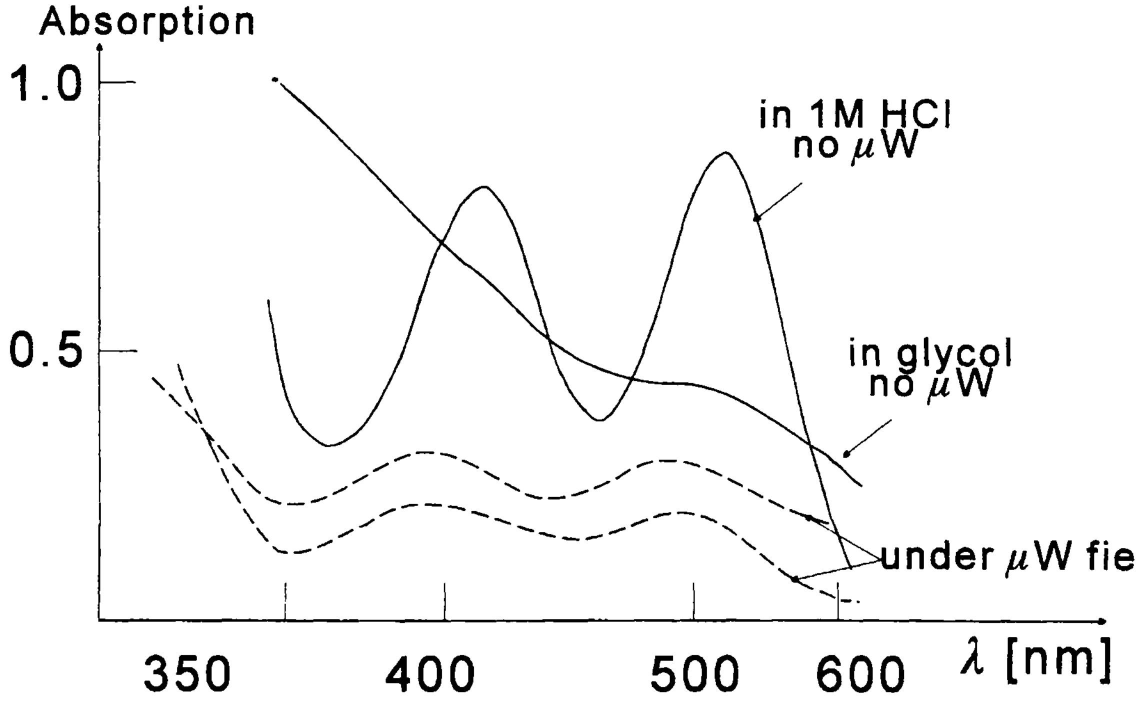


FIGURE 16. Spectrum of rhodium complexes in 1 *M* HCl and in glycol under a microwave field with and without μW. (C_{Rh} = 50 μg/ml.) (From Reference 66. With permission.)

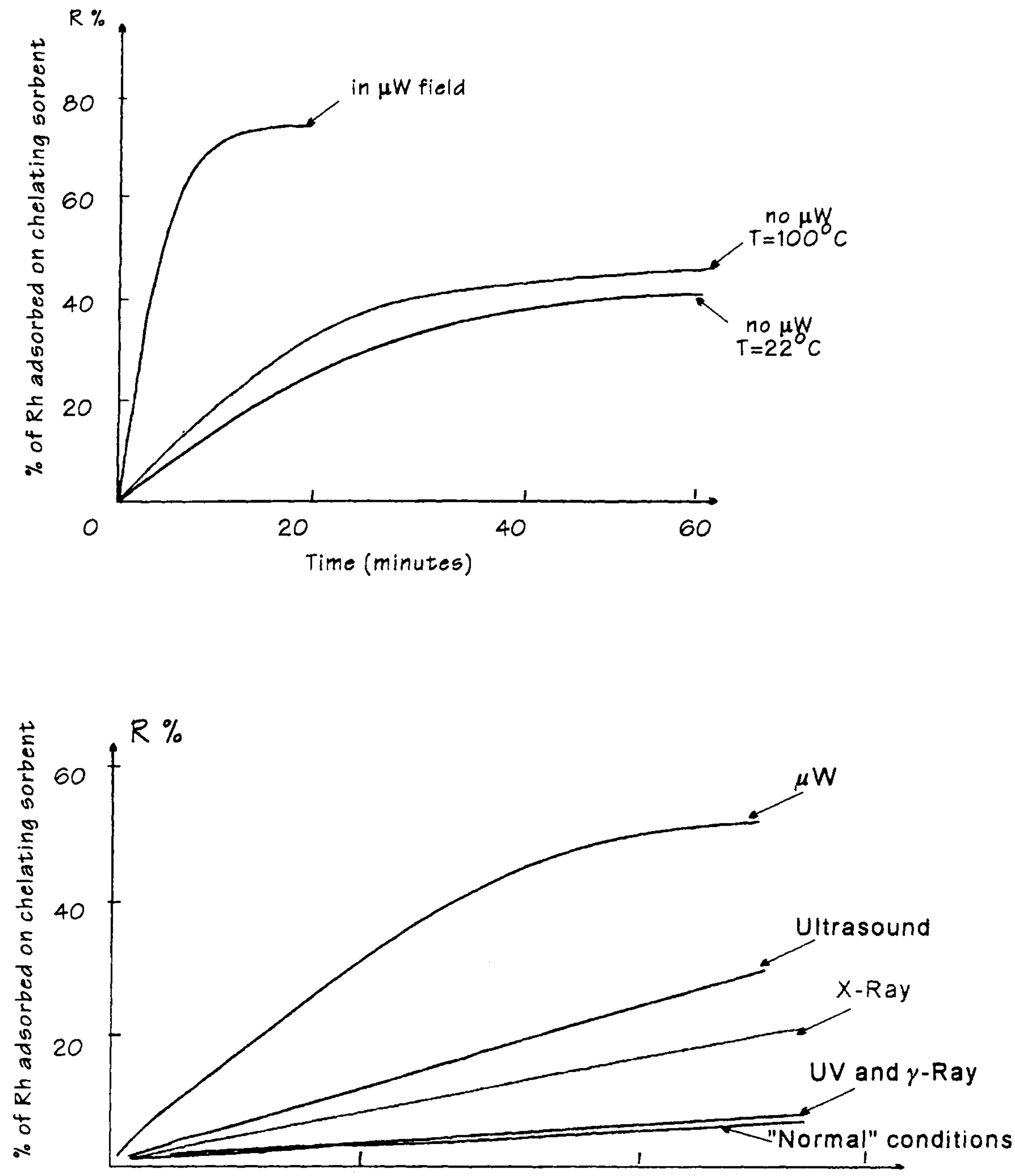


FIGURE 17. Percentage of rhodium absorbed on chelating sorbent as a function of time and (a) temperature, (b) different electromagnetic radiation plus ultrasound.

tional thermal treatment. The speed of adsorption by microwave processing was faster than adsorption under an ultrasound field. Irradiation by UV or γ-ray radiation did not bring about any substantial changes of speed of adsorption.

D. Desorption of Solid Traps by Microwave Energy

Adsorption by active charcoal is commonly used for collecting trace components in air samples prior to gas chromatographic analysis. Desorption of the collected compounds can be performed either by extraction with a solvent (e.g., carbon disulfide) or by heating and purging with an inert gas. The volume of the solvent needed in the first case is usually of the order of milliliters. Because only a few microliters of the extract are transferred to the gas chromatography (GC) column, only a fraction of the compound originally adsorbed is analyzed. Thermal desorption is superior in this respect, as the whole amount collected is introduced into the GC column and detection limits are therefore greatly reduced. A general disadvantage of thermal desorption is the necessity of trapping the desorbed compounds before analysis. The adsorbent in a sampling tube cannot be heated quickly enough from outside to allow direct introduction of the vaporized compound into the chromatography column, mainly because of slow heat transfer within the packing. This difficulty can, however, be overcome by using microwave heating. In 1983 Rektorik[67] took out a European Patent on thermal desorption of solid traps using microwave energy. An adsorbing medium with a high dielectric loss factor $-\varepsilon''$ (e.g., active charcoal or graphitized carbon black) is placed in a removable tubular trap made from material of low ε''. The microwave energy heats the adsorbing material only, at a very high speed, up to 300° per second. The desorbed analyte is swept onto the analytical column by a carrier gas. More information on this system is published by Rektorik.[68]

The application of microwave-induced thermal desorption from activated charcoal traps to analysis of the volatile compounds in industrial waste water was investigated by Neu et al.[69] They found that chromatographic peaks obtained by direct thermal desorption of an analyte onto the GC column are comparable to those obtained by injection by syringe, but the method had some drawbacks, that is, they noticed the formation of some artifacts. They suggested that artifacts result from reaction of adsorbed oxygen with the charcoal. However, because the new peaks have retention times close to those of the analyzed compounds, the possibility of analyte decomposition must be considered. Moreover this method cannot be used for thermally labile compounds, which will react with other adsorbed molecules or with the carbon itself.

Liardon et al.[70,71] used microwave desorbed traps to investigate coffee aroma and volatile flavor compounds from foods. They found that in spite of some signs of the degradation of analytes, a microwave desorption system was useful in the study of volatile compounds in foods. The use of dual adsorbent traps — first desorption by moderate heating for a relatively long time and then desorption from the second trap directly onto the GC column — can improve performance of the method.

In spite of their relatively long time on the market (over 10 years) commercially available microwave desorbers have not become established as a popular tool for the analytical chemist.

V. ENVIRONMENTAL APPLICATIONS OF MICROWAVE ENERGY

A. Soil Decontamination

Thermal processing is a popular treatment method for environmental solids contaminated with volatile or semivolatile hazardous constituents. Problems occur when the exterior of the solid must be heated to an elevated temperature in order to effect conductive heat transfer to the center. This can cause a "skin effect" — outer regions of the treated material will lose the contaminant much faster and evaporation of water will be much faster on the outside of the object. This can change the structure of the surface region, preventing decontamination of the inside. Because microwave and RF heat from the inside out, treated material can be heated without any "skin effect."

This approach has been the subject of several studies. Zhu et al.[63,72] and Windgasse[64] analyzed the removal of volatile and semivolatile organics from soil using microwave-induced steam distillation. Water present in the soil serves as a strong microwave absorber and when steam is developed in the presence of organic pollutants the contaminants are volatized as a result of steam distillation. This process requires temperatures of less than 100°C. Contaminants enter the gas phase without being destroyed or forming detectable byproducts and they are collected outside the system. Compounds of lower volatility can be removed successfully by using a multiple-stage distillation — the repeated addition of water followed by additional microwave treatments.

George et al.[73,74] decontaminated sandy and clay soils spiked with toluene and *p*-xylene at a low temperature without decomposition when soil samples were heated with microwave energy under vacuum conditions. They found that the solvents' removal rate was increased several times when the soil samples contained moisture in the form of about 3% by weight of water. Clay soil was found to be more microwave energy absorptive than sandy soil, thus yielding more rapid extraction of organic contaminants.

The same group[75] studied a technique to enhance microwave adsorption by the addition of carbon particles to the soil or sludge. Solid carbon particles having an average diameter of 3 mm were added to the materials being treated. This technique takes advantage of the ability of the carbon to strongly absorb microwave energy by the Maxwell-Wagner effect. The carbon particles are heated by the microwave energy and the soil is heated indirectly by conduction of the heat from carbon. Because the carbon particles are dispersed in the whole volume of the soil, the conduction path is short. Temperatures reached in the system can be in the range of 1000°C. This approach removed over 99% of phenanthrene from a simulated sludge containing 110 ppm of phenanthrene (90% of 40 mesh sand and 10% heptadecane) when 40% by weight of carbon was added. The removal efficiency of pentachlorophenol (PCP) from spiked soil was much lower (about 60% of the PCP can be removed from soil spiked to 300 ppm PCP in these conditions). The difference in normal boiling point, 340°C for phenanthrene compared with 310°C for PCP, does not explain the differences in removal rates. It is worth noting that carbon becomes a significantly more reactive material in the presence of microwave radiation.[76,77] For example, irradiation of activated charcoal taken from adsorption tubes in the presence of pure benzene or toluene as extraction solvents produced measurable yields of biphenyl and bibenzyl, respectively, showing that their use in such experiments may be problematic.

Zlotorzynski[76] investigated microwave-assisted extraction of PCP from a variety of reference soils. Quantitative PCP release from moist clay soil to acetonitrile was observed but in contrast the PCP was strongly adsorbed by dry soil. Microwave treatment did not affect or improve the extraction efficiency from either dry or wet soils. PCP was found to be strongly adsorbed by dry soil and not displaced by microwave-assisted extraction. However, 100% recoveries were readily achieved in the presence of water (which probably displaced PCP hydrogen bonded to the dry matrix) by conventional solvent extraction. Similar results were obtained by Lopez-Avila et al.[62] Microwave-assisted extraction from SRS103-100 standard reference soil yielded 80% PCP recovery from dry matrix yet they obtained 100% recovery from a moist sample.

Zhu et al.[63] used soil contaminated with 9,10-anthraquinone as a surrogate *model to* study the desorption of dioxins from microwave-treated soil. They concluded that after microwave treatment, at temperatures up to 500°C, 9,10-anthraquinone did not volatilize or diffuse from the soil but did become non-extractable. A model was proposed that postulated that as water was removed from soil aggregates, 9,10-anthraquinone is adsorbed directly on the humus and clay fraction. Further, work however,[64] showed that the nonextractability of anthraquinone was only due to a deficiency of water in the soil. Addition of water to the system makes extraction of 9,10-anthraquinone possible.

B. Oil Recovery by Microwave Radiation

In a petroleum refinery, natural gas processing, gas transmission, and oil and gas production, oil-water emulsions are generated. These include bottom sediments in crude oil transport facilities, oil slop discharge from flotation units, waste oil from gas compression stations, and emulsions left in pits and dump sites. Some of these emulsions are very old and very "tight," that is, they are hard to separate. They must be separated, however, either for the recycling of the oil or for the purpose of disposal.

Conventional methods of demulsification, such as chemical addition or heating, do not always work and moreover the added chemicals can also harm the environment. An alternative method of demulsification has been developed by Klaila[78] and Wolf.[79] This new technology uses microwave energy to speed up the demulsification of oil in an aqueous emulsion.

When an oil-water emulsion is heated by microwave radiation two phenomena take place simultaneously. The first is a reduction of viscosity as the temperature of the emulsion increases. The second, microwave-induced molecular rotation, neutralizes the zeta potential of emulsified oil droplets. Microwave radiation provides faster separation than does conventional heating. Fang et al.[80] presented results for laboratory and technical scale tests of this new technology. Figure 18 shows various percentage recoveries of vegetable oil from oil-water-diatomaceous earth emulsions by microwave and by conventional heating. The microwave energy appears to heat the sample faster. Furthermore, at the same temperature, it provides a better separation of oil from the emulsion than conventional heating. The oil recovery at room temperature was very poor, no separation of the emulsion being observed in the first 60 min.

In one field test 120 barrels of slop oil (emulsion of 50% of oil, 22.5% bottom sediment, and 27.5% water) were placed in a large tank as shown in Figure 19 and microwaved for 10 h at 20 kW of power. The temperature in the tank rose to about 35°C, and no water was found in samples drawn from sampling lines 2 through 6. It is worth noting that this mobile system is completely self-contained and can be used in remote areas.

Microwaves were also used for the liquifaction of sandy tar formations in Athabasca (Alberta, Canada).[81] These formations consist of a granular matrix of mostly quartz with some kaolinite and illite, the interstitial space being occupied by water and tar. Athabasca tar sand contains approximately twice the conventional world oil reserves. The tar is recovered on site by heating to between 50 and 100°C.

The traditional techniques of conduction or hot gas injection are not satisfactory, and microwave and RF[82] (longer penetration ranges) heating seem to achieve much better results than classic methods.

C. Microwave Catalysis

Selectivity of energy deposition by microwaves was utilized in a heterogeneous catalytic reaction by J. Wan et al.[83-86] The basis for this technology is that materials having a high dielectric loss factor can be

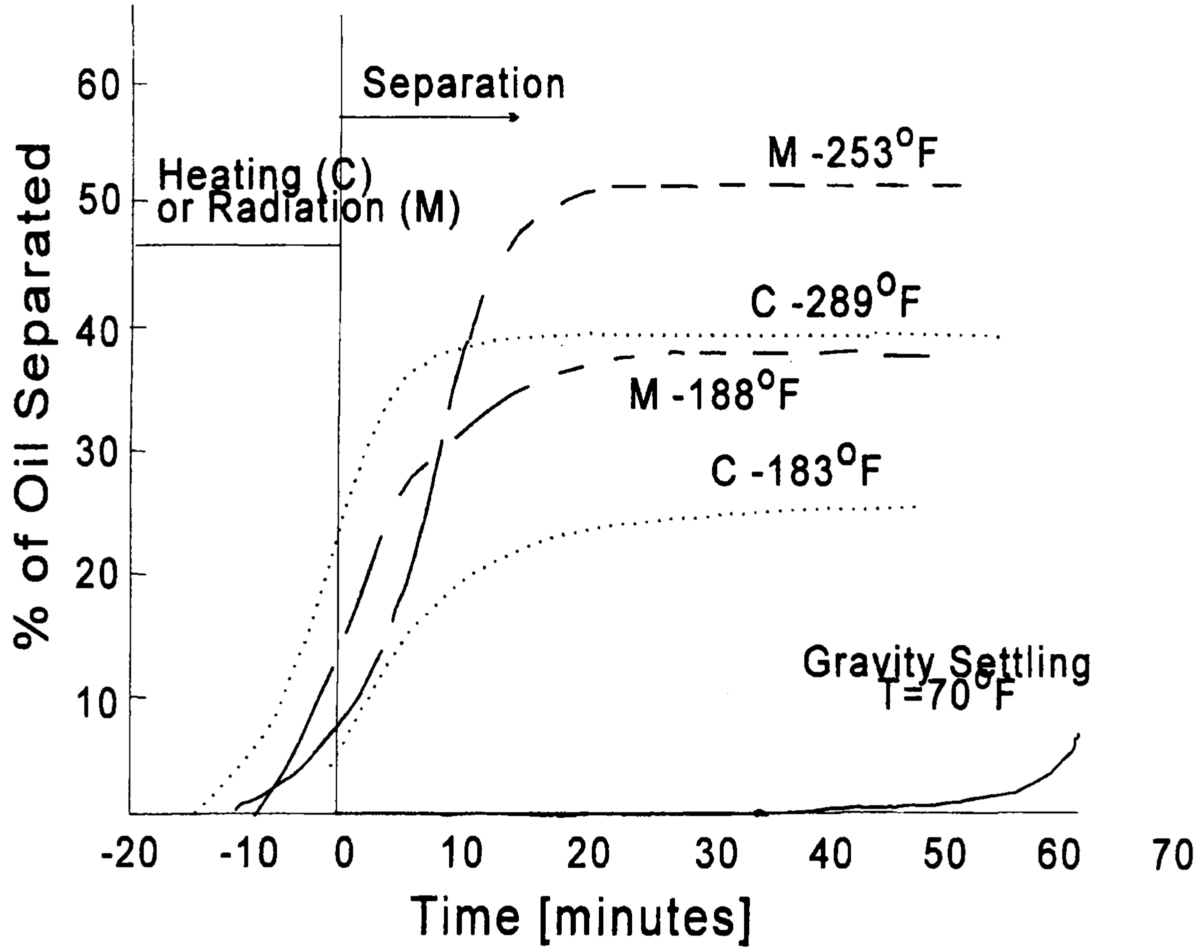


FIGURE 18. Separation of a vegetable oil-water emulsion. (From Reference 80. With permission.)

heated rapidly by microwaves and to a very high temperature, even if they are surrounded by other less lossy substances. This, plus extremely fast temperature control, achieved by switching the microwave radiation on and off, allows for very selective heating of the catalyst whose purpose is principally to focus the microwave energy, thus providing a hot surface on which reaction may be induced. Because the heating is extremely fast, the bulk of the reagent material not in contact with the catalyst surface remains at or near ambient temperature. This serves to limit desorption of the reagent from the catalyst surface, precluding the need for high-reaction pressures in the gaseous region, as well as limiting unwanted side or back reactions. This approach was used in the conversion and oxidation of methane,[83] the conversion of CO_2 to methane,[84] the decomposition of polychlorinated hydrocarbons,[85] and the decomposition of bitumens[86] utilizing nickel and copper wire mesh or powder as a catalyst and microwave energy receptors. Other work includes oxidation of 1,1,1-trichloroethane over silicon carbide as a microwave receptor[87] and pyrolysis of neopentane on a microwave-irradiated molecular sieve X-13.[88]

D. Reduction of SO_2 and NO_x Emission by Microwave Radiation

Microwaves were used by Blum et al.[89] for the purification of coal by reducing its

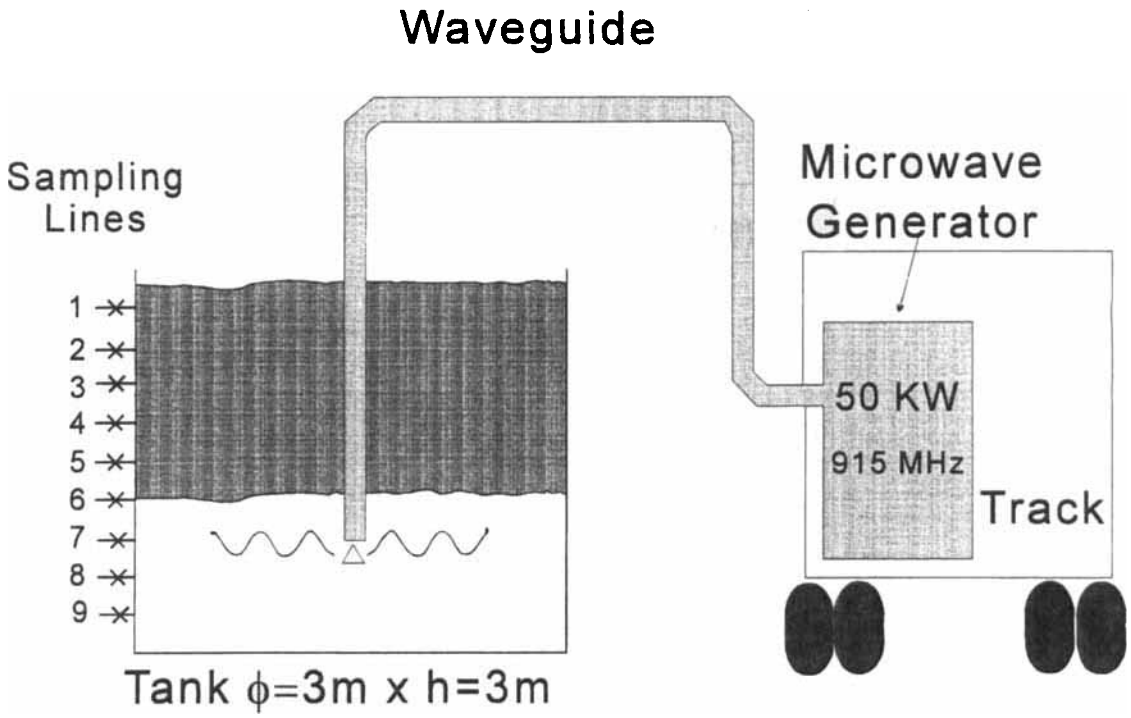


FIGURE 19. Apparatus used in field test of slop oil separation. (From Reference 80. With permission.)

ash and sulfur content. Microwave irradiation of between 30 s and 3 min took place in an inert atmosphere between an alkaline solution treatment and an acid water rinse. The relative reductions in ash and sulfur content were 98 and 66%, respectively. The mechanism exploited in this treatment is not fully understood.

Chang-Yui Cha[77] used microwave energy to remove NO_x from flue gas by a two-step process. First, NO_x is adsorbed onto a carbonaceous material, then the NO_x-laden carbon is irradiated with 2.45 GHz microwave energy, producing N_2 and CO_2. The char was recycled to adsorb more NO_x until it is consumed. Simple, classically heated regeneration of char produced NO_2 and NO, but when microwaves were used to irradiate NO_x adsorbed on char, the NO_x converted to N_2 and the carbon on which it was adsorbed was converted to CO_2. The conversion efficiency was typically better than 99%. A second advantage of the microwave-char process was that starting with char that has a surface area of approximately 7 m^2/g, after about 20 cycles of use, the surface area increased to nearly 700 m^2/g, which is in the range of activated carbon. Therefore, this NO_x abatement process can actually produce a valuable byproduct while a serious pollutant is destroyed.

E. Microwave Spaller for Concrete Decontamination

The use of microwave radiation for crushing rock and concrete is a relatively old application.[90] Concrete contains capillary water as well as water of crystallization, whereas rocks contain at least some water of crystallization. In addition, these are materials having a significant dielectric loss factor. It is therefore possible to use microwave irradiation to produce rapid heating that leads to development of internal thermal stresses that in turn generate microscopic fractures. The material thus fractured readily falls to pieces.

This approach was used recently by White et al.[91] at the Oak Ridge National Laboratory for the removal of the top few millimeters of a concrete contaminated by ^{235}U and ^{238}U.

Classical decontamination technologies use impact breaking, mechanical chisels, a high-pressure water spray, or steel shot blasters. Although these technologies can very rapidly remove a contaminated surface layer, they produce large amounts of dust that must be contained and removed. Water used produces a secondary waste stream that will require subsequent treatment. Water can also solubilize some contaminants, driving them deeper into the concrete.

The microwave spaller used by the researchers at Oak Ridge National Laboratory produced particles in the range of 1 to 10 mm. Fewer than 1% of the particles were <1 mm. Therefore, airborne contamination was not a significant hazard. The best concrete removal efficiency was achieved using 10.6 GHz frequency with a power of 3.6 kW directed by a 35.5 × 7 cm applicator. Microwave irradiation of 2.45 GHz failed to remove concrete efficiently. Based on these experiments it was concluded that at the higher frequency, heating is faster and more effective. Future work involves optimization and scaling equipment and developing a mobile unit for an actual decommissioning demonstration.

F. Microwave Vitrification of Radioactive Waste

Incorporation into a suitable glass is a well-established process for conditioning waste contaminated by long-lived radioactive elements, but radioactive waste is often too corrosive for furnaces or crucibles when processing temperatures of about 1100°C are used. Aubert et al.[92] have developed a new process for melting radioactive ashes in a microwave waveguide. The monomodal waveguide was cooled by circulating water in a cooling jacket, thus creating a cold glass layer that protects the waveguide against corrosion. Because heat for melting cannot be taken from cooled furnace walls, it was generated directly in the ashes by microwaves. Two furnaces of this type are operated by the French Atomic Energy Commission: a 2.45-GHz, 6-kW pilot plant with a capacity of 3 kg/h and a 915-kHz, 25-kW pilot plant with a capacity of 10 kg/h.

Another method for solidification of radioactive waste has been proposed by Petersen et. al.[93,94] The waste was loaded into 30-gal stainless steel drums connected to a waveguide from a 915-kHz, 60-kW microwave generator, allowing the interior of the drum to become a part of the resonant cavity. Microwave heating raised the temperature of the material inside the drum to approximately 1100°C causing it to melt. The advantages of this microwave treatment include the following:

- Selective heating of the waste eliminates thermal cycling which could lead to stress-related failure of the process equipment.
- The "in-drum" process eliminates the need to transfer the final waste to another container.
- The equipment is inexpensive and easily maintained. Only the drums are in contact with radioactive materials.

A full-scale system based on these principles has been in operation at Rocky Flat Nuclear Plant since 1991.

Jantzen and Cadieux[95] compared the microwave and conventional thermal vitrification of radioactive wastes. The results of these tests demonstrated that microwave fusion required a shorter process time, 10 to 15 min, and produced a more homogenous glass phase than conventional thermal processing, which required 4 h. The improved homogeneity observed for microwave vitrification was attributed to rapidly induced convection currents.

VI. CONCLUSIONS

As can be seen from the above examples, the unique ability of microwave radiation to induce a variety of physical and chemical phenomena can play an increasingly significant role in the development of new and existing technologies in analytical and environmental chemistry. It is clear that in certain circumstances, the use of microwave radiation can greatly speed up the extraction procedure that is a necessary prelude to many analytical techniques. Care must, however, be taken to ensure that the irradiation does not cause the chemical loss of the targeted molecule. The maturity of microwave generators, especially designed for a given application, and the improved communication among chemists, microwave, and electrical engineers that takes place (e.g., at the International Microwave Power Institute Symposia) should lead to further advances of this relatively new area of science and technology.

A few related topics were not discussed here. These include microwave plasma, microwave drying, polymerization, sintering, or microwave-induced distillation. The applications that were described provided only a part of the story, in part because many manufacturers and developers of microwave technologies tend to be secretive due to the great commercial potential of their microwave technique.

ACKNOWLEDGMENTS

The author greatly appreciates the valuable discussions and helpful manuscript review by Professor Dr. John L. Holmes and gratefully acknowledges the financial support provided by the Environmental Technology Centre of the Environment Canada during work on the discussed subject.

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