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Exploratory Studies in the Use of Microwave Radiation to Assist the Extraction of Pollutants from Various Matrices

by Andrzej Zlotorzynski

A thesis submitted to the School of Graduate Studies
in partial fulfillment of the requirements for
the degree of Master of Science
in the Department of Chemistry
University of Ottawa
Ottawa, Canada

February, 1994

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Abstract

The microwave assisted extraction of organic contaminants from heterogeneous environmental solids was investigated.

The mechanisms for the interaction of a microwave field with matter, and the basic equipment used in microwave processing are presented in Chapter 1, followed by a review of the publications dealing with applications of microwave energy to chemical and environmental problems.

Results from the investigation of the role of different soil properties such as water content, static dielectric conductivity, pH and soil composition on the deposition of microwave energy into the soil are presented in Chapter 2. It was found that water content is the most important factor in the transfer of microwave energy to the soil structure. The first portion of water added, adsorbs on the soil surface very strongly and the microwave field cannot move these adsorbed water molecules. As the water content increases, excitation of the loosely bound outer layers facilitates the transfer of microwave energy to the soil-water system. Other soil parameters have a insignificant role in the soil microwave heating when appliance grade microwave ovens (2.45 GHz, low energy density) are used.

Chapters 3 deals with the extraction of pentachlorophenol (PCP) from soil. It was found that water present in the soil significantly improves extraction recovery of PCP from soil. A simple extraction with water, acetonitrile and mixing action, proved to be fast and the most effective method for quantitative recovery of PCP from a spiked soil. This simple process can also be used in the case of environmental emergency. Recovery

of PCP with microwave assisted extraction provided no enhancement. An explanation for this is provided in Chapter 3.

Chapter 4 presents results of the microwave assisted extraction of polycyclic aromatic hydrocarbons from the surface of an activated carbon. Changes in the composition of aromatic solvents in the presence of charcoal and microwave field was noted, probably resulting from free radical reactions. This poses possibly serious problems for the use of microwave radiation as a means for recovering compounds adsorbed on activated carbon.

Acknowledgments

I wish to express my sincere gratitude to Professor John Holmes, my research supervisor, for his generous help, guidance and support throughout the course of this work. The scope of this project was outside of his main research interest, but Dr. Holmes was willing to undertake this difficult task and provide much professional advice. For not only is he an outstanding scientist and educator but he also is a person of very humane personality, ready to support his students in all aspects of their professional career. I would like to express my special thanks to Dr. John Holmes.

As a graduate student of the University of Ottawa, I was given the opportunity to do the research necessary for this dissertation at The Environmental Technology Centre of Environment Canada (ETC). This has been a very positive and rewarding experience. The research laboratory in which I have been working has an atmosphere of excellence and state-of-the-art analytical equipment. During my stay at Environmental Emergencies Science Division I was able to meet many outstanding scientists, two of whom are my co-supervisors; Mervin Fingas and Jocelyn Paré.

Mervin Fingas has provided me with the freedom to explore and learn. Above all I am indebted for his readiness to accept me into his group and generous financial support from Environment Canada.

Jocelyn Paré has helped me to understand how important and fruitful a microwave technique can be. His passion and persistence in promoting microwave technologies has guided me during of all critical moments in the course of my work in the Environmental Technology Centre.

Over my two years stay at ETC I have come to appreciate the community in which I worked. There are a number of people whom I would like to

acknowledge for their helpful discussion, input, and friendship. These people are my fellow graduate students Marc Lafontaine and Christiane Aubry, and staff of Environmental Technology Centre namely Jacqueline Bélanger, Martine Bissonnette, Tim Caron, Mike Landriault, Ken Li, Lise Sigouin and Zhendi Wang; true experts of environmental analytical chemistry, always ready to help, despite their busy schedules.

I would like to express my gratitude to the members of my family and all my friends on both sides of Atlantic for the ongoing care and warmth which they have offered me over the years. Finally this thesis would not have started and reached an end, if I has not had the good fortune to be married to Ewa and to be the father of Maria.

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Chapter 1

1. Theoretical Bases of Microwave Heating

1.1. 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, but from the first article published by Adel Abu-Samra *et al.* [1] in 1975 it took ten years to really spark the wide interest of the analytical chemistry community in the application of

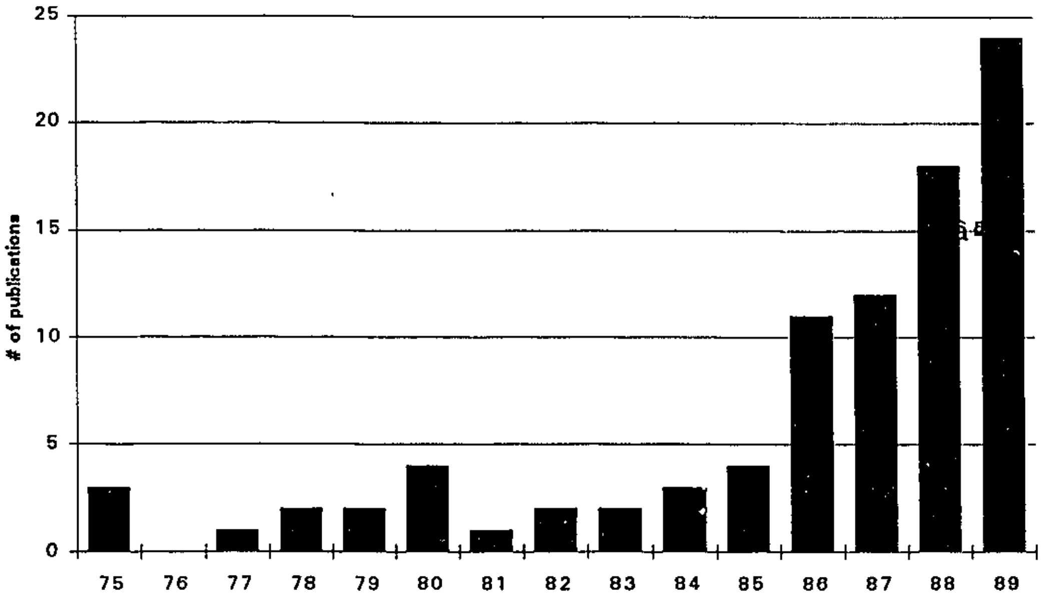


Fig 1.1. Annual literature citation (excluding conference abstracts) on microwave sample digestion [2]

electromagnetic energy to sample preparation. Data presented in **Fig. 1.1** 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 19-th century and large-scale facilities using dielectric heating (up to 10^8 Hz) were in operation in the first decades of the 20-th century [3]. However the first compact and simple microwave ovens were only available in the fifties [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; conduction, radiation and convection. The average prospective user of microwave equipment has no knowledge of microwave fundamentals and the properties of processed materials. The designers of the microwave equipment, electrical and telecommunication engineers, are lacking in 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:

"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 chapters deal with the interaction of microwaves with matter and with microwave equipment requirements for chemical laboratories. Then follows a review of current publications dealing with the application of microwave energy to environmental and analytical chemistry.

1.2. Macroscopic Properties of Dielectric.

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 Munchausen device requires of course, a variety of equipment for its practical realization in order

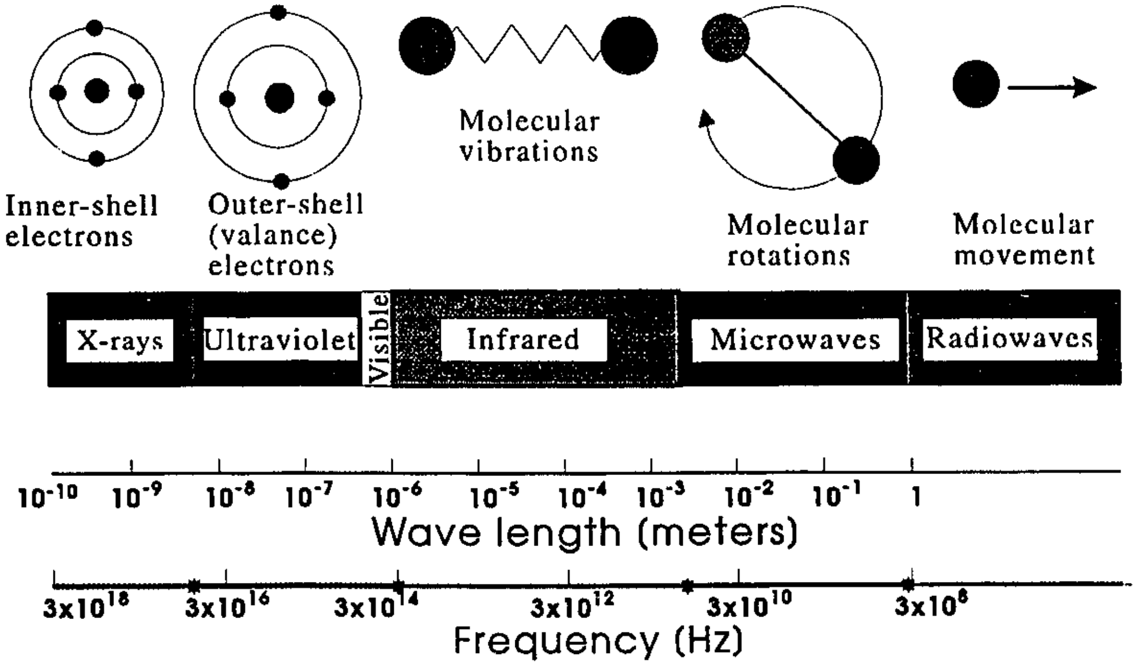


Fig 1.2. Electromagnetic spectrum

to cover the whole frequency range. The electromagnetic spectrum is shown in **Fig. 1.2**.

A condenser or a coil is used for frequencies from 0 to 10^8 Hz (radio frequencies). In the microwave region from 10^8 - 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 (IR, 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 become comparable to the incident wavelength, and so the interference technique can be used to measure dielectric properties of the materials in this frequency range.

1.2.1. Complex permittivity

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

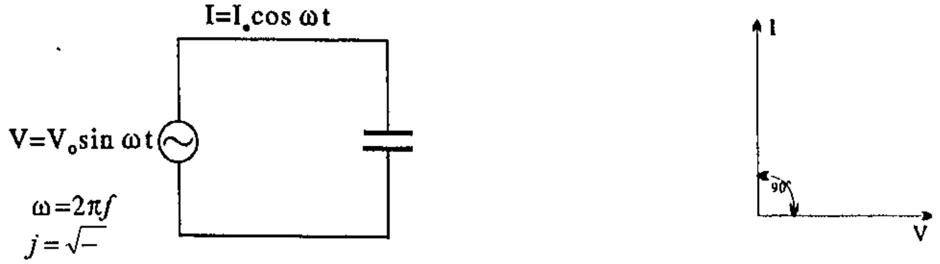
$$Q = C_0V = C_0V_0\sin \omega t$$

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 $2\pi f$.

This condenser draws a charging current I_c, given by

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

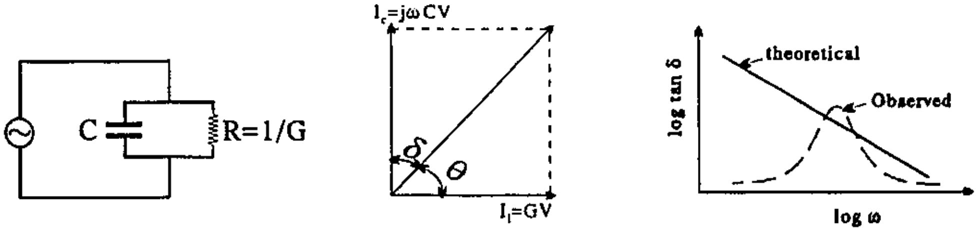
The current is out of phase with the voltage by 90°. C_0 is the vacuum capacitance of the condenser. When filled with some substance, the condenser increases its capacitance to $C = C_0\ \varepsilon'/\varepsilon_0$ where ε' is called the *real permittivity* (often called dielectric constant, but note that this "constant" is a function of frequency and temperature) and ε_0 is a free space permittivity $\varepsilon_0 = 8.85$ pF/m.



$$V=V_0\, e^{j\omega t} \qquad I_c = \frac{dQ}{dt} = j\omega C_0 V \qquad C = C_0\frac{\varepsilon}{\varepsilon_0} = C_0\varepsilon'$$

Fig. 1.3. Electric model of ideal capacitor.

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 **Fig 1.4**.



$$I_l=GV \qquad I=I_c+I_l=(j\omega C+G)V \qquad \tan\delta = \frac{I_l}{I_c} = \frac{1}{\omega RC} \equiv D$$ - *Dissipation Factor*

Fig 1.4.. Electric model of a capacitor with loss

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 is equivalent to a dielectric conductivity $\sigma = \varepsilon''\omega$ and numerically expresses all dissipative effects; the conductivity 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 Happel Dielectric and Waves [7].

Examples of materials having different dielectric loss factors and different permittivity are shown in **Table 1.1**.

Table 1.1. Dielectric Permittivity and Dissipation Factors of Different Materials at Frequency 3 GHz and Temperature 25°[7]

Material	ε'	ε''	**tan δ x 10^4**
Ice	3.2	0.00288	9
Water T=25^{0}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	10000
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 data presented in **Table 1.1** 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 energy. The dielectric loss factor can be calculated from "dielectric constants" only when the values of dielectric permittivity are known in the whole frequency spectrum.

1.3. 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] 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 which 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, because we shall mainly concern ourselves with dielectric effects associated with molecular movement, for which classical 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 **Fig.-1.5**.

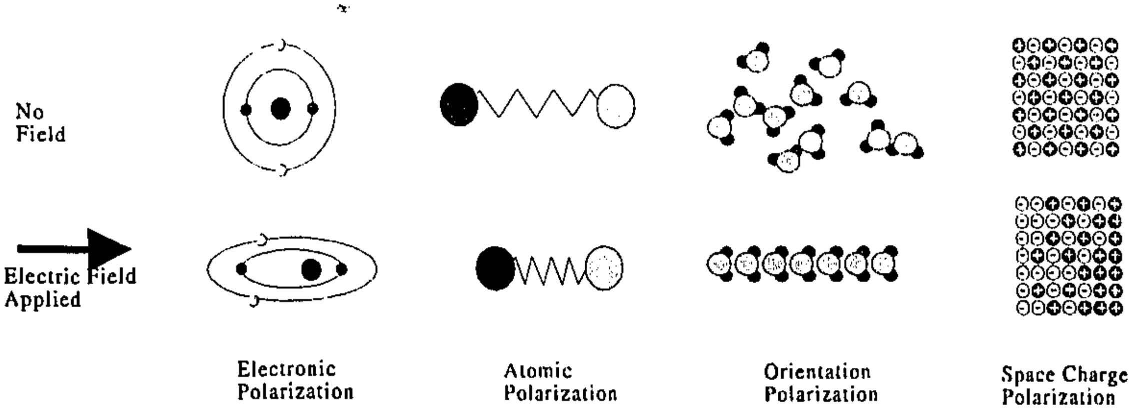


Fig 1.5. Mechanisms of polarization.

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 radio 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.

1.3.1. 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

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

where ξ is a coefficient depending on the size of the molecule and its intermolecular attraction forces. For a spherical molecule of 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 $\omega >> \frac{2\pi}{\tau}$. These values, $\varepsilon'_s$and ε'_∞, are often called the static dielectric constant and optical dielectric constant respectively. The loss factor ε" has a maximum when ω = 1/τ. A classical Debye plot is presented in **Fig 1.6.**

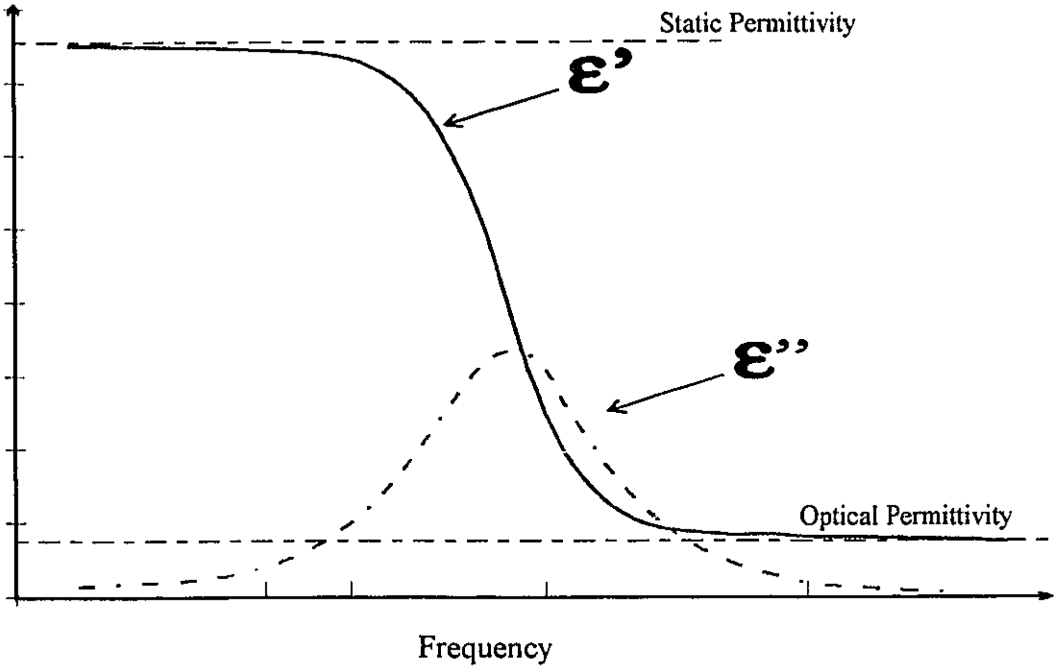


Fig 1.6. Real and imaginary components of dielectric permittivity as a function of frequency. (Debye plot)

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 which the molecule has to cross in the process of reorientation.

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

where τ_0 is a relaxation time calculated from Debye equation and U is a value of the potential barrier which 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 **Fig. 1.7**.

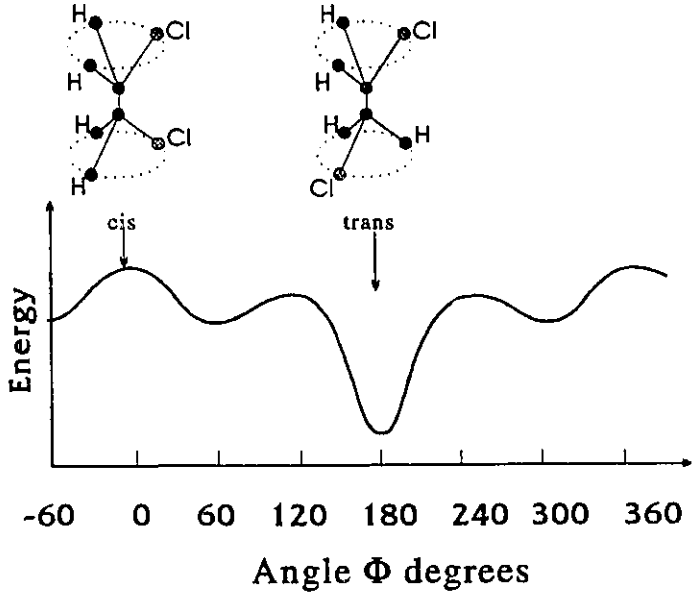


Fig. 1.7.. Orientation of dipoles in the molecule of 1,2 dichloroethane.

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 be 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, but long-range phenomena, such as interaction within a crystal lattice or interactions between long-chain molecules, can have a big impact on the relaxation time (the frequency with maximum efficiency of conversion of electromagnetic energy to heat energy). Other complications can arise for macromolecular or conducting systems as a result of the Maxwell-Wagner effect. The simple mechanical model derived by Debye can no longer explain, by the introduction of a simple microscopic relaxation time, all processes occurring during electromagneticly induced molecular rotation. The value of the relaxation time is no longer singular, but is distributed around the central value τ. **Fig. 1.8** shows a Debye plot for vulcanized rubber plus the theoretical function of dielectric permittivity and dielectric loss calculated from the Debye equations.

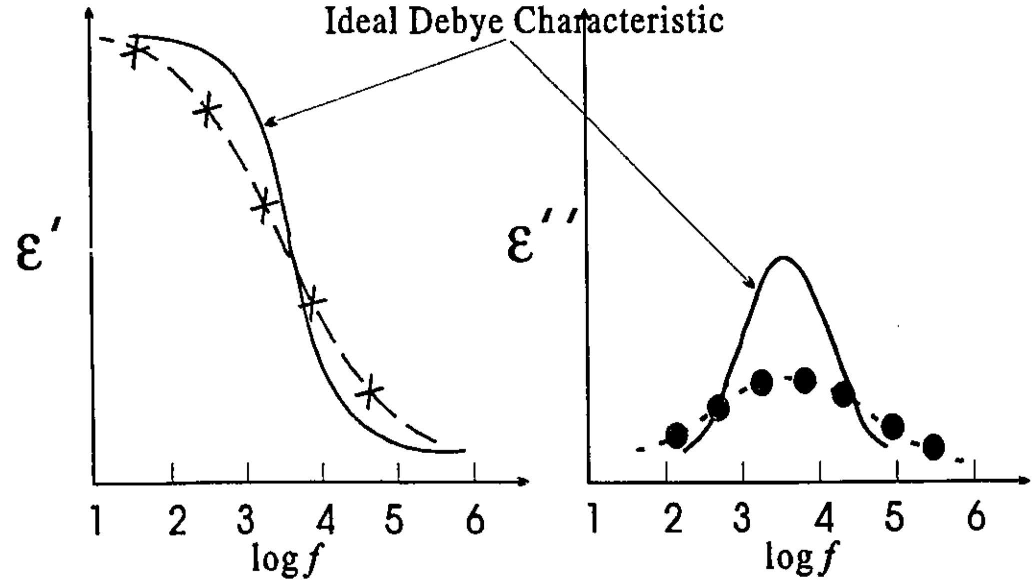


Fig. 1.8.. Dielectric permittivity and dielectric loss of vulcanized rubber as a function of frequency.

1.3.2. 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:

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

where λ_o 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 **Fig. 1.9**.

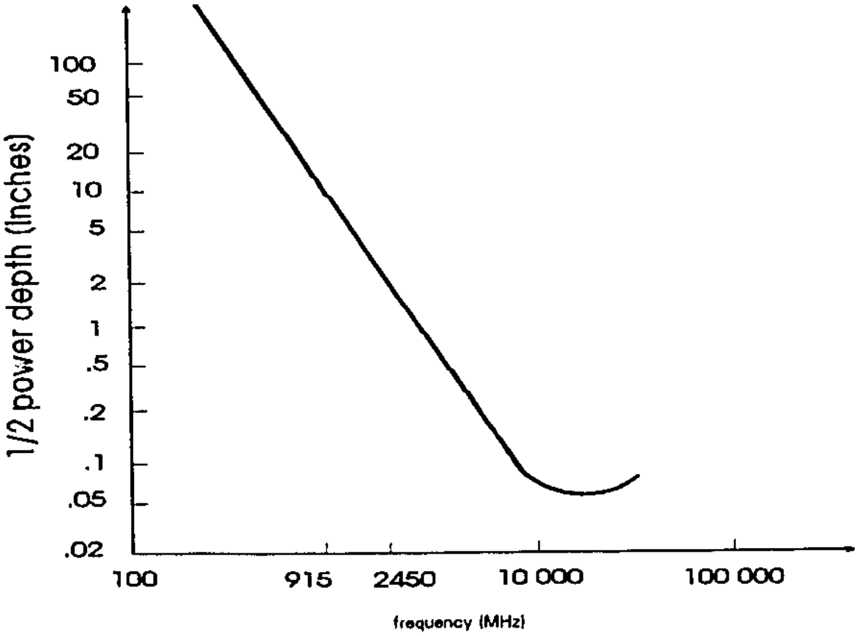


Fig. 1.9. Variation of the penetration depth with frequency for water at 25°C [14].

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 inside the volume 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 Hz.

This type of heating can be realized only by electromagnetic heating in the microwave and radio frequencies (RF), other forms of electromagnetic radiation have a penetration depth too small 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 dielectric 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.

1.3.3. 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 the temperature. Solids' dissipation factors 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 microwave field of "microwave transparent" materials such as fused quartz or PEEK (polyetheretherketone) [17]. Detailed analysis of thermal runaway can be found in a paper by Roussy *et al.* [18].

1.3.4. 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 heated object can be heated without mediation of conductive heating and usually temperatures inside of heated materials are much higher than near to the surface, especially for solids with low thermal conductivity. 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 the most of the microwave heating applications, the microwave 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 both 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. In 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 processed material.

Graphic presentation of this aspect of microwave heating is presented in **Fig. 1.10**.

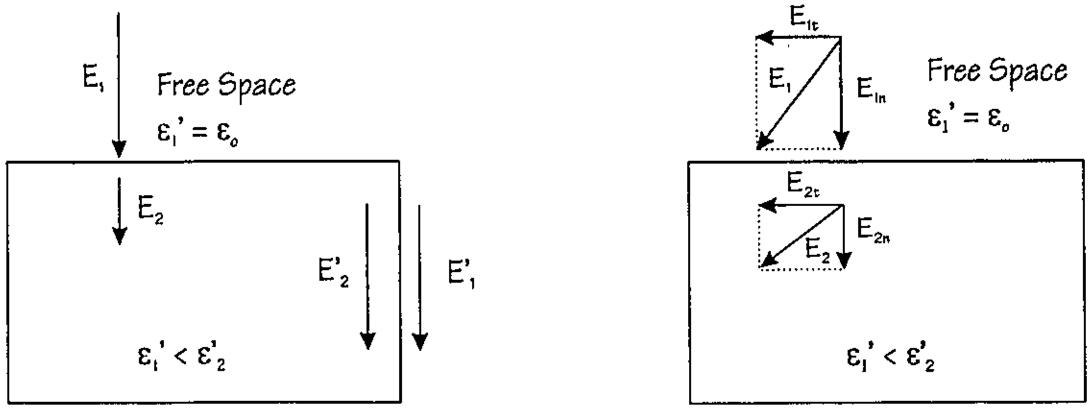


Fig. 1.10. Bending of microwave field on the phases boundary.

From the observation of the bending of a microwave frequency field, it is expected 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 centre. For more complicated shapes the distribution of the electromagnetic field inside the processed object can be very complicated and some places can receive much more energy than others.

In addition, predicting 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 were produced which burned carbonized spots placed 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 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 processed material 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. In homogeneous materials which 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 in the form of spherical particles in 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 simple examples show how complicated can be the prediction of the distribution of electromagnetic energy inside a processed material, and how different microwave heating is from classical means. Unlike classical modes of heating, microwave processing of materials is very dependent on the shape and the size of the irradiated objects.

1.4. Equipment for electromagnetic heating.

1.4.1. Frequencies used for electromagnetic heating.

Microwave and radio frequencies 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 this purposes (ISM bands) are given in **Table 1.2**.

Table 1.2. ISM Bands [21]

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

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 radio frequency are most often used for industrial (large scale) electromagnetic heating. Applications which use frequencies from outside the band allocated for non-telecommunication or RADAR have to be properly shielded in order for the radiation not to leak outside the applicator.

1.4.2. 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 (<400W) power transmission. When the applicator is a cavity, it is coupled to the transmission line by an antenna-type junction. There are two main types of generators of microwave energy; 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 phones has led to the construction of compact and very reliable power amplifiers generating 400 W of microwave energy in the frequency range of 900-915 MHz [22].

There are two types of vacuum tubes; linear beam tubes (Klystrons or Traveling Wave tubes) and cross field tubes (Magnetrons).

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

Traveling wave tubes (TWT) can generate very wide bands of microwaves. They are used mainly in RADAR jammers or for medical diathermy equipment. A traveling wave tube 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 United Kingdom 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.

1.4.3. 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 the anode and the cathode. The presence of a strong magnetic field causes the electrons to follow curved paths spiraling away from the cathode.

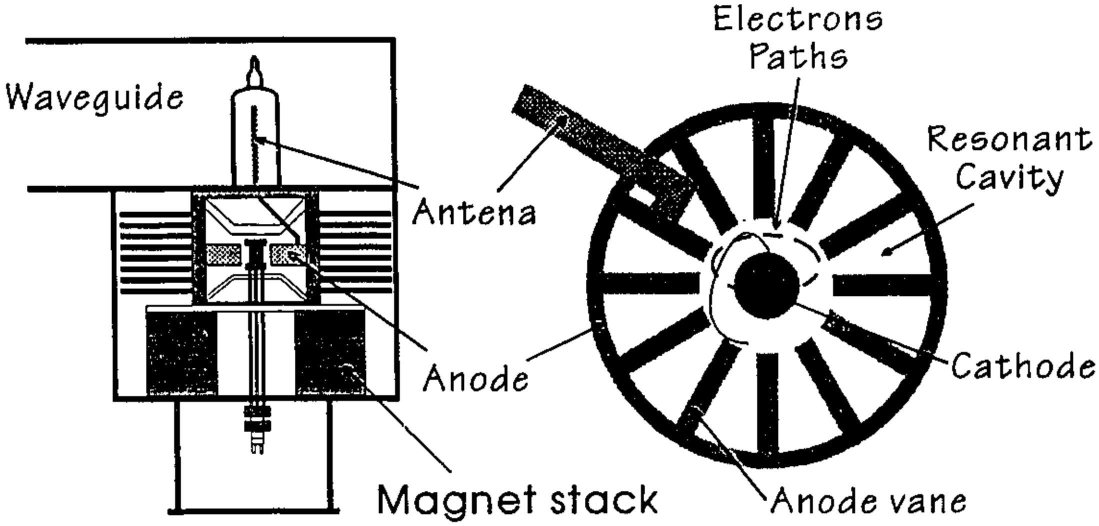


Fig. 1.11. Schematic diagram of the magnetron.

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.

(i) Electrons are accelerated by the RF field, experiencing a greater "curling force" and are accelerated back to the cathode, or

(ii) 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 **Fig. 1.11**)

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 60-65%. 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 system.

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 10-30 seconds. 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 one minute. In order to overcome this, short pulsed systems have a continuously heated cathode.

1.4.4. 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 designs 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 to 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 while 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 also 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 **Fig. 1.12**.

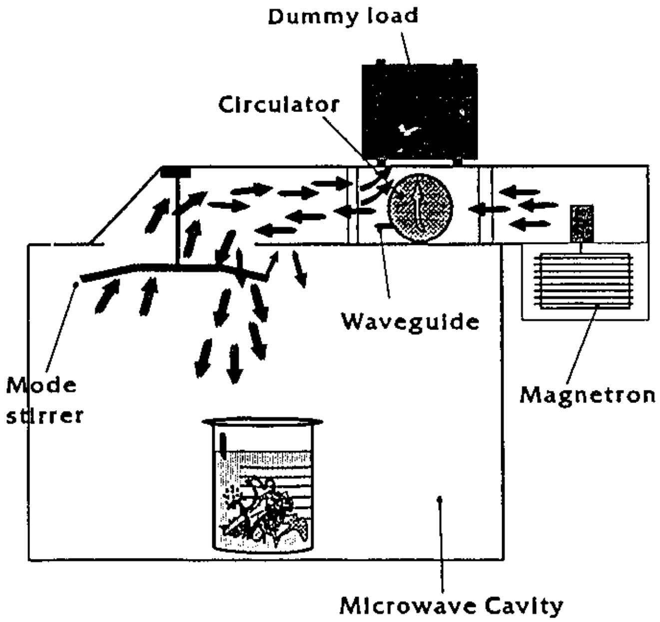


Fig 1.12. Schematic view of the microwave oven

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 in relation 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. In order to prevent this a circulator (a three way 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. **Fig 1.13** illustrates the decrease in the amount of absorbed microwave energy with decrease in the water sample size.

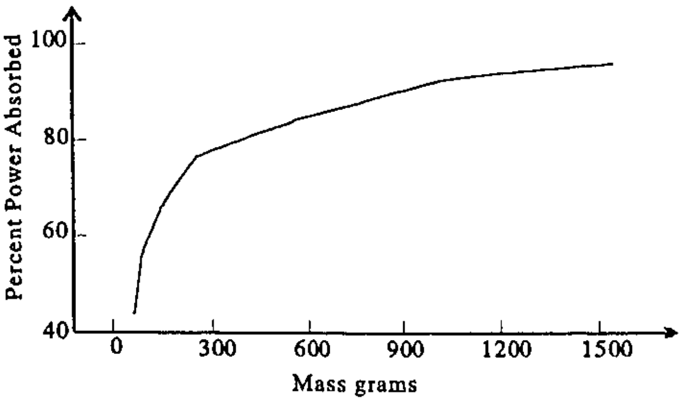


Fig 1.13. Percentage of microwave power absorbed by water in appliance grade microwave oven [25].

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 references concerning the utilization of appliance grade microwave ovens in a chemical laboratory are [27-33].

1.4.5. Applicators with Single Mode Cavity

When the materials which are being processed by a microwave field are poor absorbers of microwave energy or are only available in small amounts, the multimode microwave oven no longer represents 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 **Fig 1.14**.

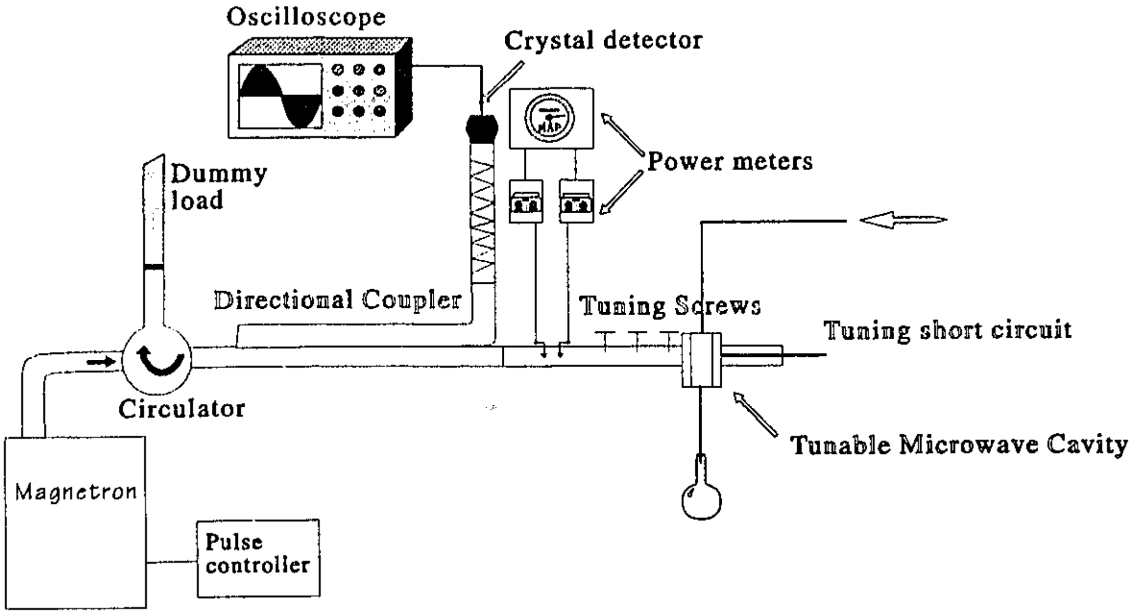


Fig 1.14. Single mode, resonant heating system.

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 is 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.

The efficiency of matching can be controlled by measurement of the forward and reflected power by a network analyzer. Since 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 small power. Further information about utilization of microwave resonant cavities in chemistry can be found in [35-38].

1.3. 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.

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

1.3.1. Microwave Digestion for Elemental Analysis.

Microwave assisted mineralization of samples for elemental analysis has been established as a routine, well developed technique. Since the first experiments carried out by Samra [1] in 1975, the application of microwave energy for digestion of a wide range of matrices has been investigated. A recent literature review [39] has 163 citation of papers 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.

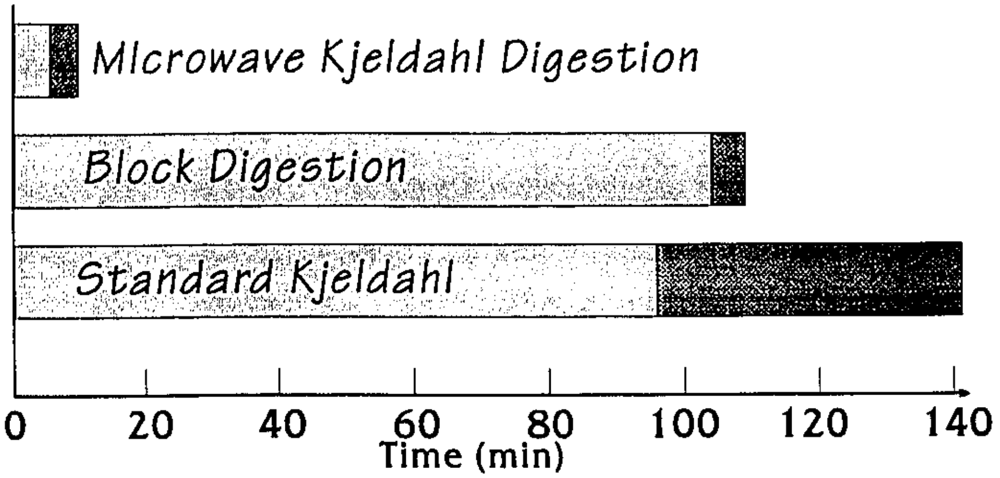


Fig 1.15. Comparison of digestion times for the microwave and standard Kjeldahl digestion methods [41].

Other reviews of methods of microwave dissolution are by Matusiewicz and Sturgeon [2] and by Sinquin *et al.* [40]. All published reports show a substantial speed-up of the microwave digestion compared with classical 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 **Fig 1.15**. One reason for such a remarkable development of microwave sample dissolution is the availability of specialized microwave ovens designed for such applications. Both types, multimode and resonant cavity microwave ovens are on the market. The book edited by Kingston and Jassie [41] has had a significant impact on the attitude of analytical chemists towards microwaves as an alternative source of energy.

1.3.2. Organic Synthesis

The application of microwave ovens to organic synthesis was initiated by Gedey *et al.* [42] in 1986 and another early report was published by Giguere [43]. Since then a wide range of organic reactions have been successfully conducted with microwave irradiation. Literature reviews can be found in references [44-46]. The time necessary to complete most organic 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 (120-J·mol^{-1}), less than Van der Waals bond 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 collapse 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 having appeared in the literature in the past year, this debate is becoming better resolved [47], [48] and 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 *et al.* [49] has the potential to be able to more precisely monitor the microwave irradiated systems.

1.3.3. Microwave Catalysis

Selectivity of energy deposition by microwaves was utilized in a heterogeneous catalytic reaction by J. Wan *et al.* [50-53]. The basis for this technology is that materials having a high dielectric loss factor can be 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. Since 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 [50], the conversion of CO_2 to methane [51], the decomposition of polychlorinated hydrocarbons [52] and the decomposition of bitumens [53] 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 [54] and pyrolysis of neopentane on a microwave irradiated molecular sieve X-13 [55].

1.3.4. 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.* [56-58]. Samples were ground and mixed with an appropriate solvent, and the resulting suspensions were irradiated with 2450 MHz microwaves for 30s 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 1.3.**

Table 1.3. Comparison of the Recovery Obtained and Time Required in (a) the Traditional and (b) Microwave Assisted Extraction Methods [57]

Compound	**Recovery %**		**Time Needed**	
	a	b	a	b
Crude Fat from Food	100	98	> 3 h	< 5 min
Antinutritives from Fava Beans	40	100	> 3 h	< 5 min
Pesticides from Soil	90	100	> 1.5 h	< 1 min

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 which could be found in the corresponding Soxhlet extracts. This method could be also suitable for the fast extraction of 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.* [59]. 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 minutes of microwave irradiation had no qualitative differences compared with the mixture obtained by 1.5 hours 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.* [60] 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 (10-20s) to 2450 MHz irradiation. The microwave technique is rapid, requires only 10 minutes for the final eluate preparation after the sensitized red blood cells are washed. Conventional methods take from 1 to 1.5 hours to obtain comparable results. The microwave assisted extraction of antibodies from the surface of red blood cells was also investigated by Torloni *et al.* [61].

In 1991 a USA Patent on Microwave Assisted Natural Product Extraction was issued to Paré *et al.* [62]. 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 by 30s microwave irradiation is comparable to 1- 2 hours of steam distillation and the quality of the extracts has been reported to be superior to that obtained by traditional methods.

Rapid separation of stabilizers from plastics was studied by Freitag and John [63]. 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 3-6 minutes. The traditionally used Soxhlet extraction requires up to 16 hours to achieve the same recovery. The same approach was used by Jassie *et al.* [64] 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 .

In the 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 Dauerman *et al.* [65] 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 non-extractable from the soil. Further work [66] 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 [67] reported that 5 x 30s microwave assisted extraction of pesticides from sediments provided better recoveries than 8 hours 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.

1.3.5. Speed-up of Preconcentration of an Analytical Sample under a Microwave Field

Kuzmin *et al.* [68] 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 on 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 molecules. As a proof they presented the visible light absorption spectrum of Rhodium complexes in 1M HCl and glycol in the presence and absence of a microwave field. This is shown in **Fig. 1.16**

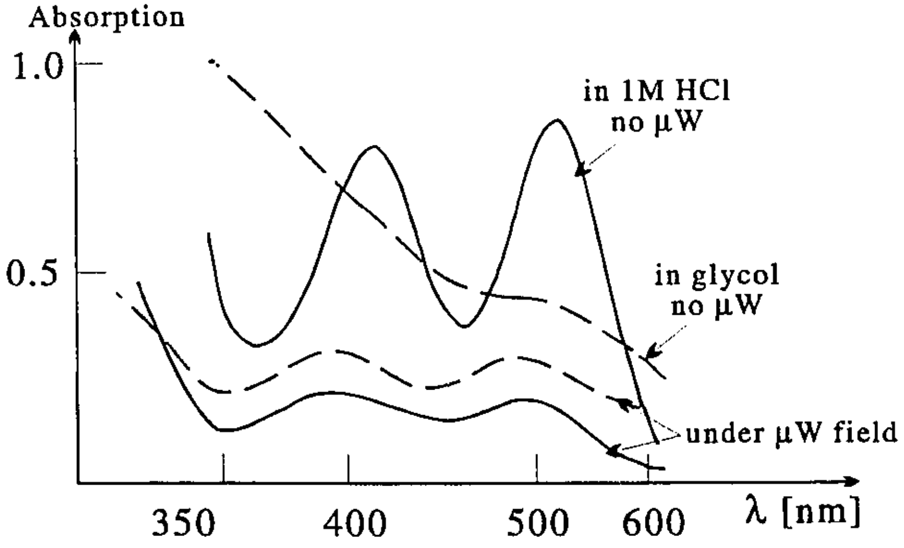


Fig 1.16. Spectrum of Rh complexes in 1M HCl and in glycol under a microwave field and without (C_{Rh} = 50 µg/mL) [68]

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.

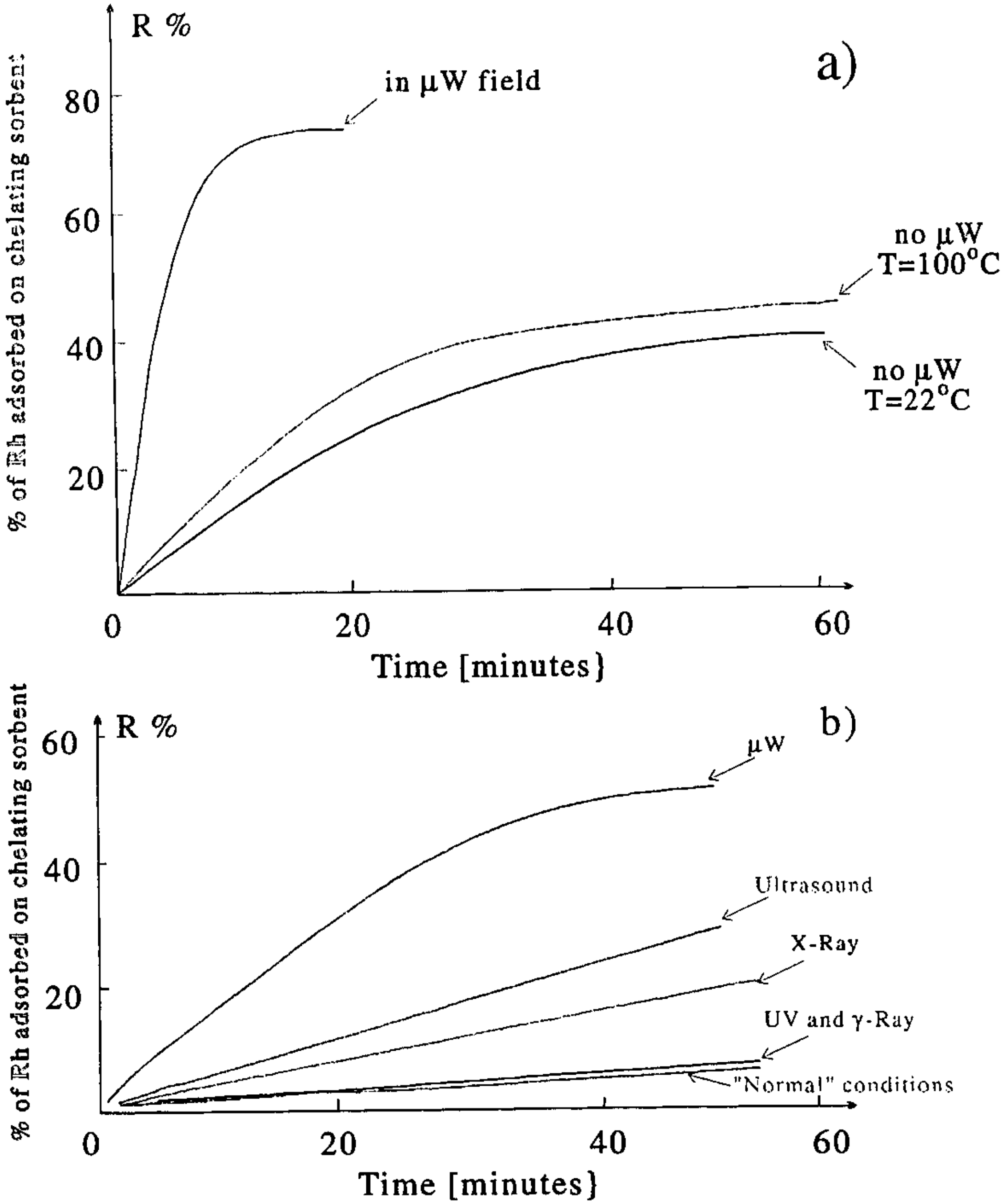


Fig. 1.17. % of the Rh adsorbed on chelating sorbent in function of time and a) temperature, b) different electromagnetic radiation plus ultrasound.

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 and so there is a different interaction between solvent and solute when the microwave field is in place.

The percentage of Rh adsorbed on a chelating sorbent as a function of time for different conditions is shown in **Fig. 1.17**. A substantial speed-up of adsorption of rhodium onto the chelating sorbent was achieved by microwave irradiation relative to conventional 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.

1.3.6. 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 GC, the fraction of the compound originally adsorbed that is analyzed is small. Thermal desorption is superior in this respect, since the whole amount collected is introduced into the gas chromatography column and detection limits therefore are 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 chromatographic column, mainly because of slow heat transfer within the packing. This difficulty can however be overcome by using microwave heating. In 1983 Rektorik took out a European Patent [69] on thermal desorption of solid traps by means of microwave energy. An adsorbing medium with a high dielectric loss factor - ε" (*e.g.*, active charcoal or graphitized carbon black) are 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 Rectorik in [70].

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.* [71]. They found that chromatographic peaks obtained by direct thermal desorption of an analyte onto the GC column are comparable to injection by syringe, but the method had some drawback, in that they noticed the formation of some artifacts. They suggested that artifacts are formed as a product of reaction of adsorbed oxygen with the charcoal, but because the new peaks have retention time 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.* [72,73] 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 a useful tool 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, can improve performance of the method.

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

1.4. Environmental Applications of Microwave Energy

1.4.1. 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 also 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. Since microwave and radio frequencies heat from the inside out, treated material can be heated without experiencing the "skin effect".

This approach has been the subject of several studies. Douerman and Wingasse [65,66,74] 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 by products and they are collected outside the system.

Compounds of lower volatility can successfully be removed by using a multiple stage distillation - the repeated addition of water followed by additional microwave treatments.

George *et al.* [75,76] 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 % wt. of water. Clay soil was found to be more microwave energy absorptive than sandy soil, thus yielding more rapid extraction rates of organic contaminants.

The same group [77] 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 the carbon. Since 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 to 310°C for PCP does not explain the differences in removal rates.

Dauerman *et al.* [65] 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 which postulated that as water was removed from soil aggregates, 9,10-anthraquinone is adsorbed directly on the humus and clay fraction. Further work however [66] showed that the non extractability 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. A detail discussion of the role of water in the extraction of contaminants from soil is presented in Chapter 3 of this thesis.

1.4.2. 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" *i.e.* 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 harm the environment as well. 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. **Fig. 1.18** 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 is very poor, no separation of the emulsion was observed in the first 60 minutes.

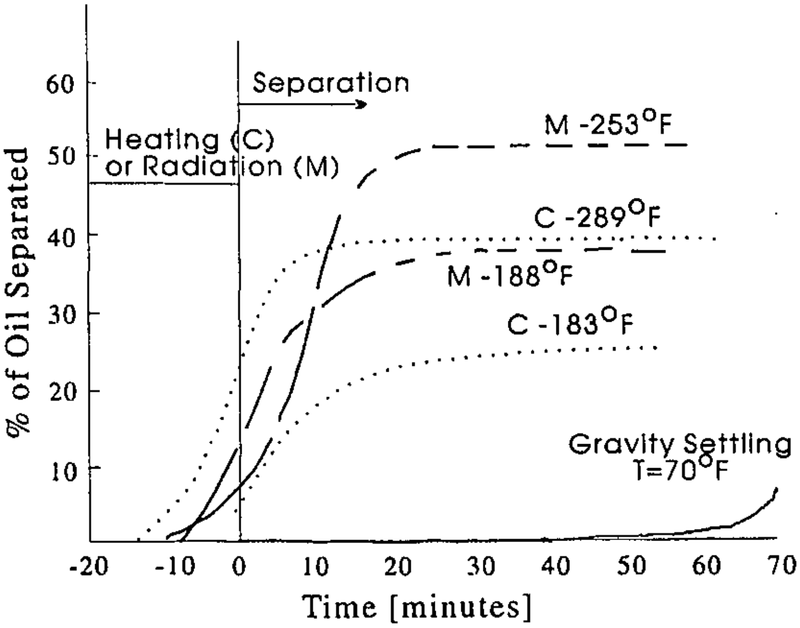


Fig. 1.18. Separation of vegetable oil- water emulsion [80].

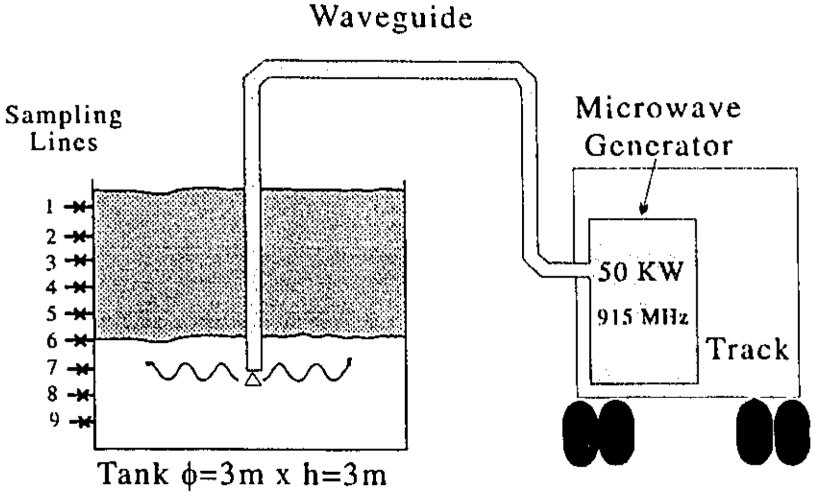


Fig. 1.19. Apparatus used in field test of slop oil separation [75].

In one of the field tests 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 **Fig. 1.19** and microwaved for 10 hours 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 Nos'. 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 sand tar contains approximately twice the conventional world oil reserves. The tar is recovered on site by heating to between 50-100°C.

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

1.4.3. Reduction of SO_2 and NO_x Emission by Microwave Radiation

Microwaves were used by Blum *et al.*[83] for the purification of coal by reducing its ash and sulfur content. Microwave irradiation of between 30 s and 3 min took place between an alkaline solution treatment and an acid water rinse. It is carried out in an inert atmosphere. 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 [84] used microwave energy to remove NO_x from flue gas by a two step process. First, NO_x is adsorbed onto a carbon material, then the NO_x laden carbon is irradiated with 2.45 GHz microwave energy, producing N_2 and CO_2. The carbon material is 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 is 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.

1.4.4. Microwave Spaller for Concrete Decontamination.

The use of microwave radiation for crushing rock and concrete is a relatively old application [85]. 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.* [86,87] 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. While these technologies can very rapidly remove a contaminated surface layer, they produce large amounts of dust particles 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 cm x 7 cm applicator. Microwave irradiation of 2.45 GHz failed to removed 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.

1.4.5. Microwave Vitrification of Radioactive Waste

Incorporation in a glass having suitable characteristics 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 approximately 1100°C are used. Aubert *et al.* [87] have developed a new process for melting radioactive ashes in a microwave waveguide. The monomodal wave guide is cooled by circulating water in a cooling jacket, thus creating a cold glass layer that protects the waveguide against corrosion. Since heat for melting cannot be taken from cooled furnace walls, it is 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.* [88,89]. The waste is loaded into 30 gallon stainless steel drums which are 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 raises 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 *et al.*[85] compared the microwave and conventional thermal vitrification of radioactive wastes. The results of these tests demonstrated that microwave fusion required a shorter process time, 10-15 min, and produced a more homogenous glass phase than conventional thermal processing, which required 4 h. The improved homogenity observed for microwave vitrification was attributed to rapidly induced convection currents.

1.5. Conclusions

As can be seen from the above examples, the unique ability of microwave radiation to induce a variety of physical and chemical phenomena is playing an increasingly significant role in the development of new and existing technologies in analytical and environmental chemistry. The maturity of microwave generators, especially designed for a given application, the improved communication between chemists, microwave and electrical engineers that takes place (at *e.g.* 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 tremendous commercial potential of their microwave technique.

Chapter 2

2. Dielectric Properties of Soil in a Microwave Field

2.1. Introduction

Electromagnetic systems in the microwave frequencies are extensively used in applications that interface with soil. A speed-up in the extraction of contaminants by microwave radiation has been reported [74-77]. In order to better understand the mechanism of these phenomena one needs to know the main parameters influencing energy transfer from the electromagnetic field to the soil system. To date very few measurements have been reported on real, well-characterized soil systems, involving radiation frequencies above 10^8-Hz.

Von Hippel [7] reported a series of measurements on soils of various water contents using frequencies from 10^2 to 10^{10} Hz. When the water content of the samples exceeded 10% by weight, a substantial increase in the dielectric loss factor was observed at frequencies between 10^8 to 10^{10} Hz. His report did not give any information about specific properties of the investigated soils such as the organic and clay contents or static electric conductivity . The investigated soils were simply called: sandy, loamy, clay and magnetic soil.

Hoekstra *et al.* [91] measured the complex dielectric constant of four soils, including a sand, a silt and two types of clays, over a frequency range from 10^8 Hz to 2.6 x 10^9 Hz. Their results showed that the relationship between volumetric water contents and the complex dielectric permittivity in the microwave region is relatively independent of the soil type. Microwave energy was absorbed mainly by water and absorption of microwave energy by soil was negligible compared to water. There were no differences in energy transfer from the microwave field to different types of soil.

Olhoeft *et al.* [92] investigated the electrical properties of lunar soil samples from the Apollo 15 landing site. Measurements were made in an ultravacuum at less than 10^{-7} torr. The sample was processed in dry nitrogen without exposure to the atmosphere. Such processed samples exhibited a dielectric loss factor nearly an order of magnitude below that determined for samples processed in ambient air, in other words those having had contact with moisture.

In this chapter the results of temperature measurements of microwave processed well-characterized reference soils are presented. Since the temperature of the soil after microwave treatment is related to the dielectric loss factor of the investigated system, such data can help determine the proper conditions for microwave soil processing.

2.2. Materials and methods.

2.2.1. Apparatus

Water Quality Checker U-10 (Horiba Ltd., Kyoto, Japan) was used to measure electric conductivity of the soil-water systems.

An Omega 871A digital thermometer equipped with a NiCr-NiAl thermocouple was used for temperature measurements. Because the thermocouple has a very low heat capacity, temperature measurements were relatively fast. After moving the thermocouple from ice water to the hot object this digital thermometer reading stabilized in less than 10 s.

The appliance grade microwave oven (Sanyo model EM 573 TWS) operating on full power at 2450 MHz was used for irradiating the investigated soil systems.

2.2.2. Investigated soils

In 1987 the Land Resources Research Center of Agriculture Canada initiated a round robin analysis of eight main types of Canadian soil [93]. Two hundred kilograms of each soil were air dried, ground to pass a 2 mm sieve, fully mixed and very detailed analyses of the physical and chemical properties were made. The main findings of these investigations are presented in **Table 2.1**.

All 8 types of reference soil were obtained from Agriculture Canada and used in this work. Soils were stored in closed polypropylene boxes at room temperature (the same storage conditions were used by Agriculture Canada) and were used as received. Because of the limited quantity of reference soil samples, not all types of soil were investigated to the same extent.

2.2.3. Temperature Measurements

Two gram samples of soils having different water contents were placed in 20 mL headspace vials and 10 mL of hexane were added to each vial. Since hexane does not mix with water, it stays on top of the soil and any added water remained in direct contact with the soil. The headspace vial was then placed inside a hole in a styrofoam block. The cavity in the styrofoam exactly

Soil ECSS #	**1**	**2**	**3**	**4**	**6**	**7**	**8**
Great Group	P.E.I. humo-ferric podzol	Quebec ferro-humic podzol	Rideau humic gleysol	Grenville gray brown luvisol	Uplands sand duystric brunisol	Manitoba black	Alberta solonetz
pH in water(1:1) soil:water	5.4±0.2	4.4±0.2	7.3±0.4	8.2±0.3	6.3±0.1	7.3±0.2	7.6±0.3
pH in 0.01 mol /l $CaCl_2$(1:2)	4.7±0.1	3.7±0.1	6.4±0.3	7.6±0.2	5.4±0.2	6.9±0.1	7.1±0.1
% total carbon	0.08±0.05	5.95±0.71	0.26±0.12	3.34±0.3	0.38±0.03	4.43±0.36	1.46±0.07
% organic carbon	0.06±0.04	5.32±0.36	0.21±0.05	0.15±0.04	0.37±0.14	4.24±0.58	1.32±0.13
% nitrogen	0.02±0.01	0.17±0.02	0.02±0.01	0.01±<0.01	0.02±0.01	0.35±0.01	0.14±0.02
% sand	62.6±3.6	84.9±5.8	1.7±1.4	57.9±5.7	96.8±1.6	32.9±2.6	45.3±3.6
% clay	6.3±2.7	2.5±1.4	52.8±6.2	12.4±3.0	1.4±1.4	29.1±2.7	28.1±1.2
Cation exchange capacity[meq/100 g]	3.1±1.3	33.6±6.8	23.2±3.5	3.9±1.3	2.7±1.0	33.4±4.5	21.7±2.4
Electric conductivity mS/cm	0.04-0.38	0.05-0.16	0.06-0.35	0.13-0.48	0.02-0.7	0.23-0.71	0.29-2.07

Table 2.1. Properties of Reference Soils of Agriculture Canada. [93]

matched the size of the headspace vial. A styrofoam cover having a small opening for insertion of the thermocouple was then placed on top of the styrofoam block with the headspace vial inside.

Next the initial temperature inside the styrofoam enclosure was measured with the end of thermocouple positioned in the middle of the hexane layer. The thermocouple was removed and the whole system was then irradiated for 30 s at full power in the microwave oven.

Immediately after microwaving had stopped, the thermocouple was re-inserted in the hexane layer and temperature changes were monitored as a function of time. The styrofoam isolation slows the exchange of thermal energy with the surroundings, and the measured temperature rise was due to the microwave radiation alone.

Microwave energy absorption by the styrofoam and hexane was found to be negligible compared with absorption by the soil-water system. The absorption of microwave energy by the borosilicate glass of the head space vial caused a temperature rise of 2°C in hexane layer, when there was no glass turntable in the microwave cavity. Since variations from vial to vial were very small (less then 0.2°C), this parameter was taken to be constant in all measurements.

The power output of the present magnetron is temperature dependent, so in order to achieve reproducible behavior, each run was preceded by five blank runs. This ensured the thermal stability of the magnetron before the experimental samples were exposed to microwave radiation.

All results presented below are the mean of at least three replicate measurements.

2.3. Results and Discussion

2.3.1. Soil Conductivity Measurements

Because the soils were stored in a dry state for a relatively long time, and because soil characteristics can be changed in the course of dry storage [94], electric conductivity and pH of soil suspensions in water were measured.

A Horiba Water Quality Checker U-10 was used to measure the static electric conductivity of a suspension of 30 g of soil in 120 mL of deionized water. Because the electric conductivity cell has a volume of 120 mL and because of the limited quantity of the reference soils, the ratio of water to soil in the suspension was changed from the standard 1:1 to a ratio of 4:1. These measurements were performed to find the order of electrical conductivity values, rather than the "absolute" values of electrical conductivity of the soils, so that the ratio of water to soil used in the experiments will not affect the distribution of electrical conductivity among the soil types.

The results of the measurements together with comparative data reported by Wang *et al.* [93] are presented in **Table 2.2.** The water suspension of soil # 8, Alberta solonetz exhibits the biggest electric conductivity, while that of soil # 6, uplands sand, is the lowest. These two soil types plus two soils from the middle of the range, # 5 and # 7, were chosen for further investigations. These four soils cover a static electrical conductivity range from 0.3 mS/cm to 0.005 mS/cm and their sand, clay and organics contents are different enough for the purposes of this study.

Table 2.2. Results of static, electric conductivity and pH measurement of reference soils.

Soil ECSS #	Electric Conductivity (from ref. [88]) [mS/cm]	Electric Conductivity (measured) [mS/cm]	pH in water 1:1 soil:water (from ref. [88])	pH in water 1:4 soil:water
1	0.04-0.38	0.022±0.005	5.4±0.2	5.51±0.1
2	0.05-0.16	0.043±0.05	4.4±0.2	4.41±0.1
3	0.06-0.35	0.029±0.005	7.3±0.4	7.74±0.1
4	0.13-0.48	0.073±0.005	8.2±0.3	9.11±0.1
5	0.07-0.48	0.100±0.008	6.6±0.2	6.73±0.1
6	0.02-0.70	0.005±0.001	6.3±0.1	6.42±0.1
7	0.23-0.71	0.163±0.01	7.3±0.2	7.62±0.1
8	0.29-2.07	0.305±0.01	7.6±0.3	8.26±0.1

2.3.2. Temperature Rise After Microwaving

2.3.2.1. Microwaving With Turntable Present

The following samples were prepared: 2 g soil plus 10 mL of hexane, 2 g of soil plus 10 mL of hexane plus 1 mL of deionized water (added 5 min before microwave treatment) and blank runs on hexane and hexane-water mixtures. The samples, enclosed in the styrofoam container were placed on the outer edge of the turntable in the microwave oven and irradiated for 30 s. A separate study of the reproducibility of irradiation showed that irradiation of a sample placed in the middle of the microwave oven cavity produced a temperature rise of 36.5°C ± 3.0°C in 10 mL of water irradiated for 30 s.

Placement of the same sample at the edge of the turntable, rotating at 6 r.p.m. resulted in a temperature gain of 32.7°C ± 1.4°C. These results are the mean of ten measurements. The placement of the sample on the edge of the rotating turntable gave better reproducibility of the microwave irradiation.

The temperature changes in the hexane layer after microwave irradiation of the soil-water-hexane systems placed on the edge of turntable as a function of the time after irradiation are presented in **Fig 2.1**. There are no substantial differences between heating patterns for the different soil types, except for soil # 6, upland sand. This soil was heated less than the others after irradiation without any water addition, and it was heated more than the others after addition of 1 mL of the water to the two grams of soil. A reasonable explanation for this phenomenon is the inability of pure sand to retain water. After addition of one mL of water to two grams of sand, a layer of free water was seen above the sand. The addition of the same amount of water to the other soils resulted in soil without any visible free water, all water being held inside the soil's structure.

The lower adsorption of microwave energy by soil # 6 without water addition, compared to the other soils, can be explained by the relatively low adsorption capability of pure sand. The other soils investigated have higher clay contents and absorb more water vapor from the air than the sand, so that even without addition of water, their water contents are higher than that of the sand. This explanation is in agreement with Olhoeft *et al.* [92] who drew similar conclusions from experiments with lunar soil *in vacuo*.

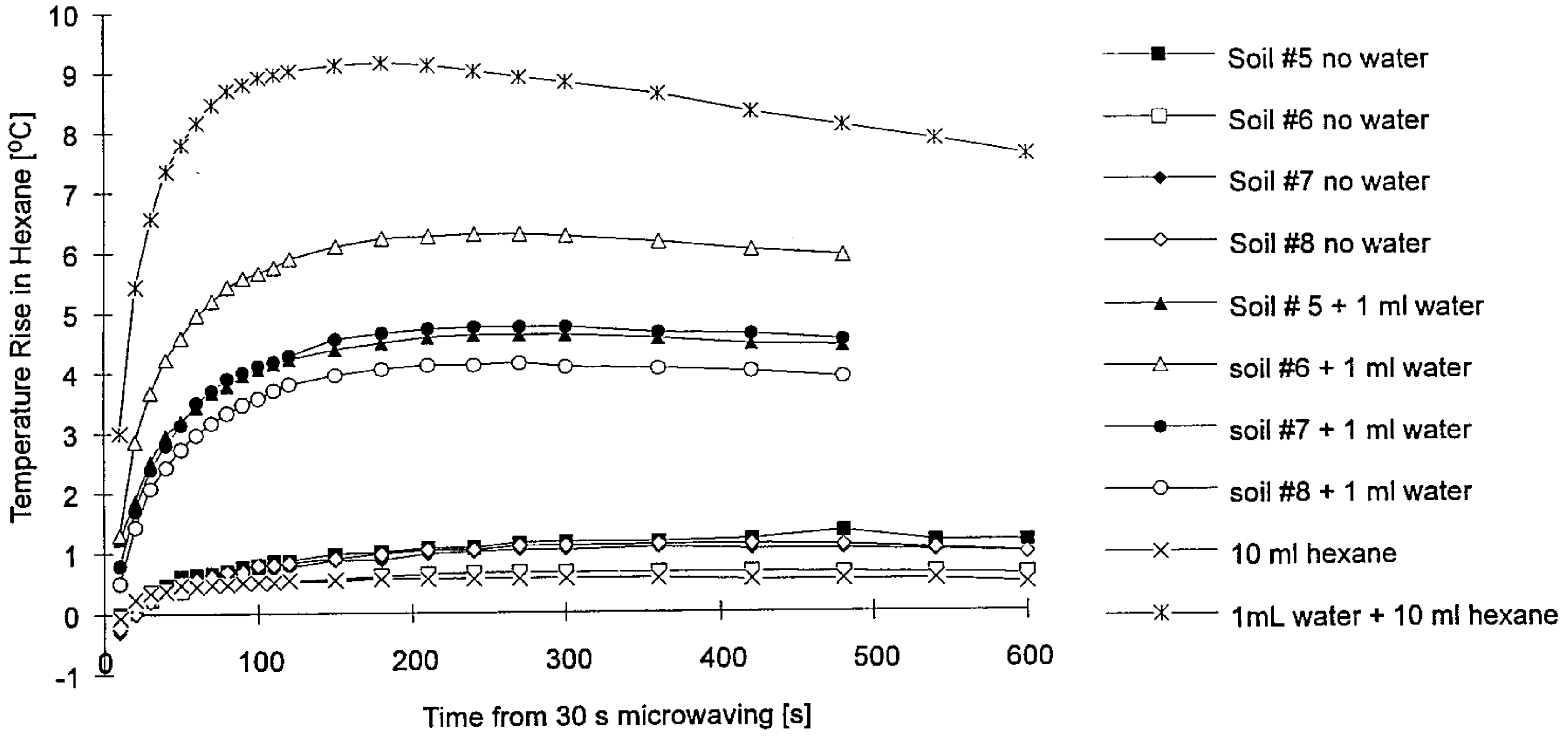


Fig 2.1. Temperature gain in hexane layer as a function of time and water contents.

Microwave irradiation on turntable.

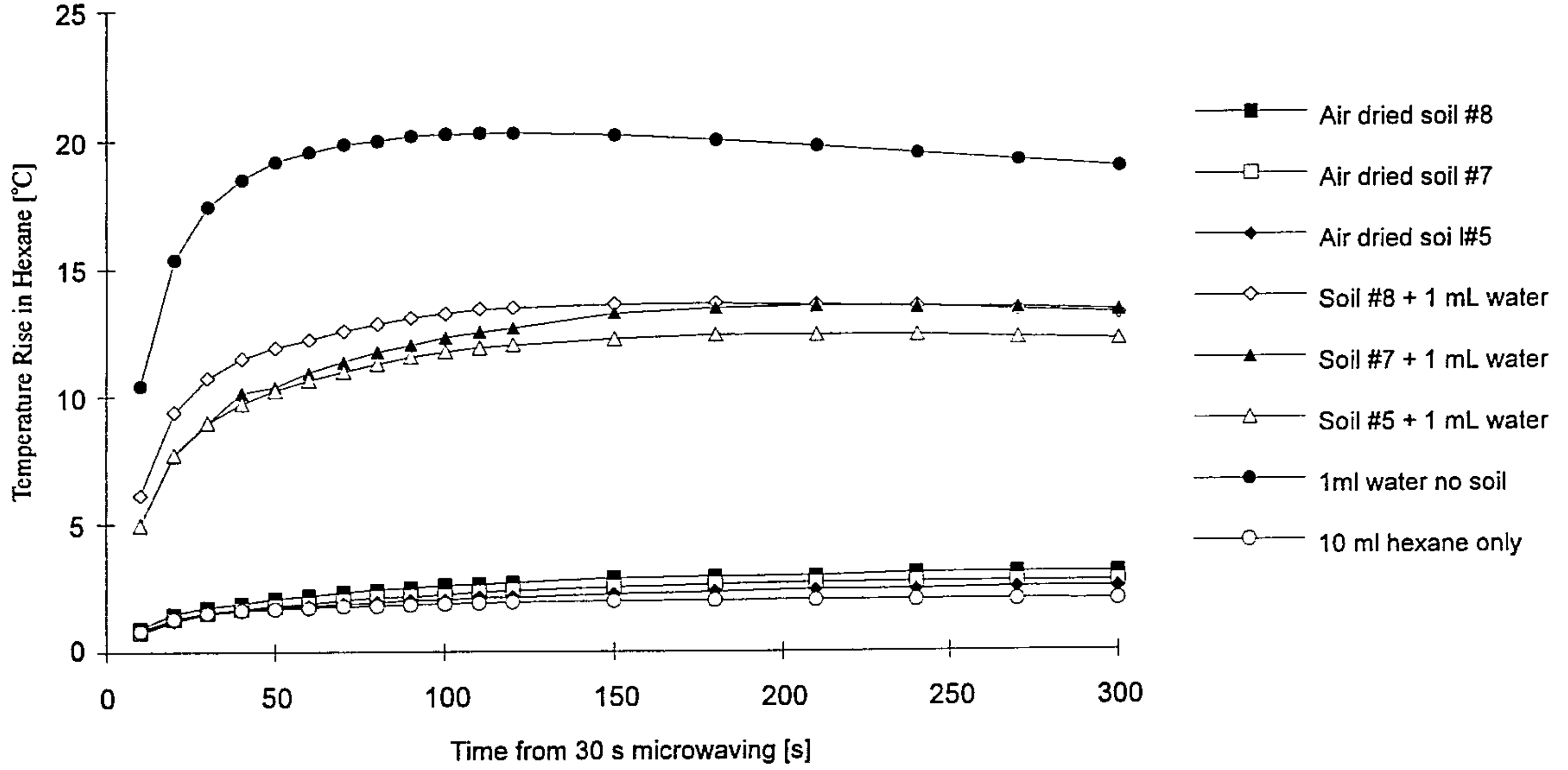


Fig 2.2. Temperature gain of the hexane layer as a function of time and water contents.

Turntable removed from microwave cavity.

2.3.2.2. Microwaving Without a Turntable

Irradiation of soils # 5 to 8 at the edge of the turntable showed in **Fig. 2.1** that there were no substantial differences in heating rates for the soils. Their adsorption of microwave energy was very low and comparable with the adsorption of the glass turntable. The turntable temperature itself rose during irradiation, indicating that a substantial part of the microwave energy was absorbed by the turntable itself. Irradiation of a sample without the turntable present showed that the measured temperature rise after a 30s irradiation approximately doubled. Soils # 5,7 and 8 were irradiated under these new (no turntable) conditions in order to determine if there are any differences in the heating patterns of the different soils in this stronger microwave field. The results of these investigation are presented in **Fig 2.2.** In spite of the differences in soil composition, their microwave absorption capabilities (loss factors) were very similar; all were heated to the same degree. Water added to the soils caused an increase of the loss factor of the system, but the temperature gain of the soil-water system was smaller than when water alone was irradiated.

Soil # 8 was chosen to investigate the influence of water present in the soil on the loss factor of the system. The temperature rise after 30 s microwave irradiation as a function of water added to soil # 8 is shown in **Fig 2.3**. In comparison, the temperature rise as a function of added water without the soil, is shown in the same figure. From a comparison of these two graphs it is evident that the presence of the soil changes the loss factor of the system. Additions of water to the headspace vial with no soil, resulted in a steady rise of the loss factor (temperature) throughout the investigated

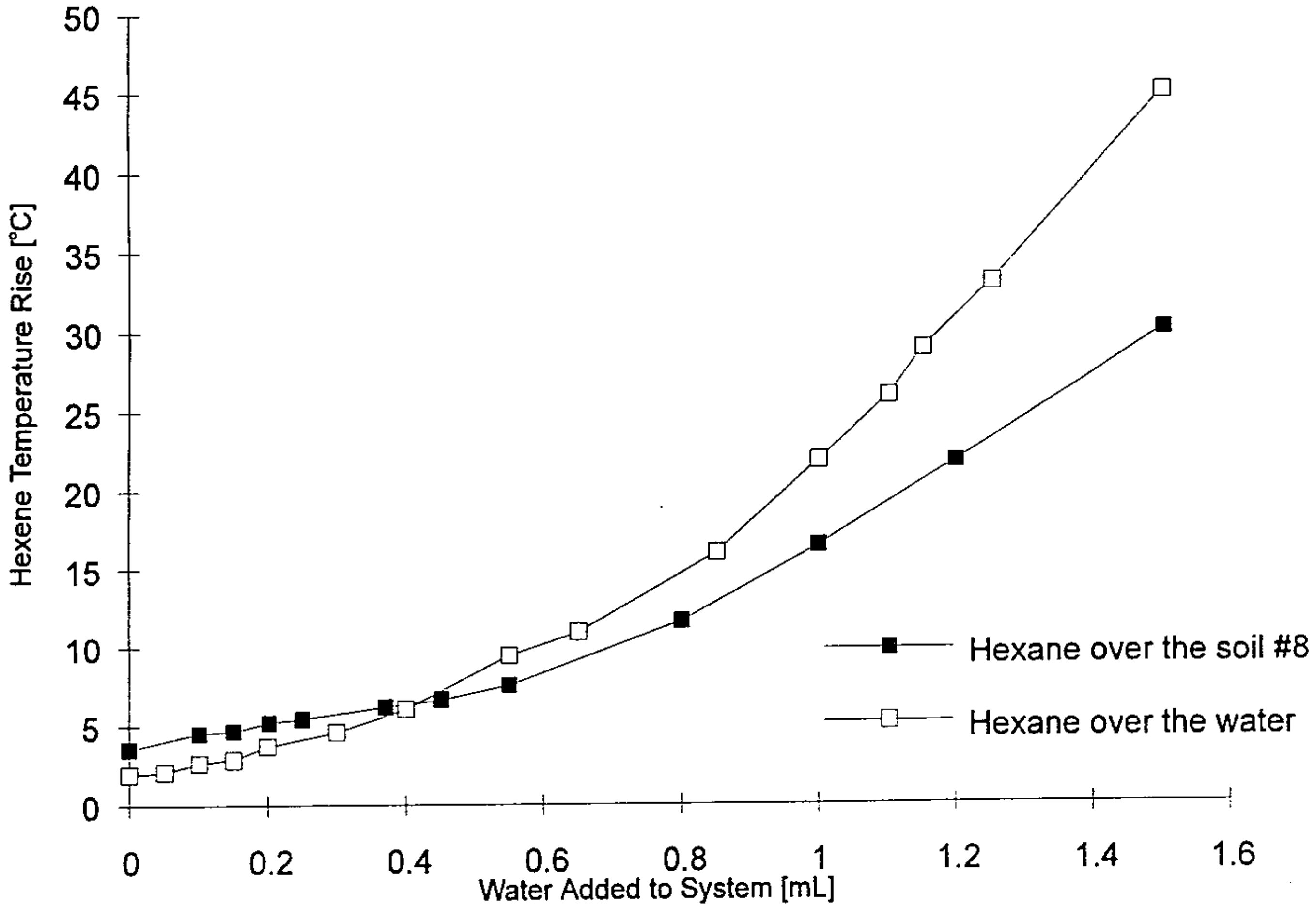


Fig 2.3. Temperature in hexane layer over soil #8 or only water as a function of volume of water added to the system. Temperature values measured 180 s after stoping microwave irradiation.

water range. Additions of water to the soil-hexane mixtures produced an increase in temperature rise. However when the added water was less than 0.5 mL per 2 g of soil, the changes in the dielectric loss factor of the system produced by the added water are different from those when the total water content was higher. For soil # 8 this threshold water content is about 25 % of the water contents in the soil. Addition of water beyond this 25 % limit produced more rapid changes in the loss factor of the system. Similar dielectric loss behavior when water was adsorbed on aluminum oxide was reported by Baldwin and Morrow [95]. They found that the first added water molecules adsorb to the surface as a monolayer and are held very tightly. The value of the loss factor is very low because the adsorbed molecules cannot move freely. Following completion of the monolayer, the enhanced ability of water molecules to orient in the field causes an increase in dielectric loss factor. In the present system, as water contents increase, the influence of the soil phase decrease rapidly and water furthest from the soil tends to resemble a pure condensed phase.

A similar study was done by Schwan [96] who studied the dielectric properties in a wide range of frequencies of water adsorbed on macromolecules such as hemoglobin. He found that bound water relaxes at frequencies between those characteristic of ice and normal water. Moreover, the relaxation spectrum of the bound water was very broad indicating that the activation energies for movement of bound dipoles occupy a very wide range. A maximum absorption of microwave energy by bound water was found to be in the range of 300 MHz, about one tenth of the value 2450 MHz used in appliance grade microwave ovens.

2.4. Conclusions

Four different soil types were investigated for factors which influence their absorption of microwave energy. One soil type, pure sand, exhibited singular behavior in the microwave field. Other soil types, despite their differences in composition, showed very similar dielectric properties. Significant heating of the soils can be achieved only by adding water to the system, but for each soil a certain minimal water content is required. The small dielectric loss factor of air dried soils showed that the microwave system used is unable to reorient adsorbed molecules. Part of the water is tightly bound to the soil surface and is not affected by the microwave field. We propose that the same will happen to other adsorbed species having strongly dipolar characteristics. Energy deposition in the soils can only be achieved by excitation of the loosely bound outer (non or weakly adsorbed) layers of water.

Recent advances in the construction of devices measuring dielectric properties, such as very precise network analyzers can help answer the question; how is it possible to excite adsorbed molecules by means of a microwave field? Other frequencies, better tuned to the relaxation time of strongly held monolayer molecules, plus a higher density of microwave field should help desorb such molecules. Unfortunately appliance grade microwave ovens do not have this capability. The common frequency of 2450 MHz is probably too high to excite molecules tightly bound to the rigid soil surface. Schwan [96] found that the maximum absorption of microwave energy by water bonded to hemoglobin can by achieved at a frequency of about 300 MHz. Microwave sources working at this frequency are not readily available, but detailed studies of dielectric properties as a function of frequency are needed. Unfortunately, to date, the literature on this subject is very scarce.

The results acquired in the course of this work have not helped to resolve the problem but rather, have restated it. The microwave system used during investigation of dielectric properties of soil was too simple and its power output was inadequate for the selective deposition of microwave energy directly into the soil. A substantial part of the energy was deposited outside the soil-water system *e.g.* into the turntable or the glass of headspace vial. This experimental set up was able to put only a few percent of the nominal power output into the investigated object. For further investigation of the role of soil composition, a more advanced, single mode microwave setup is necessary in order to perform precise measurements of the absorbed microwave power. Investigations of the role of soil composition on its dielectric properties have to involve much higher densities of energy than can be achieved using appliance grade microwave ovens together with much precise monitoring of the energy transfer (*e.g.* direct and real-time measurement of temperature of the soil under the microwave field). The experimental set-up used in this work was only able to notice changes due to different water contents of the soil and not arising from the different compositions of the soil types.

Chapter 3

3. Extraction of PCP from Soil.

3.1. Introduction

Pentachlorophenol (PCP) was first prepared by Erdmann in 1841 but was not produced on a commercial scale until 1936 [97] . PCP is a fairly weak acid, although the presence of chlorine makes it more acidic than phenol. It reacts quantitatively with strong alkalis to form the corresponding salts, which are water soluble. PCP itself is almost insoluble in water (8 mg in 100 mL) and freely soluble in a variety of organic solvents. It is quite stable and does not undergo decomposition even when heated for an extended period at elevated temperature (m.p. 190°C -191°C , b.p. 293°C).

PCP is widely used as a fungicide and insecticide in commercial wood treatment [98]. Heavy PCP contamination of the soil surrounding wood treatment facilities has been reported by Lamar [99]. This widespread contamination has raised concerns regarding the environmental impact of PCP, since it is known to be toxic toward a broad spectrum of organisms and is possibly mutagenic [100]. PCP is a priority pollutant, a member of The Top Ten Materials from The 1990 Chemical Spill Priority List of Environment Canada.[101].

3.2.Extraction Of Environmental Pollutants From Soil

In order to quantitatively determine PCP in environmental samples, PCP must first be extracted from its matrix. It is vital that the extraction procedures be highly effective, since extraction recovery is often the limiting step in the quantitative analysis of organic pollutants from environmental solids [102].

In the past, chlorinated insecticides have been isolated by Soxhlet extraction - a time consuming technique involving many manipulation steps after actual extraction and large consumption of pure organic solvents. Consequently, numerous alternative methods have been proposed.

Johnson and Starr [103] compared Soxhlet extraction, shaking extraction, ultrasonic extraction and a Polytron, a high specific intensity ultrasonic generator and homogenizer, for the extraction of insecticides from various soils. Polytron extraction is based on two interrelated forces: direct mechanical shearing and cavitation. In general they concluded that a Polytron is the superior extraction device even for very short (30 s) blending times. Further, acetone was a superior solvent and moist soil was more efficiently extracted than dry soil.

Bertuzzi *et al.* [104] evaluated a variety of parameters applied to the extraction of dieldrin, DDTs and methoxychlor from nonfatty samples containing less than 10% water. A number of conclusions were derived from this work:

1. Acetonitrile/water combinations were the best solvent.
2. Hydration of the sample was critical to efficient extraction, but the manner in which hydratation was accomplished was not important.
3. Differences in sample size, solvent volumes used for extraction (assuming sufficient was present to "wet" the sample), and blending times (2 min and 5 min) did not affect the extraction efficiency.

Chiba and Morley [105] evaluated a number of variables which influenced the extraction efficiency of aldrin and dieldrin from three soil types. It was concluded that water added to soil prior to extraction allowed the most efficient extraction of both insecticides. Saha *et al.* [106] pointed out that the addition of 20% water to a soil immediately before extraction resulted in the highly efficient extraction of dieldrin from four soil types and of chlordane from a clay loam soil. [107]

Wall and Straton [108, 109] investigated the efficiency of extraction of pentachlorophenol from two types of soil. using standard Soxhlet extraction, shaker extraction, sonification and Vortex extraction. All four methods were equally effective, but they found that PCP was more strongly adsorbed in dry soil. They recommended that when storing soil samples prior to extraction, the moisture status of the soil should be carefully controlled, especially with soil containing relatively high amounts of clay and organic matter.

Ganzler *et al.* [56-58] applied microwave irradiation to the extraction of various types of compounds from soil, seeds and food. Samples were ground and mixed with an appropriate solvent, methanol or methanol-water for polar compounds and hexane for non-polar compounds. The suspensions were irradiated for 30 s, but not allowed to boil. The irradiation was repeated several times after cooling. Samples were then centrifuged, and an aliquot of the supernatant fluid was injected into a chromatographic column. The microwave extraction method was found to be more effective than the conventional methods.

A new microwave assisted extraction method was used by Paré *et al.* [62] for extraction of natural products from materials of biological origin and by Craveiro *et al.* [59] for the extraction of essential oils from the leaves of *lippia sidoides*. Both groups found much shorter times for extraction plus a better "quality" of extracted oils. Due to the shorter extraction time degradation of the extracted components was reduced.

3.2.1. Extraction of Real World, Aged Contaminants from Soil

Determining the extraction recovery of spiked analytes from environmental samples is a routine procedure to develop and validate new extraction methods. While the use of spiked samples to determine extraction efficiencies from homogenous samples such as sorbent resins may be valid, spiking analytes onto heterogeneous environmental matrixes, such as soil or sludge, may not be a reliable means of representing the extraction behavior of native analytes. Hawthorne *et al.* [110] studied the relative extraction rates of native PAHs and spiked deuterated PAHs from environmental solids including petroleum waste sludge, railroad bed soil and urban air particulate matter using supercritical fluid extraction and sonication with methylene chloride. Regardless of the spiking method and aging time (up to 14 h), the extraction rates of the spiked d-PAHs were substantially (up to 10-fold) higher than these of same native PAHs. Differences in extraction rates of the spiked and native PAHs were most dramatic for the lower molecular weight species.

Pignatello *et al.* [111] on the basis of a study of the extraction of 1,2 dibromoethane (EDB) from agricultural top soil fumigated with EDB 19 years previously, found that residual EDB is trapped in soil micropores (other than the interlayers of expandable clays) where release is influenced by extreme tortuosity or steric restriction. Since soils possess a graduation of pore sizes, increasingly "remote" sites will become populated with time. They found also that aged soils contaminated with EDB are very resistant to biodegradation and EDB degradation was negligible after 38 days compared with the rapid removal and mineralization of added [^{14}C]EDB. They concluded that the resistance to biodegradation of native EDB was prevented by the small size of the soil pores occupied by EDB. Microbes cannot enter these pores due to steric restrictions.

Boyd *et al.* [112] compared the sorption/desorption behavior of field weathered (aged) simazone (2-chloro-4,6-bis(ethyloamino)-s-triazine) residues from a 20 year continuous corn field with sorption/desorption of recently added ^{14}C-simazone to the same soil. The apparent sorption coefficients of the aged residues were approximately 15 times higher than the sorption coefficient of added simazine.

These findings show that despite the common practice of using spiked recoveries to develop and validate extraction methods for native contaminants, this approach is frequently invalid for achieving quantitative extraction conditions from heterogeneous materials such as environmental solids. The results of a spiked recovery should be validated by subsequent extraction by other methods or by use of a standard reference material with known composition. Only naturally aged samples, whose time of contact with the targeted compounds is in the range of years, can be used for validation of new extraction methods for heterogeneous environmental solids.

The objective of this work was to study in more detail the extraction of PCP using microwave assisted extraction, shake extraction, and Soxhlet extraction, and find fast, efficient method of extraction of PCP from different types of soil. The new method should be suitable for use in a mobile laboratory unit at a spill site. Since the spill situation involves non-aged samples, the spiking procedure can be used for validation of the analytical method. To validate the usefulness of the microwave assisted extraction of native contaminants, the extraction of naturally weathered soil samples from a wood treatment facility was also investigated.

3.3. Materials and methods.

3.3.1. Apparatus

A household microwave oven (Sanyo model EM 573 TWS) operating at full power at 2450 MHz was used for microwave assisted extraction which was performed in 7 mL Teflon screw-cap wet digestion vessels (CEM, Matthews, N. C.)

The HPLC equipment was a Waters (Milford, Mass.)model 590 piston pump, a Rheodyne injection valve with a 20 μL sample loop, Waters (Milford, Mass.) model 440 UV Absorbance detector working at 254 nm and Spectra-Physics (San Jose Ca.) SP-4270 integrator.

GC analyses were performed on a Hewlett-Packard (Palo Alto, Ca.) model 5890 Series II gas chromatogram equipped with an autosampler and a Hewlett-Packard 5971A mass selective detector.

3.3.2. Soil samples

Eight soil samples having a variety of clay, mineral species and organic matter contents were obtained from Land Resources Research Centre of Agriculture Canada. A brief description of the soils' physical and chemical properties is given in **Table 2.1** (page 53). All soil samples were air-dried, ground to pass a 2 mm sieve, thoroughly mixed and stored in polypropylene boxes at room temperature.

Contaminated weathered soil samples were taken from a wood preserving facility located on the shore of the St. Lawrence River in Quebec, that has been in operation from the beginning of the 1950's. Because of the high volume used and the improper disposal of creosote and PCP over this 40 year period, soil at this site has been extensively contaminated. Relatively high PCP concentration, up to 1300 ppm, in the soil from this site was reported by Hawari *et al.* [113]. On June 28 1993 soil samples were collected from the upper 30 cm of the site. The soil was air-dried, sieved through a 2 mm sieve and stored in amber glass wide-mouth bottles, which were closed with Teflon-lined caps. The soil was stored at 4°C in the dark and used as needed.

3.3.3. Chemicals

Pentachlorophenol (99+% purity; Supelco, Inc., Bellefonte, Pa, USA, Lot- No.LA21469) was dissolved in acetonitrile and stored as a 500 μg/mL stock solution. Concentrations of 2.5, 10, 50, 100 μg/mL were employed in absorption and spiking experiment. All solvents used for HPLC analysis and sample extraction were HPLC grade (BDH Inc., Toronto)

3.3.4. Analytical procedures

The PCP concentrations in extracts from the spiked samples were quantified by the high performance liquid chromatography method published by Wall and Stratton [108,109], using Zorbax Rx-C18 4.6 mm x 150 mm column. The mobile phase was acetonitrile: 5 % aqueous acetic acid (70:30 v/v) at a flow rate 1.1 mL/ min.

Since samples with native PCP contamination contained other pollutants, mainly polyaromatic hydrocarbons, HPLC using UV detection failed to resolve the extracted mixtures even after extensive clean up. Gas chromatography with a mass specific detector was used instead to quantitate PCP in extracts from weathered soil. PCP present in the extract was separated on a DB-5 (Supelco, Bellafonte, Pa.) capillary column. The temperature program was as follows: 60°C for 1 min followed by a linear increase of 10°C/min to 180°C and then 15°C/min to 300°C where it was held for 10 min. Injector and detector temperatures were maintained at 280°C and 300°C respectively. The concentrations of PCP were calculated by comparing peak areas obtained from duplicate 1 μL injections using external standards. A maximum of four determinations were made between standard injections.

3.3.5. Adsorption Experiments

The Adsorption of PCP on soil was determined by the batch equilibration technique. Approximately one gram of air-dried soil or soil having a known water content was placed together with 2-3 mL of acetonitrile PCP solution in a Teflon, screw-capped vial. The vials were shaken for times of from one minute up to 24 hours. After shaking, the vial was centrifuged for five minutes (Damon/iec Division, Needham Hts., Mass.). The supernatant liquid was analyzed for its PCP concentration. The quantity of PCP absorbed on the soil was calculated from the changes in PCP concentration in the supernatant liquid.

3.3.6. Extraction experiments

3.3.6.1. Spiked Soils

Extraction was performed on spiked soils, prepared by adding a known amount of an acetonitrile solution of PCP to the slurry of soil in acetonitrile.

After spiking, the soil was dried under a gentle stream of nitrogen and stored in screw-capped Teflon 250 mL Erlenmeyer flask at 5°C until further use.

a) Soxhlet Extraction Ten grams of spiked soil was placed in a 33 x 80 mm Whatman Cellulose extraction thimble and extracted for 6 to 12 hours on a Soxhlet apparatus with a mixture consisting of 10 mL of ethanol and 125 mL of toluene. After extraction, the solvent was evaporated to 5 mL using a rotary evaporator with a 55°C temperature water bath, dried over anhydrous sodium sulfate and evaporated a second time with about 150 mL of acetonitrile using the rotary evaporator with a 35°C water bath temperature. The residue was dissolved in 5 mL of acetonitrile and the concentration of PCP was determined by HPLC.

b) Shake extraction: About one gram of spiked soil was shaken by hand with 2- 3 mL of solvent for 1-5 minutes, followed by centrifugation and filtration of the supernatant liquid through a syringe 2 μm filter and then the PCP was determined by HPLC.

c) *Microwave Assisted Extraction* The spiked soil samples (about one gram) were suspended in a Teflon screw-capped vial with 2-3 mL of solvent. The suspensions were irradiated for 15-30 seconds in the microwave oven operating on the full 700 W power with a frequency of 2450 MHz. The samples were cooled to room temperature in 2-5 min and then irradiated and cooled again when necessary. Following the extraction, the samples were centrifuged for 5 minutes and filtered through a 2 μm syringe filter and a 0.15 mL aliquot was injected into the 20 μL sample loop of the HPLC system.

3.3.6.2. Weathered Soil. Extraction and Clean-up

The procedure used for extraction of PCP from weathered soil was a modification of that developed by Mueller *et al.* [114]. Triplicate 5.0 g samples of soil were each placed in a clean 125 mL Nalgene flask fitted with a screw capped . To each bottle was added 2 mL of deionized water and 15 mL of methanol. The soil slurry was acidified to pH = 2 with concentrated sulfuric acid. The transfer of PCP to the organic phase was facilitated by mixing in a mechanical tumbler or by microwave irradiation as described above for the spiked soil. Ten mL of 0.1 M HCl/0.1 M KCl was added to the soil-methanol slurry which was then filtered under vacuum through a 0.2 mm Nalgene filter unit (Sybron Corporation, Rochester, N.Y.) lot no. 10609A. The filter was washed successively with 5 mL of hexane and 5 mL of deionized water. The wash solution was added to the filtrate. The combined filtrate was then extracted three times with 5 mL of hexane. The combined hexane phases were dried over Na_2SO_4 and evaporated under a stream of dry nitrogen at room temperature. The final volume was adjusted to 10 mL. The recovery of PCP after these operations was found to be better than 90%.

3.4. Results and Discussion

3.4.1. Effect of Soil Type on PCP Absorption.

Adsorption experiments were carried out with seven types of soil obtained from Agriculture Canada, in order to evaluate the effect of the pH of the soil, the organic matter content, the particle size distribution and cation exchange capacity of the soil on the PCP adsorption.. The results obtained after ten minutes contact of two mL of acetonitrile PCP solution with one gram of soil are given in **Table 3.1.**

Table 3.1. PCP adsorption from acetonitrile solution to different types of soil after 10 min contact.

Soil type	**PCP Added [μg]**	**PCP Concentration in Soil [μg/g]**	**% of PCP Adsorbed**
# 1 P.E.I. humo-ferric podzol	4.89	1.10±0.05	24%
# 2 Quebec ferro humic podzol	4.89	0.08±0.03	2%
# 3 Rideau humic gleysol	4.89	3.72±0.05	80%
# 4 Grenville gray brown luvisol	4.89	4.33±0.06	96%
# 6 Uplands sand	4.89	1.69±0.07	38%
# 7 Manitoba black	4.89	1.60±0.09	36%
# 8 Alberta solonetz	4.89	1.45±0.07	31%

As can be seen from the **Table 3.1**, soil samples can be classified into three groups according to the magnitude of adsorption. The greatest adsorption occurred in soils # 3 and # 4. In contrast there was practically no adsorption by sample # 2.

Inspection of the properties of the soil samples shown in the **Table 2.1** (page 54), indicates that the pH of the soil may be the primary factor governing the magnitude of apparent adsorption. The relationship between the pH of the soil sample to the magnitude of adsorption is shown in **Fig. 3.1**. No relationship could be found between the concentration of PCP in the supernatant solution and the contents of clay, cation exchange capacity or the organic matter contents of the soil

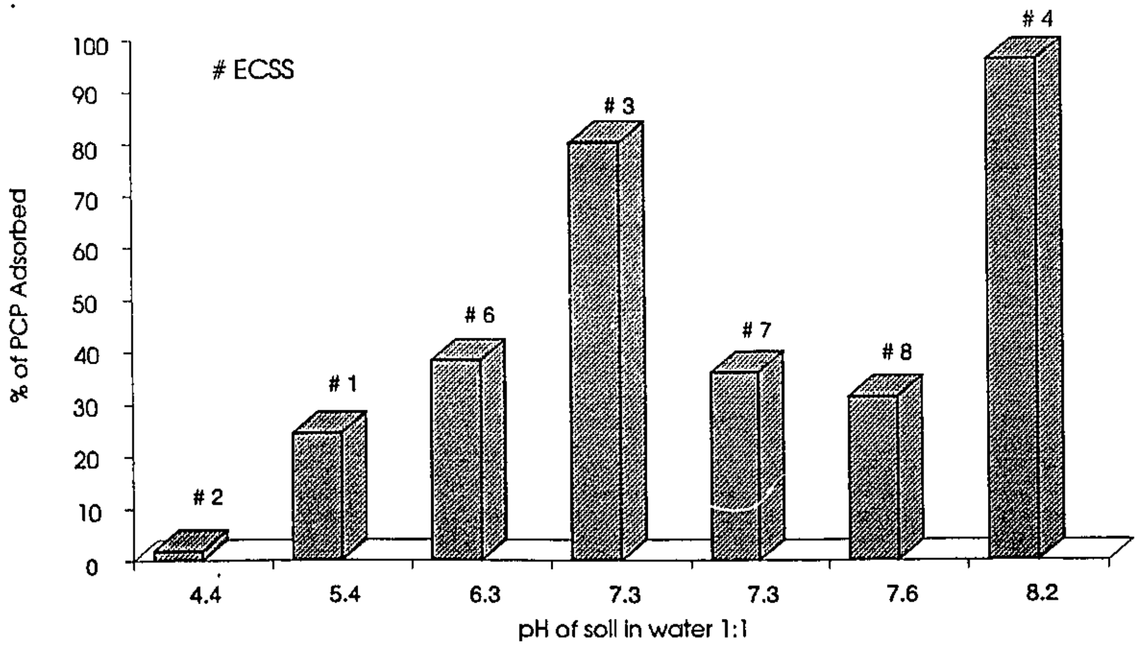


Fig 3.1. Influence of pH of soil on adsorption of PCP

For further examination of the adsorption behavior of PCP, a Rideau Gleysol (ECSS # 3) with high clay content was chosen. This soil exhibits a

Soil origin	**Initial PCP conc. [μg/mL]**	**Time of contact**	**PCP conc. after contact with soil [μg/mL]**	**PCP adsorbed [μg /g of soil]**	**PCP adsorbed [%]**
Soil straight from the box	4.71	**1 min.**	2.36	4.19	**57%**
	2.44	**10 min**	1.80	3.27	**80%**
	4.71	**24 hours**	0.90	7.03	**98%**
Soil after one week equilibration with water vapor at room temperature	2.44	**10 min**	1.80	1.27	**26%**
	2.44	**24 hours**	1.68	1.36	**31%**
Soil plus 0.4 mL of water	2.44	**10 min**	2.13	0.00	**0%**
	2.44	**24 hours**	2.11	0.03	**3%**

Table 3.2. Influence of water content of soil and time of contact on adsorption of PCP from acetonitrile solution.

good adsorption capacity and the supernatant solution after contact with this soil is relatively clean, there being no need for any purification before HPLC determination.

The affinity of PCP for the soil # 3 as a function of the water content of the soil, and as a function of contact time was measured. Results are presented in **Table 3.2**. There is no significant increase in the quantity of PCP adsorbed on the soil after the first 10 minutes of contact. Even after 24 hours of shaking, the adsorption of PCP is mainly the same as that found after 10 minutes. This indicate that during first few days of contact, PCP adsorption is not limited by diffusion to adsorption sites.

PCP is strongly retained on air-dried soil but the affinity of PCP for the soil decreases with increase of the water contact. There is no significant adsorption of PCP on a soil having a water content greater then the water-holding capacity of the soil. These results indicate a competition between water and PCP for adsorption sites on the soil. The pH dependency of the adsorption shown in **Fig 3.1** suggests that PCP is adsorbed on the soil mainly as an anion.

Weber *et al.* [115] found that the adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) on an anion-exchange resin was reduced in phosphate buffer solution showing that the phosphate ion competed with 2,4-D anions for adsorption sites on the resin. The competition between PCP and water, for adsorption sites on a soil might well be of the same type as that between 2,4-D and phosphate ions in adsorption on the anion exchange resin.

3.4.2. Extraction of PCP from spiked soil.

The recovery of PCP from the spiked soil # 3 are summarized in **Table. 3.3**. High extraction efficiency was obtained with all methods, and the mean recovery of PCP exceed 90%. in all cases. Although Soxhlet extraction is often the standard procedure for organic compounds from soil, microwave assisted extraction and shake extraction yielded the same or higher recovery efficiency with lower solvent requirements and with much less time being required for the preparation of a sample for HPLC determination.

Table 3.3. Recovery of PCP from Rideau humic gleysol spiked with 5-µg/g of soil

	Recovery, (%)				
Extraction method	**mL of water added per 1 gram of soil**				
	0	0.05	0.1	0.2	0.4
Soxhlet					
6 hours	62%				
12 hours	90%				
1 min shake extraction					
with methanol	55%		78%	85%	
with acetonitrile	9%	64%	92%	101%	105%
Microwave 30 s					
with methanol	63%			87%	
with acetonitrile	10%	69%	89%	104%	101%

A 20 g sample of PCP spiked soil # 3 was put into a headspace vial, capped and stored in a refrigerator at 4°C for 17 months. This aged PCP spiked soil was extracted by standard shake and microwave methods using acetonitrile as a solvent. The results of these extractions are presented in **Fig. 3.2**. Recoveries of PCP from such treated samples were of the order of 85 % after just 2 minutes shaking, or 30 s microwaving and 2 minutes of shaking.

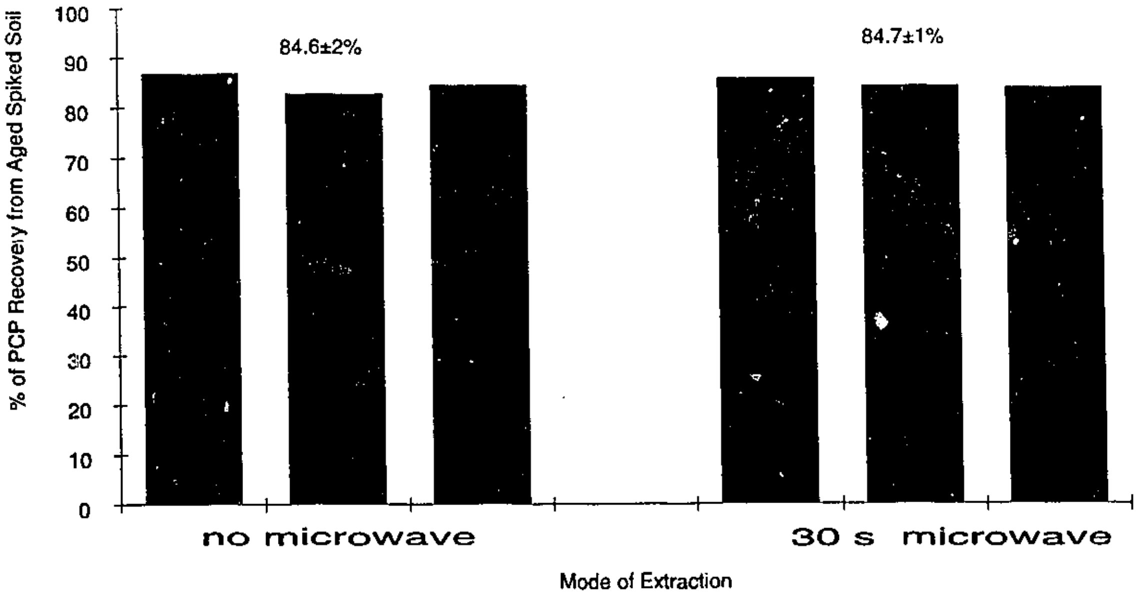


Fig. 3.2 Recovery of PCP from Aged Spiked Sample.

To find the reason for the incomplete PCP recovery, these extracts were analyzed by GC-MS in the scan mode. The GC chromatograms showed the presence of new peaks, but an NBS library search was unable to recognize the mass spectrum of the compounds eluted in these peaks. A likely explanation of the lower recovery of PCP after 17 months of storage is that some microbial biodegradation had taken place.

In all the above investigations there was no advantage in using microwave assisted extraction over shake extraction. It appears that the mechanism of desorption of PCP from a soil depends upon on the competition between water and PCP for the same adsorption sites.

The recovery of PCP from soil # 3 after shaking or microwave assisted extractions as a function of the quantity of the water added to the system is presented in **Fig. 3.3**.

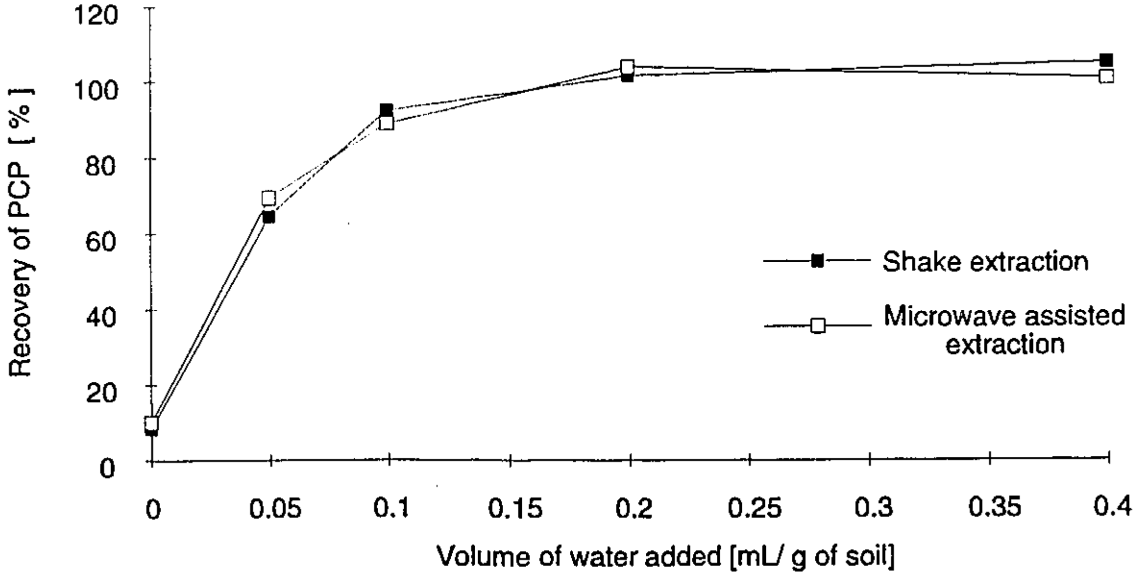


Fig 3.3. Recovery of PCP from spiked soil # 3.

There is no difference between the extraction efficiency of the two methods. Extraction is always quantitative when there is a sufficient quantity of water present in the soil. When the soil is dry, the extraction efficiency is less than 10 % irrespective of the mode of extraction. Microwave assisted extraction brought no improvement to the recovery of PCP from spiked Rideau Gleysol.

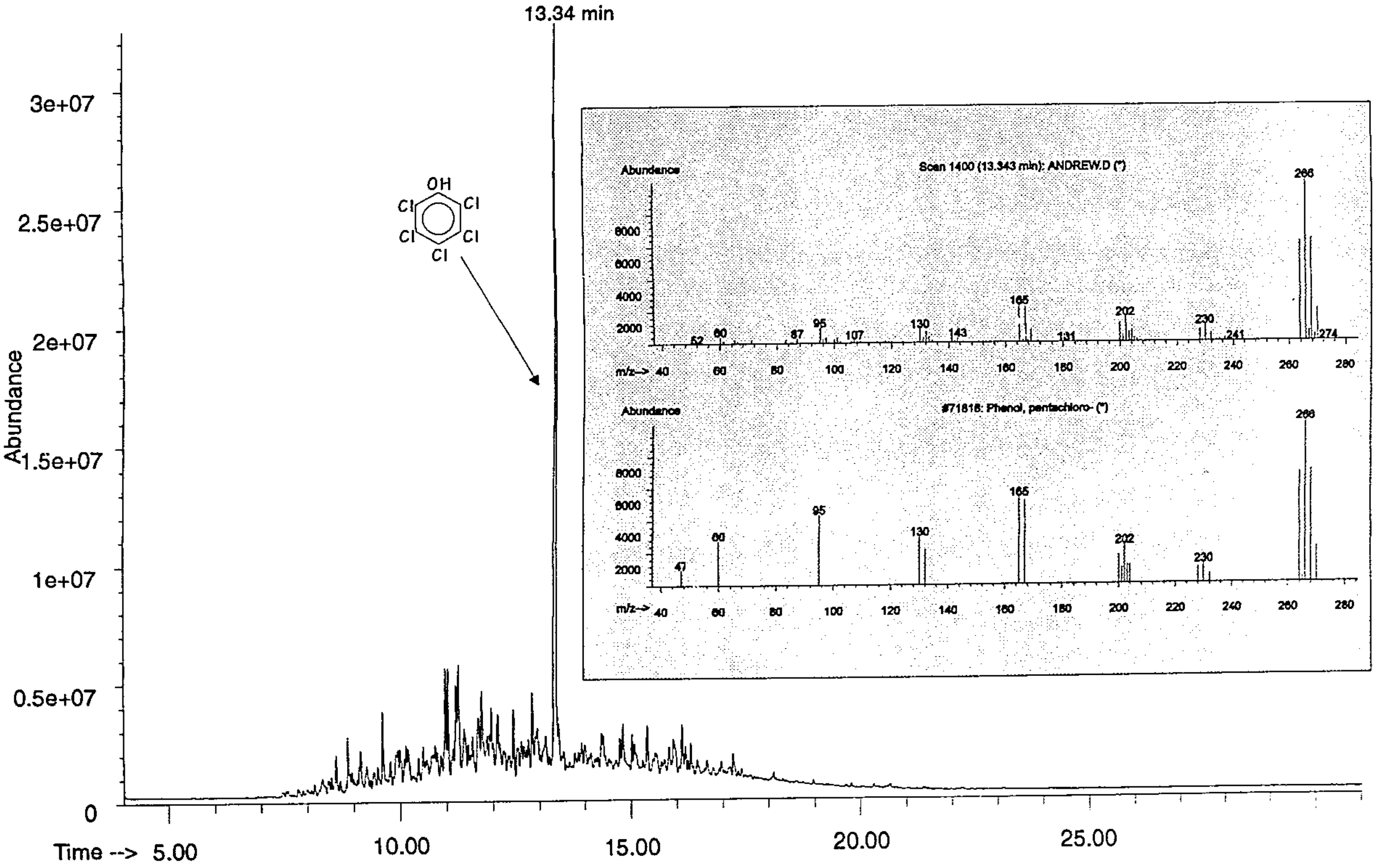


Fig 3.4. Total ion curent chromatogram and mass spectrum at 13.34 min of the cleaned extract of weathered PCP contaminated soil.

3.4.3. Extraction of PCP from Naturally Weathered Soil

A typical gas chromatogram using a mass specific detector of the extract from contaminated soil is presented in **Fig. 3.4**. As can be seen the clean-up procedure proved to be satisfactory. The PCP peak is the largest signal and is well resolved despite the heavy contamination of the soil by othercompounds. The mass spectrum of the PCP peak is very similar to that of the pure compound.

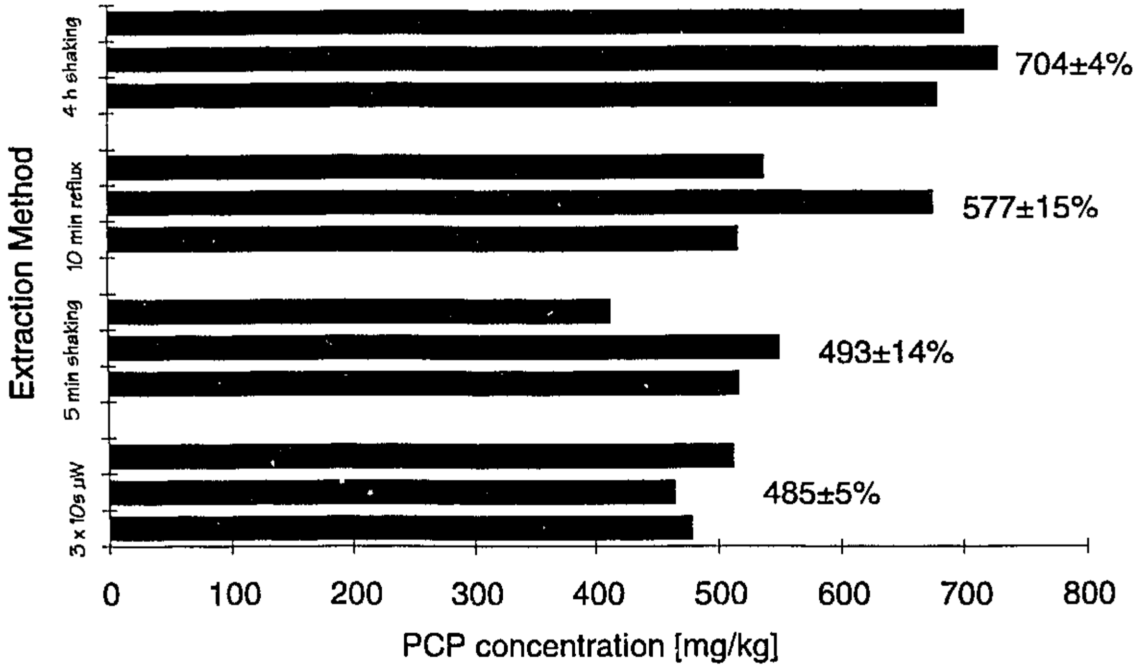


Fig 3.5. PCP recovered from weathered soil

Results for the quantity of PCP extracted from the soil from the wood treatment facility are presented in **Fig. 3.5.** The highest recoveries were obtained by extraction involving four hours shaking. The resulting PCP concentrations were in the range of 700 µg/g of soil. Microwave assisted extraction showed recovery rates similar to 5 minutes of shaking, about 500 µg/g of soil. The time of extraction for these two methods was exactly the same, the microwave extraction having been repeated 3 times with cooling periods in between.

3.5. Conclusions

The adsorption behavior of PCP from acetonitrile solution onto different types of soils was investigated. Significant differences were noted. The pH of the soil seems to be a prime factor governing the magnitude of adsorption. There is no clear correlation between adsorption and other physicochemical properties of the soils investigated. Shake extraction with water and acetonitrile proved to be a simple, fast and most effective method for quantitative recovery of PCP from spiked soil and it can also be used in the case of environmental emergency. Even recovery from samples aged for 17 months was satisfactory.

The PCP extraction recovery from a native contaminated soil was the highest following four hours of shaking with the solvent. Microwave heating and heating under reflux resulted in no improvement in extraction effectiveness.

The mechanism of microwave extraction still needs to investigated. Ganzler *et al.* [58] suggested that the disruption of weak hydrogen bonds resulting from dipole rotation of the molecule in the microwave field facilitates desorption of adsorbed contaminants. Since PCP probably bonds to soil mainly by an ion exchange type of adsorption [116-118] there is no possibility to break strong ionic bonds by means of 2450 MHz microwave radiation in a household oven.

Moreover, as was shown in Chapter 2 of this work, the microwave field generated in the appliance grade microwave oven is unable to excite water molecules bonded in a monolayer. Only more loosely bound upper layers of water can absorb microwave energy. The same could happen to adsorbed contaminants if they are adsorbed on the soil structure. Their dielectric loss factor will be much smaller than in the free, condensed phase. Microwave energy will be deposited into loosely attached surroundings *e.g.* free water in the soil structure. This can lead to further complications. Prolonged microwave irradiation will cause evaporation of free water from the soil system. This in turn will strengthen the adsorption of organics to the soil. Akgerman *et al.* [119] stated that the presence of water greatly reduces organic uptake by soils, especially at low organic concentration. The effect of humidity was attributed to adsorptive displacement of organics by water. Goss [120] investigated the effects of relative humidity on the sorption of organic vapors on clay minerals. He found that at low humidity, when the coverage of the sorbent was incomplete, sorption coefficients for organics were considerably increased. The facile release of PCP from the moist soil, in contrast to its strong adsorption on dry soil, was observed in the course of this work.

Microwave induced removal of water from the soil will slow down the extraction of organic contaminants by drying the soil. Only volatile or semivolatile organics can be removed in the first stages of this process by *in situ* steam distillation. Less volatile contaminants will remain in the soil structure and their adsorption on the soil may well be stronger than before microwave assisted extraction.

Chapter 4

4. Desorption of PAHs from a Charcoal Surface by Microwave Energy

4.1. Introduction

Polycyclic Aromatic Hydrocarbons (PAH) are ubiquitous environmental pollutants. Animal experiments have revealed that many compounds in this class of chemicals are carcinogenic and/or mutagenic in vivo and in vitro. As complete a knowledge as possible concerning the particle bound, gaseous and dissolved PAH's and their composition in an environmental sample is necessary for the evaluation of any cancer risk.

PAH's are mainly produced during the combustion (or pyrolysis) of organic materials. Such reactions produce a polymeric carbon particulate as well, so a knowledge of PAH's adsorption behavior on the surface of carbon (*e.g.*, diesel soot, fireplace soot, etc.) can also provide valuable information concerning the generation, transport and environmental fate of these priority pollutants. Moreover, many types of polymeric carbon, *e.g.*, activated carbons, are used as an adsorption medium for the clean-up and determination of PAH's in air and water. Some of the commercially produced polymeric carbons, such as lampblack or technical carbon black used in rubber tire manufacturing, have been shown to contain absorbed PAH's which are extractable in a standard Soxhlet apparatus with benzene [121]. However the finer particle size channel blacks used for pigments, or activated carbons used in water purification have not been shown to contain appreciable quantities of benzene extractable PAH's. The similarities in production methods for these different carbons have led to the suspicion that the small particle size channel black or activated carbon will contain adsorbed PAH's, but due to stronger adsorption these PAH's are not extractable by usual methods [122]

Polymeric carbon exhibits a high dielectric loss factor in the microwave radiation region [123]. The temperature of carbon particles so heated can be as high as 700°C just after one second of microwave treatment. These properties have been utilized in the regeneration of activated carbon by microwave radiation[123], in the reduction of metal oxides[124] and for soil decontamination by microwave volatilization in which solid carbon particles of an average diameter of 3 mm were used as the microwave energy receptors [77].

This chapter presents preliminary study of microwave assisted extraction of polycyclic aromatic hydrocarbons from activated carbon.

4.2. Material and Methods.

4.2.1. Apparatus

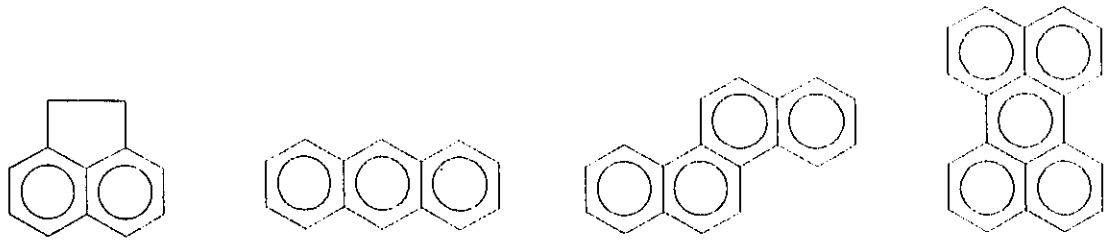
The CEM (Matthews, N.C., USA) model MDS-2000 microwave sample preparation system was used for microwave assisted extraction. Extraction was performed in 2 mL capped sample vials (Hewlett Packard, Palo Alto, Ca.)

The determination of extract composition was done by gas chromatography using a flame ionization detector GC-FID (Hewlett Packard 5890 series II)

4.2.2. Charcoal Sample

The charcoal used in the extraction experiments was taken from adsorption tubes produced by SKC Inc. (Eighty Four, Pa., USA). The charcoal was removed from the sealed glass tubes just prior to the addition of solution of PAH species.

4.2.3. Chemicals



Acenaphthene Anthracene Chrysene Perylene

Fig 4.1. Structures of aromatic compounds studied

Crystals of acenaphthene, anthracene, chrysene and perylene (Aldrich Chemicals, Milwaukee, WI.) were dissolved in hexane and stored in the dark at 4°C as a stock solution having a concentration of 800 μg/mL of each compound.

All solvents used for extraction were "distilled in glass" or equivalent quality.

4.2.4. Preparation of samples and extraction procedures

PAH's were absorbed onto activated charcoal by the addition of 100 μL of hexane solution with known concentration of four PAH's. Carbon sample weights were typically about 0.1 g. Spiked samples were dried under a gentle stream of nitrogen until the carbon particles became free flowing. The extraction procedure followed the drying step as soon as possible, usually not more than one hour after spiking.

The activated charcoal samples were suspended in 1 mL of each solvent. The suspensions were irradiated for 15-30 seconds in a microwave oven operating on the full 100W power with frequency of 2450 MHz. The samples were cooled to room temperature in 2-5 min and then irradiated and cooled again when necessary. Control samples followed the same procedure, but without microwave irradiation. After extraction an aliquot from each solution was analyzed by GC-FID or GC-MSD.

4.3. Results and Discussion

4.3.1. The Behavior of Solvents in a Microwave Field

Benzene, toluene, hexane, acetonitrile and carbon disulphide were chosen, to evaluate their utility as solvents in microwave assisted extraction of the aromatic molecules from polymeric carbon.

The properties of these solvents are given in **Table 4.1.** Except for acetonitrile, all have a low dielectric loss constant. They are transparent to microwave energy and so there is no significant temperature rise in a microwave field after 1 minute of irradiation. These solvents do not change their chemical composition. Chromatograms of acetonitrile, benzene and toluene after 30 s microwaving are presented in **Fig 4.2**.

Fig 4.2 shows also chromatograms of the pure solvents after contact with activated charcoal and 30 s irradiation in the microwave oven. The aromatic compounds, benzene and toluene, both showed signs of chemical reaction in

Table 4.1. Physical properties of solvents used for extraction of PAH from charcoal [125]

Solvent	Density [g/mL]	Boiling Point [°C]	Static Dielectric Permittivity	Dipole Moment [D]*	Viscosity [mN·s·m^{-2}]
Acetonitrile	0.783	81.6	37.5	3.92	0.375
Benzene	0.879	80.1	2.275	0	0.603
Carbon disulphide	1.263	46.3	2.641	0.06	0.363
Hexane	0.659	68.7	1.89	0.08	0.313
Toluene	0.866	110.6	2.38	0.36	0.552

* *Values of the dipole moments are shown in Debye units. The conversion factor to SI units is 1 D = 3.33564 x 10^{-30} C·m [coulomb-meter]*

the presence of charcoal and microwave energy. During irradiation the charcoal "boils" in all solvents and even some sparks between carbon particles can be visible. Carbon disulphide and hexane did not show changes in their chromatograms after microwaving with charcoal and without it. In order to eliminate the possibility that any new chromatographic peaks are due to the microwave assisted extraction of contaminants from charcoal, the same sample of charcoal was extracted 5 times with fresh benzene. Every extract showed the same chromatogram and the area of all peaks were the same. This shows that the new peaks in the chromatogram are produced during the microwave irradiation of charcoal plus solvents and not extracted from the charcoal itself. GC -MS analysis showed that the new chromatogram peaks result from reaction of the aromatic ring. For example peak 10.109 on

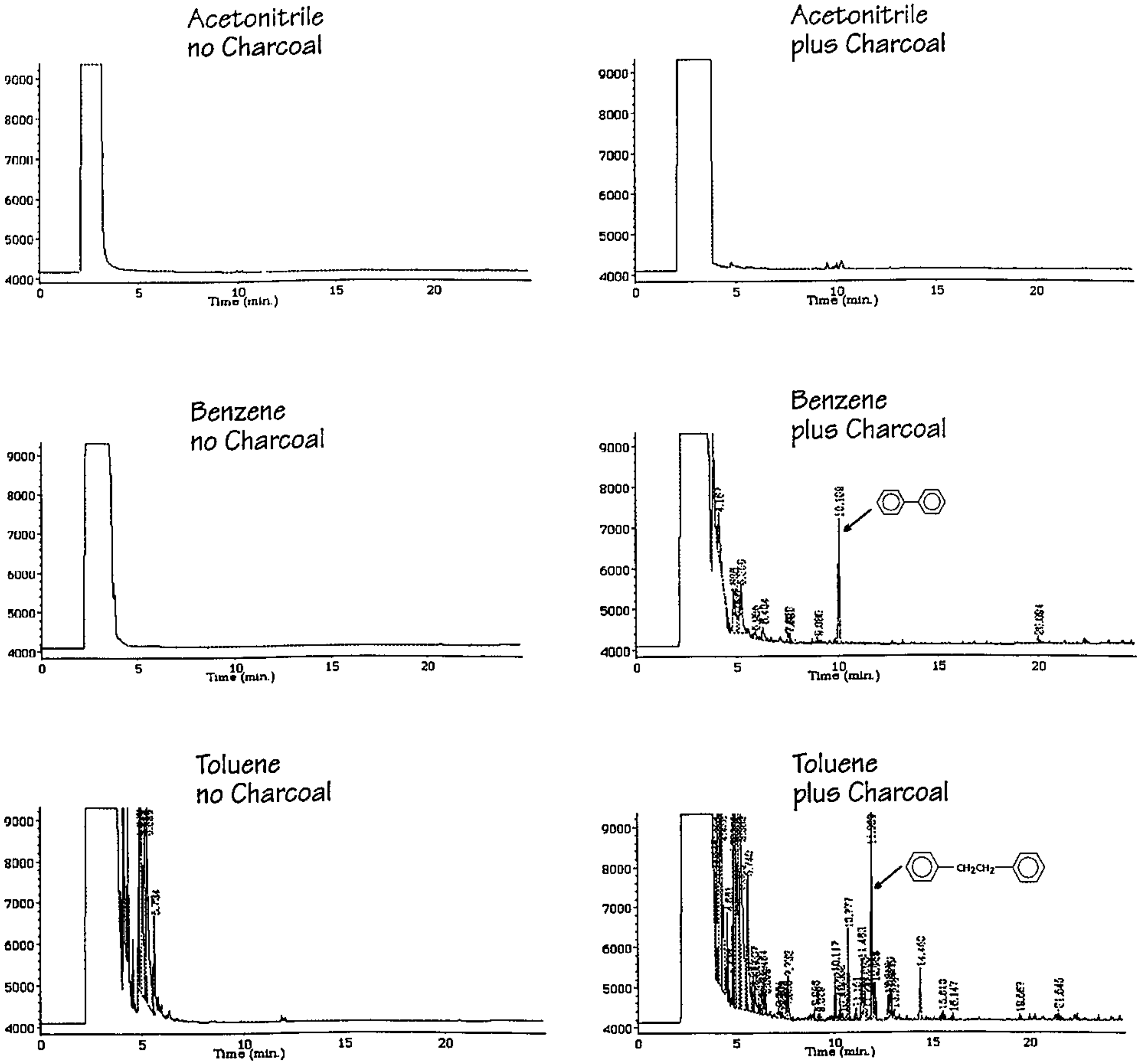


Fig 4.2. Gas chromatograms with FID detection of pure solvents after microwave irradiation

(**Fig 4.2**) was identified as biphenyl and for toluene bibenzyl was identified. Because aromatic solvents produce so rich a GC spectrum they clearly cannot be used as a solvent for the microwave assisted extraction of PAHs from charcoal. Only hexane and carbon disulphide showed acceptable blanks, allowing them to be used in future extraction experiments.

4.3.2. Microwave Assisted Extraction of PAHs from Charcoal

The recoveries of four polycyclic aromatic hydrocarbons from activated charcoal with carbon disulphide as a solvent are presented in **Table 4.2**.

Table 4.2. % Recovery of four PAH from charcoal with carbon disulphide as a solvent.

	Extracted compound recovery			
	Acenaphthene	Anthracene	Chrysene	Perylene
no charcoal 30s microwave	Taken as 100%	Taken as 100%	Taken as 100%	Taken as 100%
no microwave 1 h shake	33%	<0.1%	<0.1%	<0.1%
charcoal+30 s microwave	33%	<0.1%	<0.1%	<0.1%
charcoal+2 x 30 s microwave	29%	<0.1%	<0.1%	<0.1%
charcoal+3 x 30 s microwave	32%	<0.1%	<0.1%	<0.1%

Acenaphthene can be recovered moderately well from charcoal, but the larger compounds, with three or more aromatic rings are not visible in the GC-FID chromatograms of the carbon disulphide extracts. Irradiation of the samples with microwave energy showed no improvement.

Hexane was unable even to extract acenaphthene from a charcoal surface; recovery was less than 0.1% for all investigated compounds. Microwave irradiation brought no improvement in recovery.

4.4. Conclusions

The extractions of acenaphthene, anthracene, chrysene and perylene from activated charcoal were investigated. Changes in the chemical composition of the aromatic solvents were noted after contact with charcoal in a microwave field. The reactions are likely to be free radical type and they probably take place at the carbon surface. It is therefore proposed that adsorbed PAH's undergo the same type of metamorphosis, leading to larger and more strongly adsorbed molecular species. Natusch *et al.* [126] suggested that a coal surface can have catalytic activity towards aromatic compounds. They observed the degradation of fluorene on fly ash and carbon even without microwave irradiation.

It seems that microwave energy cannot be used to aid solid to liquid extraction of PAH's from charcoal for analytical purposes. Recent advances in short-path thermal desorption techniques [127] suggest that solid to gas extraction is a better method. The speed of diffusion of analyte from a hot charcoal surface to gas phase should be much faster to facilitate desorption of analyte without decomposition. Much shorter pulses of microwave energy, in the range of milliseconds [50] can preclude the production of localized hot spots in the charcoal and so may prevent thermal degradation of the analyte.

Literature

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