DESIGN OF MICROWAVE HEATING EQUIPMENT FOR LABORATORY APPLICATIONS

by

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ABSTRACT

General purpose pressure vessels for digestion in microwave ovens have been developed and their applications investigated. The vessels were manufactured from PTFE and polypropylene and included a safety valve. The easily manufactured vessels were found to be reliable for a wide range of samples. A small vessel of 10 ml capacity, also constructed from PTFE and polypropylene, was developed for very small samples. These were used for the digestion of blood.

A design for a simple modification of microwave ovens for use in the laboratory has been investigated. A Sharp microwave oven was lined with polypropylene and an extraction system that worked by the Venturi effect was used to remove the fumes from the cavity of the oven. This modification was found to be adequate to prevent corrosion of the oven and to provide the necessary safety features required for a laboratory system. In another modification, a thermocouple and a controller were used for maintaining the temperatures of the samples. Ports were available at the top of the cavity for insertion of suitable vessels for a variety of investigations.

A computer-controlled waveguide has been designed for general laboratory applications. The temperature of the samples could be monitored and controlled. The waveguide was used for investigating sample digestions and the heating characteristics of a wide range of materials.

A cylindrical applicator has been developed for the microwave heating of large (*ca.* 300 - 600 ml) samples. Temperature monitoring and control was achieved through the use of a thermocouple and a computer. The instrument was found useful for many laboratory investigations involving relatively large samples.

A new applicator has been developed for the even heating of multiple laboratory samples. The vessels (tubes) were introduced into the multimode cavity through ports. A choke was developed to allow rotation of the ports and the samples inside the cavity. Vapours could be extracted from the vessels outside the cavity using a fume extraction system. This system was found to be safe in terms of microwave leakages and yielded very good evenness of heating.

A number of waveguide structures have been evaluated for irradiating digestion vessels that are normally used in microwave ovens. A choke system was developed to allow the vessels to be easily inserted into the applicator. Very good heating reproducibilities of the samples were achieved in these applicators. Although these systems were found to be very sensitive to the

load characteristics, the power transfer could be adjusted by controlling the microwave power and by using matching techniques. It was demonstrated that microwaves could be used to heat the contents of a PTFE-lined steel pressure vessel by coupling the power through an aperture at the bottom of the vessel. Good power transfer was achieved and the system was found to be extremely sensitive to the load conditions. By monitoring the reflected power, large variations of power transfer were noted during the heating cycle and pressurization, but it was shown that on-line tuning could be used to control the power transfer. Digestions carried out in the pressure vessel took shorter times than normally taken in the microwave oven.

A cylindrical microwave reactor using a 1.2 kW generator has been built for the heating of relatively large loads. On-line tuning could be performed to achieve high efficiencies in different loads.

Two simple and compact on-line heaters have been developed for laboratory applications. The use of waveguide structures and on-line tuning provided very efficient heating for a wide range of applications.

A cavity has been designed for studying gas discharges excited by microwaves. Discharges of nitrogen, argon and oxygen were studied. A reactor and a manifold were developed to study the reactions of singlet oxygen species with organic molecules. Very efficient oxidation reactions were achieved in a number of samples.

The design of a gas thermometer has been evaluated for use in a microwave field. These simple thermometers were found to perform well and could be used to control temperature.

A 10 GHz microwave moisture meter has been developed and evaluated for granular and powder samples. The design was based on the absorption of microwaves by the moisture in the sample. The sample masses were approximately 20 g and the samples were held in a length of waveguide for the measurements. Calibration curves in the range 0 to 15 % moisture were constructed for molecular sieve, kaolin and rice. The simple instrument was found to give good reproducibility and accuracy.

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PUBLICATIONS

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Pougnet M A B, Schnautz N G, and Walker A M
Development and application of a microwave digestion pressure vessel.
S.Afr.J.Chem.,1992,**45**(4),86-89.

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Modification of a commercial microwave oven for applications in the chemical laboratory.
Rev.Sci.Instrum.,1993,**64**(2),529-531.

Pougnet M A B, Downing B J, and Michelson S C
Microwave irradiation systems for laboratory pressure vessels.
J.Microwave Power and Electromagnetic Energy,1993,**28**(1),18-24.

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A cylindrical microwave cavity for laboratory applications.
J.Microwave Power and Electromagnetic Energy,1993,**28**(2),114-119.

CONTENTS

CHAPTER 1

INTRODUCTION

1.1 Microwaves and microwave heating

Microwaves are part of the electromagnetic spectrum (Figure 1.1) lying between the infrared region and conventional radiowaves and having a frequency range of 0.3 to 300 GHz, corresponding to wavelengths ranging from 1 m to 1 mm. The microwave frequencies of particular interest in microwave heating are 915 MHz (896 MHz in UK) and 2.45 GHz. These frequencies correspond to wavelengths in free space of 32.8 cm and 12.2 cm, respectively, and have been set aside for industrial, scientific and medical (ISM) use in most countries [MET91]. The majority of domestic microwave ovens operate at 2.45 GHz and both frequencies are used in industrial systems.

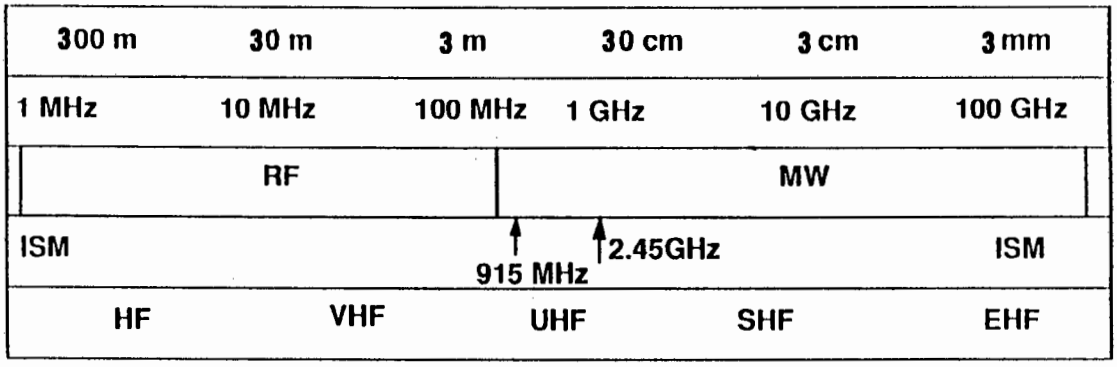


Figure 1.1 The electromagnetic spectrum.

1.1.1 The magnetron tube

Microwaves are generated in special vacuum sealed electron tubes such as the klystron and the magnetron. Magnetrons are classified into pulsed and continuous-wave (CW). The pulsed magnetron is mainly used for radar applications and the CW magnetron for microwave heating equipment. A qualitative description is given below.

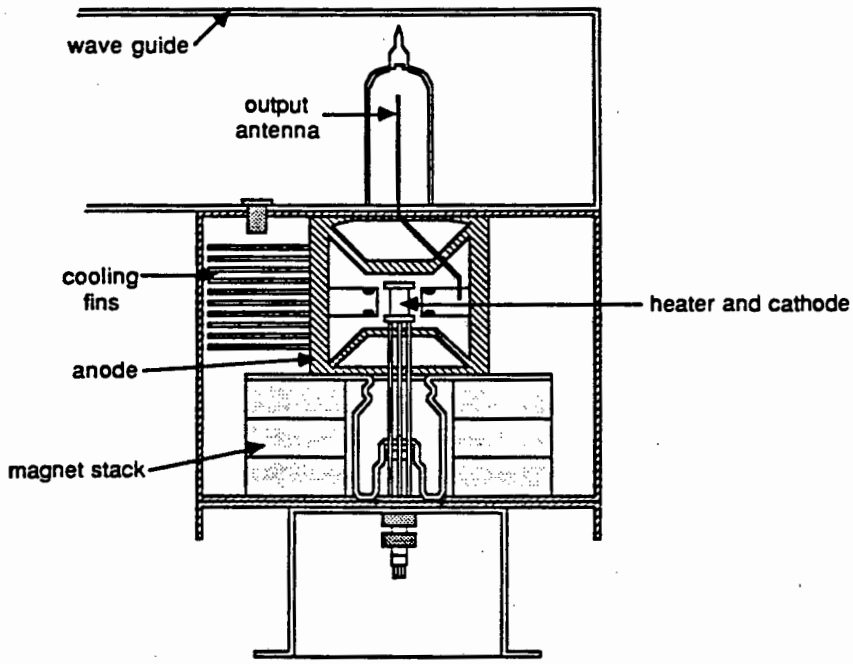
The magnetron is an electron tube (Figure 1.2) which is constructed so that electrons are controlled by a unidirectional coaxial magnetic field which passes through the interaction space (vacuum) between the cathode and the sectored anode. The anode has even numberes of resonant cavities connected in parallel, which produce microwaves through the energy transfer between electrons emitted by the cathode and the RF electrical field excited on the cavities. The copper anode consists of an even number of vanes strapped alternately. The space between two adjacent vanes forms a resonant cavity and all the spaces are arranged so as to be synchronous with the oscillating frequency.

The cathode (or filament) is directly heated (filament voltage) and is usually made of thoriated-tungsten. A magnetic field is applied in a direction parallel to the axis of the tube using permanent magnets or electromagnets (where the field strength can be varied to obtain variable power output). A high voltage (several thousand volts) is applied between the electrodes. The electrons emitted at the cathode follow a curved path to the anode under the influence of the magnetic field and a high energy rotating electron beam is formed in the interaction zone. The cycloidally-moving electrons are excited and form electron clouds due to the interaction of the DC and RF electric fields between the tips of the vanes of each resonant cavity. The electron clouds form repeatedly to give the cavities energy. Thus, the oscillation is maintained, and the oscillating energy is coupled-out by means of a probe from one of the resonant cavities into an antenna where it is launched into a transmission line or sometimes directly into a microwave cavity.

The efficiency of the magnetron is as high as 60 to 80 %. Anode cooling is required to avoid excessive rise in temperature since the rest of the input power is dissipated mostly in the anode.

The features of CW magnetrons such as compactness, ruggedness, high efficiency and stability, and also low cost, are the reasons why they are widely used as sources for microwave ovens and other heating equipment.

A



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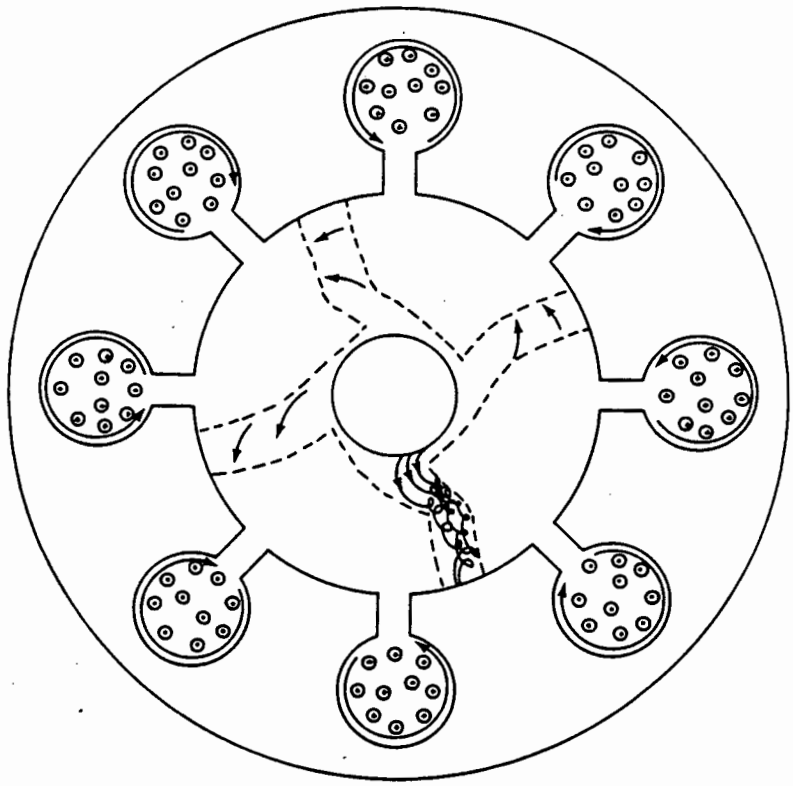


Figure 1.2 (A) Schematic of the magnetron.
(B) Cross-section of the anode and electron movement in the interaction zone.

1.1.2 Transmission of microwaves

Electromagnetic energy travels along a microwave transmission line as guided waves comprising of periodically-varying electric and magnetic fields. Several types of transmission lines are used for microwaves, including waveguides, coaxial lines and microstrip lines. Hollow metal waveguides are usually used for high power applications. Three types of wave configurations or modes can exist on a transmission line. Coaxial and microstrip transmission lines propagate TEM modes whereas waveguides propagate TE and TM modes. The transverse electromagnetic mode (TEM), has the electric and magnetic fields transverse to the direction of flow; the transverse electric (TE) mode has the electric fields transverse to the energy flow and the magnetic fields in the direction of energy flow; and the transverse magnetic (TM) mode has transverse magnetic fields and electric fields in the direction of energy flow. While the TEM mode can propagate along coaxial and microstrip transmission lines at all frequencies, the TE and TM modes which propagate in waveguide structures have a minimum frequency below which energy will not propagate (the cutoff frequency) and each mode has a different cutoff frequency.

The waveguide modes are identified by the type of mode (TE or TM) followed by two subscripts m and n. The subscript m denotes the number of half-wave variations of transverse field intensity along the wide dimension of the rectangular waveguide, a, (see Figure 1.3) and n denotes the number of half-wave variations along the narrow dimension b. For circular waveguides, m is the number of full-period variations of electric or magnetic field along a circular path concentric with the wall and n is one more than the total number of electric or magnetic field reversals along a radial path. Figures 1.4 and 1.5 show the field configurations of some modes in rectangular and circular waveguides, respectively.

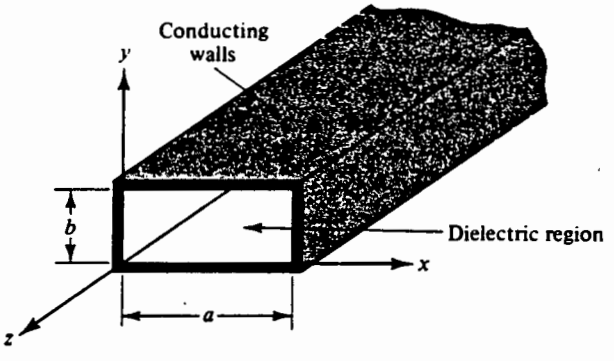


Figure 1.3 Rectangular waveguide.

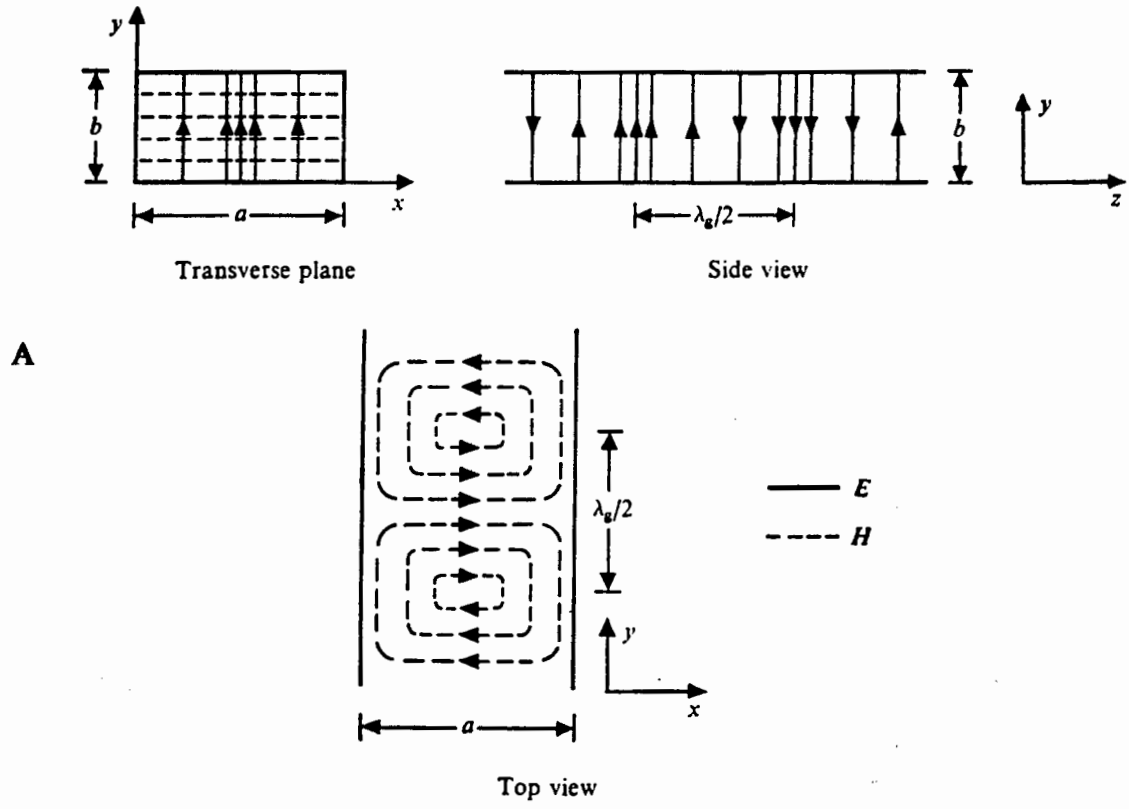


Figure 1.4 Some rectangular waveguide modes. A: TE_{10}; B: TE_{11}; C: TM_{11} (solid line: electric field, dashed line: magnetic field).

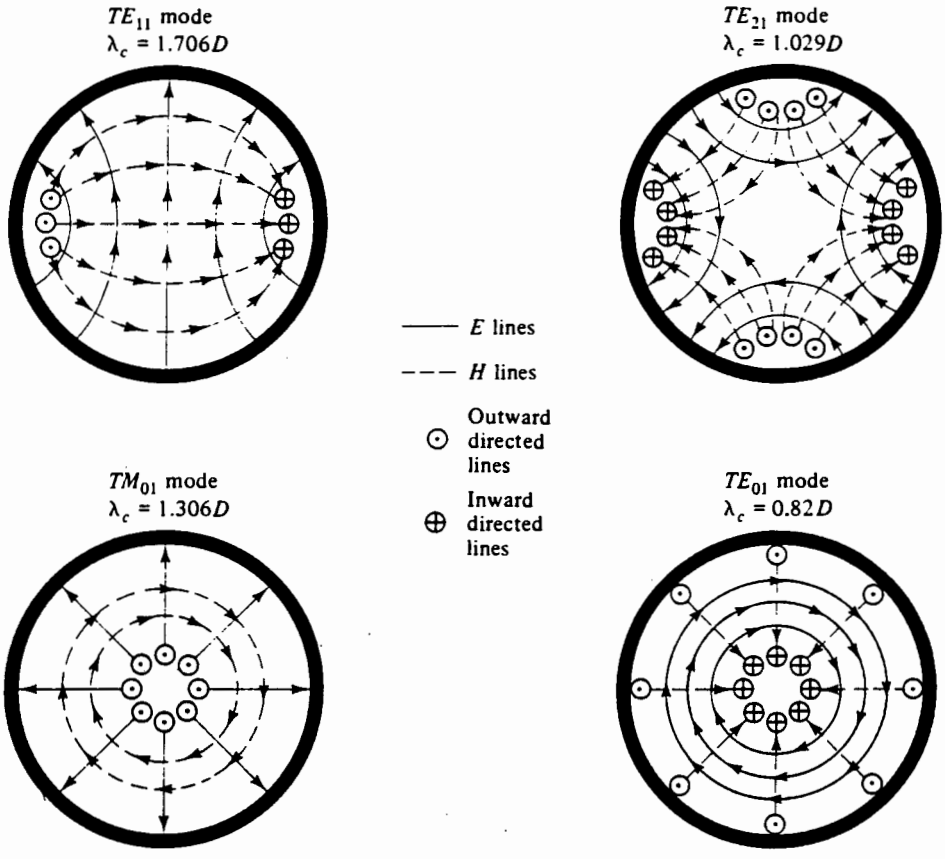


Figure 1.5 Some circular waveguide modes. D = inner guide diameter.

The cutoff wavelength λ_c for any TE or TM mode in a rectangular waveguide is given as:

$$\lambda_c = 2 \left[\left[\frac{m}{a} \right]^2 + \left[\frac{n}{b} \right]^2 \right]^{-\frac{1}{2}} \tag{1}$$

The cutoff wavelengths of a circular waveguide for the TE and TM modes are:

TE mode

$$\lambda_c = \frac{2\pi a}{u'_{m,n}} \tag{2}$$

TM mode

$$\lambda_c = \frac{2\pi a}{u_{m,n}} \tag{3}$$

where a is the waveguide inner radius, u′ is a constant, different for every TE mode and u is a constant for every TM mode. In order to propagate energy, waveguide sizes are larger at lower frequencies and the lowest frequencies used are confined by the impractical large size requirements.

The guide wavelength λ_g is different from the free space wavelength and is given as:

$$\lambda_g = \lambda_0 \left[1 - \left[\frac{\lambda_0}{\lambda_c} \right]^2 \right]^{-\frac{1}{2}} \tag{4}$$

where λ_0 is the wavelength in free space.

Waveguide sizes have been standardized for the different frequency bands in the microwave spectrum and waveguide components such as flanges, bends, twists and tapers are available commercially. The standard waveguide for operation at 2450 MHz (R26 or WR340) has internal dimensions of 86.36 mm x 43.18 mm. Non-standard waveguide sizes can also be used provided they are of the correct size for the desired mode or modes of propagation.

Coaxial lines consist of a cylindrical outer conductor with an axially-located circular inner conductor. Both conductors are made of high conductivity metals such as copper or brass. The configuration of the electric and magnetic fields in the line is shown in Figure 1.6, where the electric field is confined to the radial direction and the magnetic field lines enclose the centre conductor. The wavelength in the line filled with air is the same as the free space wavelength. However, in dielectric-filled coaxial lines the wavelength is equal to the free space wavelength divided by the square root of the dielectric constant. Both flexible and rigid coaxial lines can be used, and standard sizes are available having different frequency and power-handling limitations. The high field intensities in coaxial lines can result in arcing due to excessive heating of the centre conductor and is therefore a limiting factor for power handling. In high-power applications waveguides are preferred to coaxial lines since they are less lossy and can handle higher power.

The wave impedance (Z_W) of an electromagnetic wave is the ratio of the electric field strength to the magnetic field strength. The strength of an electric field or magnetic field is related to the permittivity and permeability of the medium, and Z_W in free space can be calculated as

377. In a waveguide the characteristic wave impedance is the ratio of the electric and magnetic field strengths transverse to the direction of energy flow and is dependent on mode and wavelength. In air filled rectangular waveguides,

$$Z_{TE} = Z_w \cdot \frac{\lambda_g}{\lambda_0} \cdot \frac{b}{a} \tag{5}$$

$$Z_{TM} = Z_w \cdot \frac{\lambda_0}{\lambda_g} \cdot \frac{b}{a} \tag{6}$$

and in coaxial lines,

$$Z_{TEM} = 138 \sqrt{\frac{\mu}{\epsilon_r}} \cdot \log \left[\frac{R_0}{R_1} \right] \tag{7}$$

where μ is the permeability and ϵ_r is the dielectric constant of the medium separating the conductors and R_0 and R_1 are the radii of the inner and outer conductors respectively.

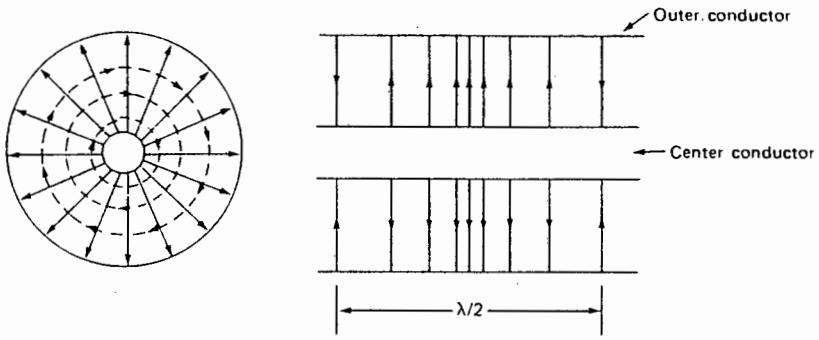


Figure 1.6 The coaxial line showing the TEM mode configuration (solid line: electric field, dashed line: magnetic field).

When a wave travels along a transmission line which is not terminated with its characteristic impedance, the wave is reflected from the termination point and travels back towards the source. Both waves are attenuated as they travel along the line according to the loss characteristics of the line. The two waves form a standing wave. The voltage and current standing waves are displaced by a quarter wavelength. The standing wave has its maximum field where the waves are in phase. The voltage standing wave ratio (VSWR) is defined as the ratio of the maximum to minimum voltages:

$$\text{VSWR} = \frac{E_{max}}{E_{min}} = \frac{1 + |\rho|}{1 - |\rho|} \qquad (8)$$

where ρ is the magnitude of the reflection coefficient.

The VSWR can be measured by inserting a movable probe through a longitudinal slot cut in the side of the line. If the reflection coefficient is zero, none of the incident microwave power is reflected from the load and the load is said to be matched to the line. If the reflection coefficient is non-zero (*i.e.*, a mismatch between the transmission line and the load), a tuner can be inserted between the line and the load and can be adjusted to create an additional reflection of power which cancels out that of the load so that no reflected power exists in the line and the VSWR = 1, when maximum power transfer to the load is obtained. Various devices are used to match impedances and they include quarter-wave transformers, tapers, transitions, and stub tuners. Transitions can be made from rectangular to circular waveguides and from waveguide to coaxial lines. Some useful transitions are shown in Figure 1.7.

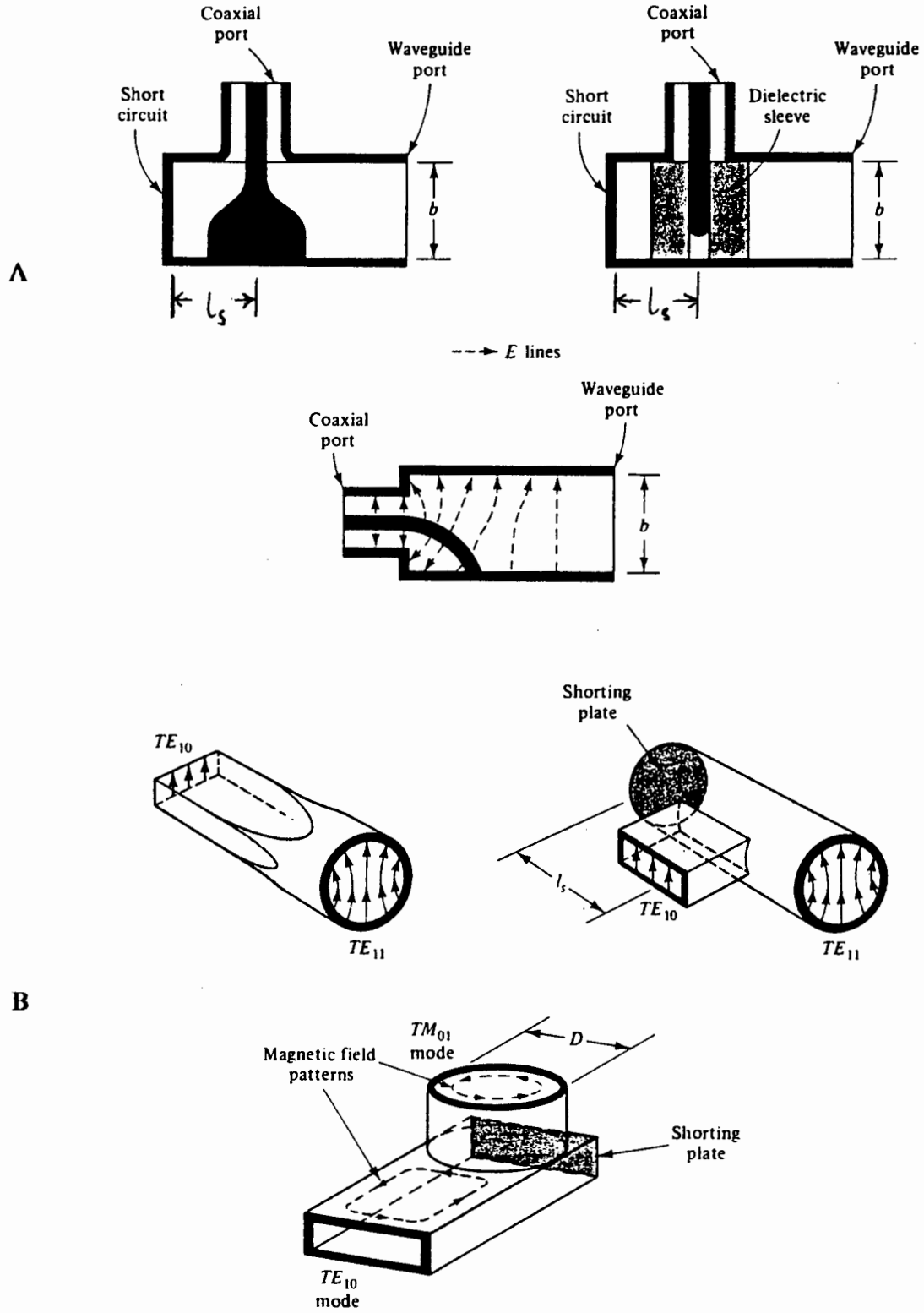


Figure 1.7 Transitions from rectangular waveguides to coaxial (A) and rectangular to circular waveguides (B). $l_S = \lambda_g/4$.

1.1.3 Microwave heating applicators

There are two basic approaches for applying microwaves to materials. Waveguide applicators where the material concerned is generally of smaller or comparable size to that of a suitable waveguide (travelling-wave applicators and single-mode resonant cavities), and multimode designs where the material is placed in or conveyed through a metal enclosure or cavity in which a large number of resonant modes are excited. By far the most widely-used microwave applicators are of the multimode type, as used universally in domestic ovens and industrial installations. The design of the microwave oven will be discussed first and this will be followed by a brief discussion of the single-mode applicators.

The important components of a microwave oven are illustrated in Figure 1.8. Most commonly, the microwaves are launched in a waveguide and enter the cavity through one or more openings. The waveguide structure can vary widely in dimension (specially in commercial domestic ovens) and direct coupling of the magnetron into the cavity can also be used. When the microwaves enter the cavity, they are reflected between the metallic walls and set up a standing-wave pattern. Thus the energy pattern or distribution is not uniform and low and high energy density spots exist. When a load (material which absorbs energy) is placed inside the cavity, part of the energy is absorbed and converted into heat and the wave pattern is also changed. While it is possible to calculate the cavity size so that the maximum number of modes are excited within the cavity and thus ensure the best energy distribution [PUS66], the non-uniformity of the field remains a major problem and much consideration has been given to minimise its effect. One method of overcoming the problem is continually to alter the geometry of the oven, thus changing the positions of the field intensity nodes and antinodes continuously so that the energy distribution over the time period of exposure to microwaves is equalized and the material more uniformly heated. This is done usually by the use of a mode stirrer, which is a rotating metallic structure (more commonly resembling fan blades), causing extra reflections of the waves. The most common and effective technique is to move the load through the field, either on a conveyor belt as in industrial microwave applicators or on a rotating turntable in the smaller ovens. Other methods that have been used include rotating antennae [SIM80], multiport feeds from a single magnetron waveguide, multiple feeds from several magnetrons, or a combination of some of the above techniques when uniform heating is very critical.

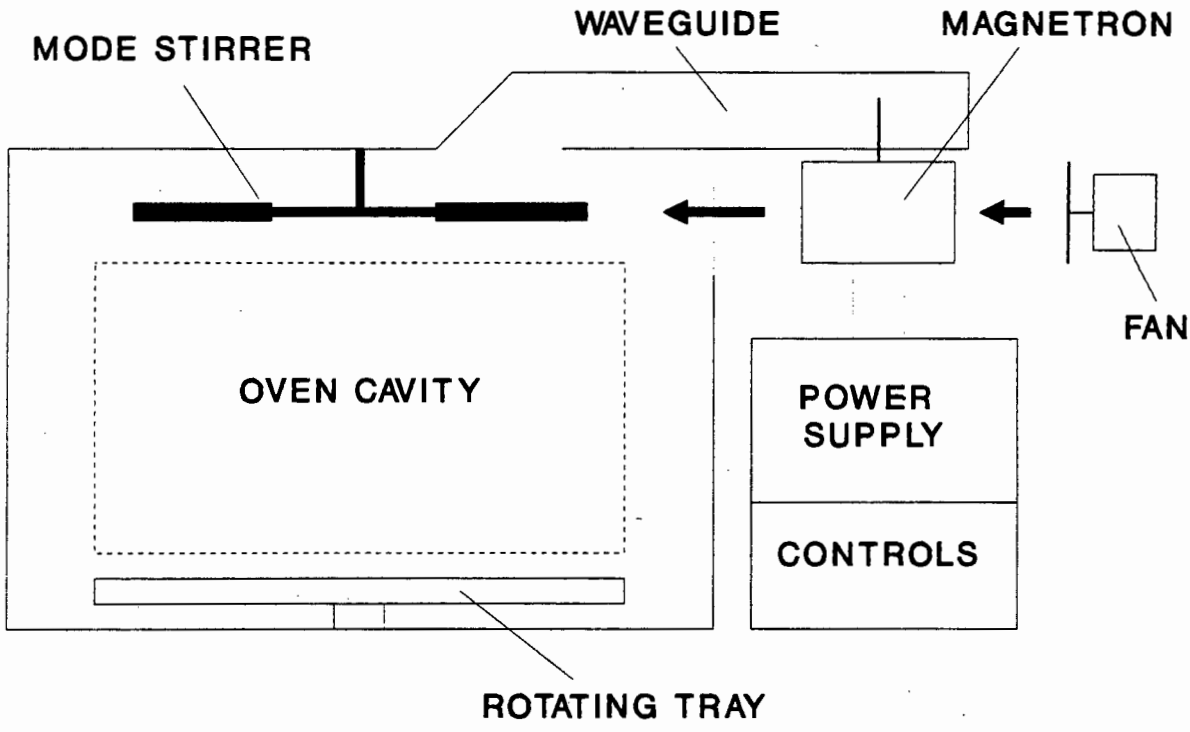


Figure 1.8 Schematic design of the microwave oven.

All microwave applicators contain some sealing structures to prevent excessive leakages of microwave energy. Currently, a maximum level of 5 mW cm^{-2} is recommended by the American National Standards Institute [KIN88]. Elaborate systems have to be used in continuous (conveyor belt) type industrial applicators [MET88]. In batch systems such as the microwave oven, a metal to metal contact seal is effective but for practical reasons, the quarter-wave choke designs are more widely used in domestic ovens and other small applicators. The principle of operation is illustrated in Figure 1.9. The two sections of exactly one-quarter wavelength long create a short circuit which prevents propagation of the waves past the door.

All ovens have primary and secondary door interlocks (electrically and mechanically independent of each other) which ensures that the magnetron is not powered when the door is opened. Additionally, a third interlock switch causes discharge of any residual power on the power supply on opening the door when the oven is ON.

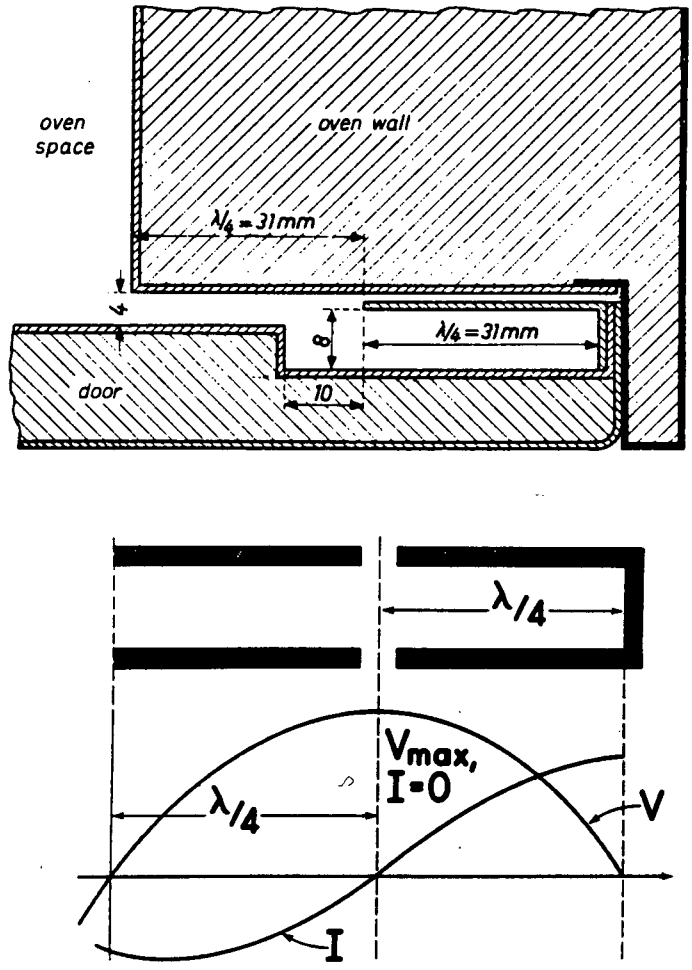


Figure 1.9 Quarter wavelength choke for door of microwave ovens [COP62]. The principle of operation of the choke is shown in the lower figure.

Most magnetrons used in domestic microwave ovens are designed to deliver a fixed power output. The power is then varied by ON/OFF control. A duty cycle control mechanism (electro-mechanical or microprocessor) switches the transformer primary voltage ON or OFF according to a selected schedule, thus varying the average output of the magnetron. A setting of 50% means that the power is ON 50 % of the time. The duty cycle (ratio of time ON to cycle time) is limited by the necessity for magnetron "warm up" time after the OFF time. This arises from the time required for the filament to attain optimum temperature for efficient electron emission. In most domestic ovens, a combination transformer (incorporating the filament and high voltage supplies) is normally switched ON and OFF. The warm-up period thus limits very fast pulsing of the magnetron to achieve fast smooth rates of heating. If the latter condition is necessary, a separate filament transformer should be used. Pulsing is then

achieved by switching only the high voltage supply. While for cooking the above mode of power control may be adequate, for many scientific and industrial applications it is desirable to use adjustable continuous power. Several techniques are used to control the power output of a magnetron. Some industrial grade magnetrons have electromagnets that allow variation of the output power. Other systems include the use of variable autotransformers, saturable reactors and phase controllers to adjust the high voltage to the magnetron [DEC86].

A problem common in microwave heating applications is that when a small load is placed in the cavity, a large proportion of the power delivered by the magnetron is not absorbed and is reflected back to the magnetron. Operation in a high reflected power situation may result in over-heating of the magnetron, unstable performance and possible damage to the tube. In domestic microwave ovens, a fan is used to cool the magnetron and a thermal cutoff switch is mounted on the magnetron and sometimes also on the cavity. Industrial high-power magnetrons are normally water-cooled. A simple precaution that has been taken in many cases where domestic ovens are used for scientific investigations is to place a dummy load in the cavity: this can be simply a volume of water. In industrial applications and properly-designed microwave heating applicators, isolators or circulators are used to protect the magnetron. The isolator is a ferrite device allowing transmission of energy in one direction but attenuating it in the other direction, reflected power being absorbed by the device and having to be dissipated. The circulator (or iso-circulator) is a three-port device as illustrated in Figure 1.10. Port 3 is terminated by a matched dummy load which effectively absorbs energy reflected from output port 2. The dummy load normally consists of flowing water into a microwave-transparent container inside a length of waveguide. These devices are expensive and therefore not used in domestic ovens.

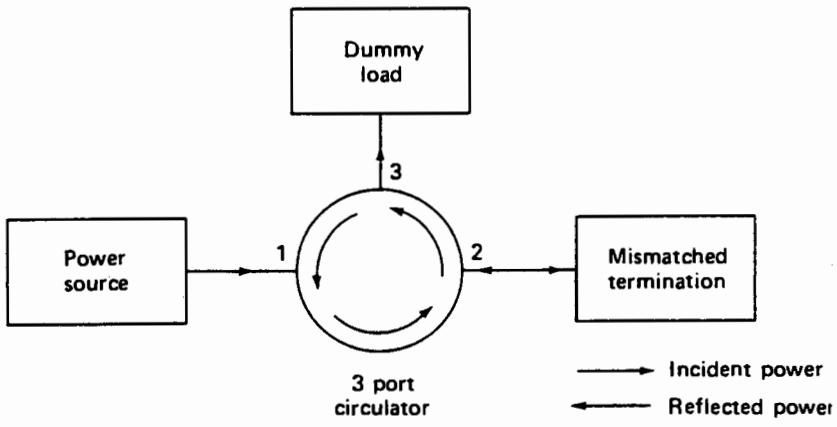


Figure 1.10 The iso-circulator.

The power absorbed by a material in a microwave field is proportional to: $f E^2 \tan\delta$ where f is the operating frequency, E is the electric field and $\tan\delta$ is the loss tangent or power absorption of the material (see below for a more detailed discussion). From the above equation it is clear that a high field intensity is desirable for materials having a low $\tan\delta$ or if very high rates of heating are necessary.

In a normal microwave oven, the cavity is quite large and when a very small load is present, the E field will increase until all the losses present within the cavity, including the cavity itself, are satisfied. The losses (apart from the load) are made up from small leakages (*e.g.*, at the door seal) and the circulating currents induced in the cavity walls. For example, the circulating currents are low for aluminium (since the skin resistance is low) compared with stainless steel. The greater the area, the greater are the losses. The difference between a substantial load and a light load gives rise to an increase of the E field. A measure of the sharpness of a cavity to respond to external excitation is the quality factor, Q, which is defined as:

$$Q = 2\pi \frac{\text{total energy stored}}{\text{energy dissipated in both the cavity and the dielectric / cycle}} \qquad (9)$$

Since in a multimode cavity there is a limitation to the magnification or Q factor achievable, the E field will never rise to a high value and the amount of energy that can be absorbed in a material will be restricted. In microwave ovens the E field will be limited which results in a low rate of rise of temperature. The amount of energy that can be dissipated depends on the source and the utilisation efficiency. When high rates of heating or the heating of low loss materials are required, high Q cavities are used. These are single-mode resonant cavities which can operate in the fundamental or higher-order mode. The superposition of the incident and reflected waves in a waveguide yield a standing wave pattern which is well-defined in the cavity (Figure 1.11). Thus, materials can be positioned at the electric field maximum for optimum absorption of energy. Since the internal dimensions are small, the losses are also small and therefore the Q factor can be very high. However, for high Q cavities, the magnetron frequency must be stable and care has to be taken in designing the power supply. Because of the dielectric material inside the waveguide, the system has to be tuned and this is achieved by using the plunger-tuner which allows the field maximum to be adjusted and placed at the position of the material in the waveguide. The function of the aperture (coupling iris) is to provide matching of the impedance of the loaded cavity to the impedance of the waveguide. The size of the coupling aperture is dependant on the material and will affect the power transfer and the Q of the cavity. Its optimal size is normally found experimentally.

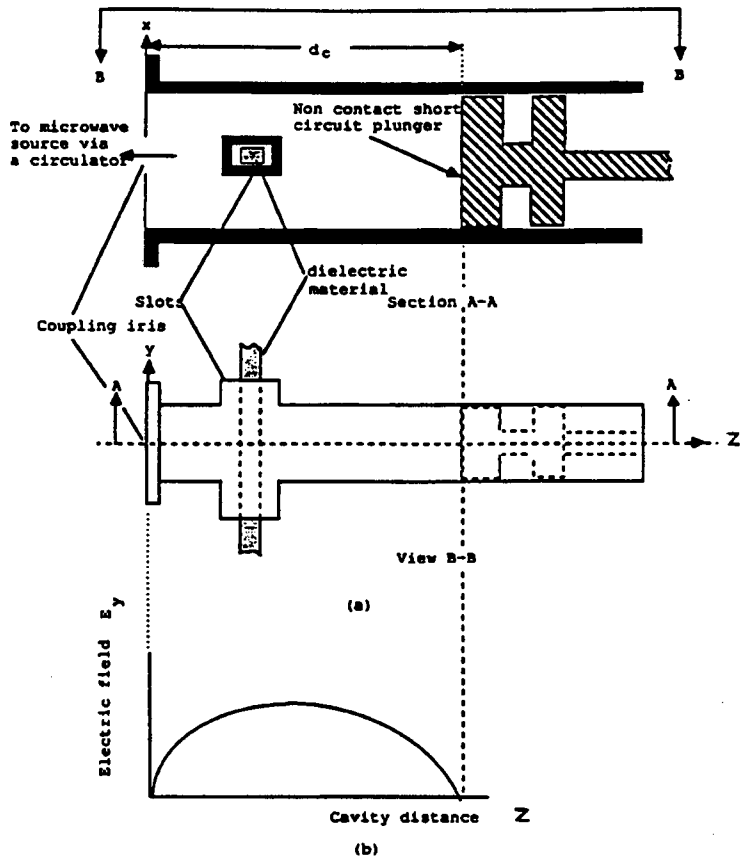


Figure 1.11 A single mode resonant cavity [MET90].

Single mode resonant cavities have been designed for a variety of applications and many examples are discussed by Metaxas and Meredith [MET88]. Asmussen *et al.* [ASM87] and Jow *et al.* [JOW89] have discussed the operation of a cylindrical cavity for a number of applications. The design of a cylindrical cavity is shown in Figure 1.12. Metaxas [MET90] developed a variable-aperture resonant applicator to process a wide range of materials. The single-mode resonant cavities have found wide applications in the processing of ceramics [BER76,BAD82,SUT89,BRO89]. Other applications include the use of microwave-induced plasmas for materials synthesis [ASM88,SAL91] and electrodeless discharges in gases for spectroscopy [FEH65,MCF75,BOZ81] .

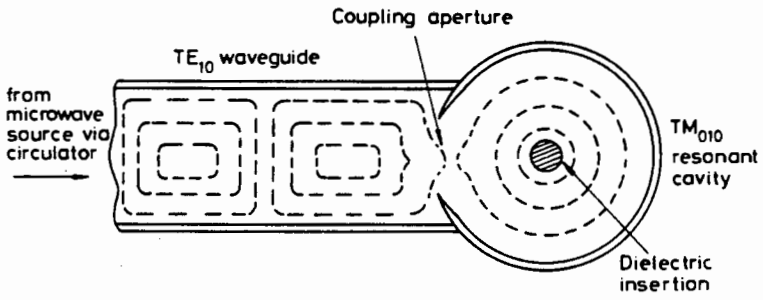


Figure 1.12 Cylindrical cavity [MET88].

In travelling wave applicators (Figure 1.13), the energy is continually absorbed by the load within the waveguide and excess energy is dumped into a dummy load which terminates the waveguide. If all the power is absorbed by the load, it is sometimes not necessary to have the dummy load and the waveguide is terminated by a short circuit plate. Several designs have been found useful for industrial applications such as axial applicators, the helix applicator and the meander (or serpentine) applicators for sheet or filament materials (Figure 1.13). The principles of operation are discussed in more detail by Metaxas and Meredith [MET88].

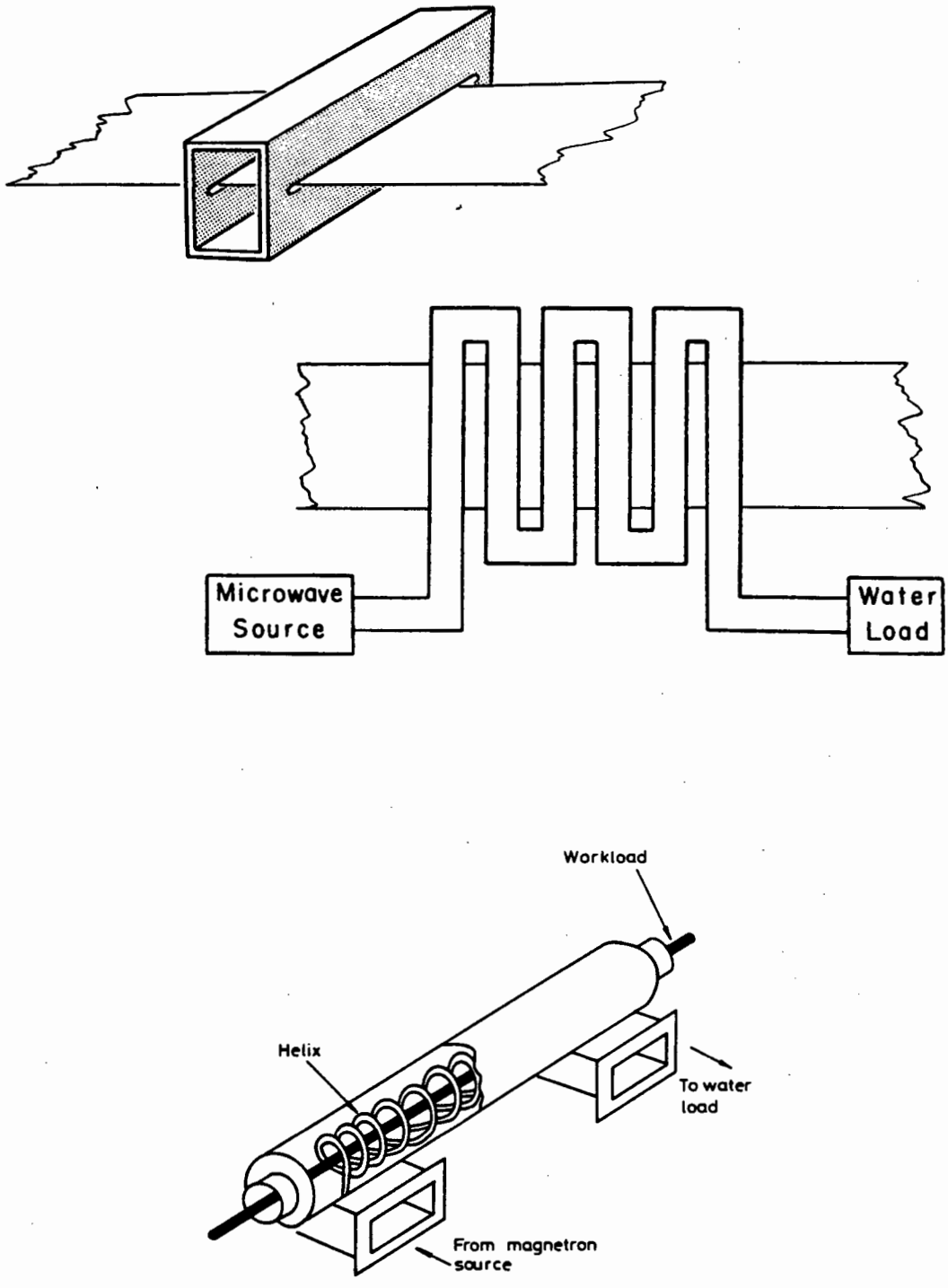


Figure 1.13 Travelling wave applicators. A : slotted waveguide and serpentine applicator for sheet material. B : Helix applicator [MET88].

1.1.4 Mechanism of microwave heating

The interactions of microwaves with materials which results in heating are related to the electrical properties of the materials. While it is beyond the scope of this work to deal with this in great detail, some basic concepts are discussed below. More details on dielectric properties and losses and the theory of volumetric heating are found in the references [FRO49,VON54,AND64,FEY64,PUS66,SCH71,MET88].

If a dielectric is inserted between two plates of a parallel capacitor, its capacitance is seen to increase by a factor ϵ_r due to the increased electric field energy being stored in the dielectric. This factor, ϵ_r, is called the relative permittivity or dielectric constant of the dielectric. In reality, ϵ_r is generally complex, since it not only accounts for stored energy within the dielectric, but for energy losses as well. Since dielectrics are insulators they have no free charges to allow for DC conduction. However, transient electric fields do result in the movement of bound charges, and hence transient conduction [AND64]. The following simple model helps to explain this. The electrically-neutral dielectric consists of positive and negative charges which are bound together and not free to separate [e.g., a symmetrical neutral atom consisting of a nucleus within an electron cloud, Figure 1.14(a)]. However, application of an electric field **E** will distort the atom, moving positive and negative charge centres apart. This displacement of the relative positions of these oppositely bound charges results in a small dipole moment **p** being induced [Figure 1.14(b)].

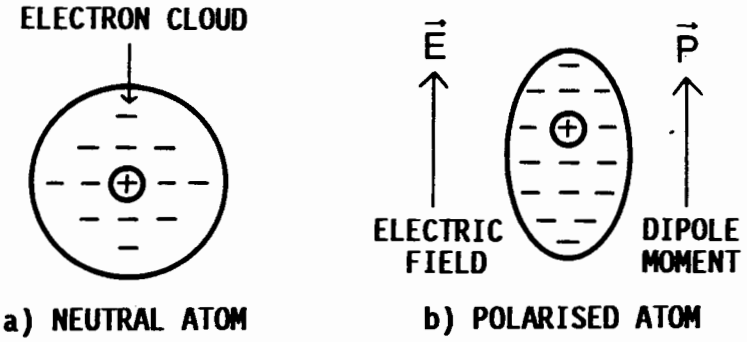


Figure 1.14 Induced polarisation in a neutral atom.

For N such atoms (or molecules), the total polarisation **P** of the dielectric is then

$$\mathbf{P} = N\mathbf{p} \tag{10}$$

Polarisation **P** is also proportional to the electric field intensity **E**. The constant of proportionality depends on the ease with which dipole moments are induced for that specific material [FEY64]. The proportionality may be written as

$$\mathbf{P} = \chi \epsilon_0 \mathbf{E}, \tag{11}$$

where χ is the dielectric susceptibility of the material, and ϵ_0 is the absolute permittivity of free space.

The relative permittivity ϵ_r is related to the dielectric susceptibility χ by:

$$\epsilon_r = 1 + \chi \tag{12}$$

Thus, the more easily the material polarises, the larger ϵ_r. The mechanism of polarisation is not limited to the above example. Two of the most common forms of polarisation are electronic polarisation and orientation polarisation [FRO49].

Electronic polarisation occurs for non-polar molecules, as in the above example. Here polarisation is due to induced dipole moments caused by the relative shifting of the oppositely-charged nucleus and electron cloud. This is a fairly weak effect, and hence non-polar molecules tend to have low permittivities.

Orientation polarisation occurs for polar molecules (e.g., water). Although polar molecules possess individual dipole moments, the average polarisation of the material in the absence of an electric field is zero, due to their random orientations. On the application of an electric field the moments become aligned, resulting in a strong net polarisation. Permittivities for polar molecules can thus be high (e.g., for water, ϵ_r = 73 to 77).

Another source of polarisation arises from charge build-up at interfaces in nonhomogeneous materials. This is termed interfacial or space charge polarisation, or is called the Maxwell-Wagner effect. For mixtures containing large amounts of conductive phases, this mechanism can contribute significantly to the overall polarisation, as shown by Wagner [WAG14].

The mechanism of power loss in a dielectric, due to an alternating electric field, will now be explained. The concept of complex permittivity, which is used to account for these losses, is now introduced. Since the dielectric permittivity is of more interest than the electric susceptibility, it is more convenient to work with the electric displacement vector **D** than the polarisation **P**, and $\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$.

When the polarising electric field is sinusoidal, $\mathbf{E} = \mathbf{E_0} \cos(\omega t)$ [$\mathbf{E_0}$ = peak electric field], as for an electromagnetic wave, the dipole moment will oscillate in orientation in an attempt to stay aligned with the field. However, due to the internal moments and restoring forces of the molecules, the polarisation will lag behind the electric field [SCH71]:

$$\mathbf{D} = \epsilon^* \mathbf{E} \cos(\omega t - \delta) \qquad (\delta > 0 \text{ since lag}) \quad \text{or} \tag{13}$$

$$\mathbf{D} = \epsilon^* \epsilon^{-i\delta} \mathbf{E} \exp(j\omega t) \qquad \text{(using phasor notation)} \tag{14}$$

where $\epsilon^* \epsilon^{-i\delta}$ is a complex factor accounting for this phase difference. Thus, the complex permittivity ϵ can now be defined as

$$\epsilon = \epsilon^* e^{-j\delta} = \epsilon_0 (\epsilon' - j\epsilon'') \tag{15}$$

where $\epsilon' = \epsilon^* \cos\delta$ and $\epsilon'' = \epsilon^* \sin\delta$

From electromagnetic theory, the energy change (per unit volume) is given by the expression **E** d**D**.

The energy loss rate L in the dielectric is thus given by

$$L = \frac{\omega}{2c} \int_0^{2\pi/\omega} E \frac{\delta D}{\delta t} \, dt \tag{16}$$

Inserting the expressions $\mathbf{D} = \epsilon_0 \mathbf{E} \{\epsilon' \cos(\omega t) - \epsilon'' \sin(\omega t)\}$ and $\mathbf{E} = \mathbf{E_0} \cos(\omega t)$ into the above and integrating, the formula for the mean energy loss rate L in a dielectric is obtained:

$$L = \frac{\epsilon_0 \epsilon'' E_0^2 \omega}{2} \tag{17}$$

The real part of the complex permittivity (ϵ') can now be recognised as the familiar dielectric constant (since $\cos\delta \approx 1$ as δ is small), whereas the imaginary part (ϵ'') is termed the dielectric loss factor. It is this loss factor that accounts for energy loss within dielectrics, and hence heating by electromagnetic waves. The ratio (ϵ''/ϵ') is often termed the loss tangent, since $\tan\delta = (\epsilon''/\epsilon')$.

A dielectric may, in addition, have a small, non-zero conductivity which will also result in energy losses. Thus energy losses within a dielectric may be due to both polarisation and resistive loss mechanisms. As far as external effects are concerned, however, these mechanisms are indistinguishable. The conductivity loss can therefore be modelled into the dielectric loss factor ϵ'' [SCH71].

This can be seen from Maxwell's equation:

$$\text{curl } \mathbf{H} = j\omega\mathbf{D} + \mathbf{J} \quad \text{(for sinusoidal fields)}$$

$$=> \quad \text{curl } \mathbf{H} = j\omega\epsilon\mathbf{E} + \sigma\mathbf{E}$$

$$=> \quad \text{curl } \mathbf{H} = j\omega\epsilon_0\{\epsilon' - j\epsilon'' - j\sigma/(\omega\epsilon_0)\}\mathbf{E} \qquad (18)$$

The new loss factor may now be thought of as consisting of the old loss factor (resulting from polarisation loss) plus a new term, $\sigma/\omega\epsilon_0$, arising from the resistive loss mechanisms.

Thus, even for a dielectric of zero conductivity, the power loss may be thought of as a result of an effective dielectric conductivity $\sigma = \epsilon_0\epsilon''\omega$, instead of as a polarisation loss.

The form of an electromagnetic wave in a lossy dielectric can easily be obtained by replacing ϵ_r in the wave solution of Maxwell's equation for a lossless dielectric, by the complex permittivity value $\epsilon' - j\epsilon''$.

The form of the electric field component of a plane wave travelling in the x-direction in a dielectric is

$$E_y = E_0 \exp[j(\omega t - kx)] \qquad (19)$$

where $k = 2\pi/\lambda = \omega\sqrt{\epsilon_r}/c$ and $\sqrt{\epsilon_r} = \sqrt{\epsilon'}\ \sqrt{(1 - j\epsilon''/\epsilon')}$

Typically $\epsilon''/\epsilon' << 1$, and thus the binomial expansion may be used to get

$$\sqrt{\epsilon_r} \approx \sqrt{\epsilon'} \{1 - j\epsilon''/(2\epsilon'')\} \quad (20)$$

Substituting this expression into (19) above, the expression for an electromagnetic wave in lossy dielectric medium is obtained [FEY64]:

$$E_y = E_0 \exp[\, j\omega \{t - x\sqrt{\epsilon'}/c\,\}\,] \exp[-\omega x \epsilon''/2c\sqrt{\epsilon'}] \quad (21)$$

This expression is that of an exponentially decaying wave (Figure 1.15). The wave has a velocity $v = c/\sqrt{\epsilon'}$ and an exponential attenuation $e^{-\alpha}$ where $\alpha = \omega x \epsilon''/2c\sqrt{\epsilon'}$.

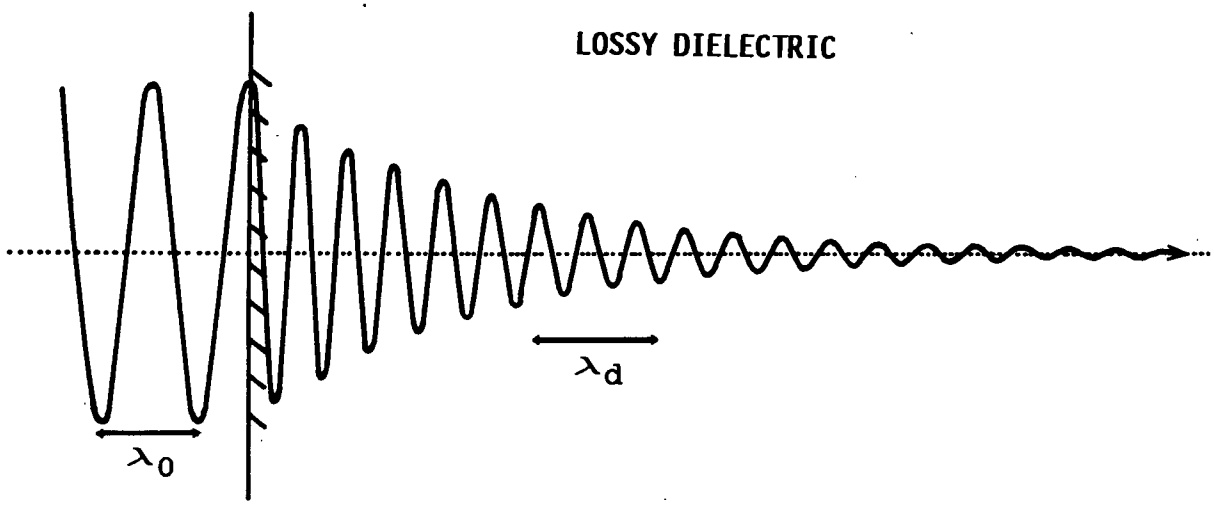


Figure 1.15 Decay of an electromagnetic wave in a lossy dielectric.

The power loss with penetration of the waves through a material is of practical value in microwave heating. The power penetration depth is defined as the distance from the surface of the material at which the incident power drops to 1/e (about 37 %) while the half-power depth is the depth at which the power density is one-half of what it is at the surface of the material. Another parameter, the skin depth, is defined as the distance below the surface at which the electric field strength is reduced to 1/e (i.e., the power density is down to $1/e^2$). The following equation (22) relates the penetration depth D_p to the free space wavelength and $\tan\delta$:

$$D_p = \frac{\lambda_0}{\pi \sqrt{8} \sqrt{\epsilon' \left[\sqrt{(1 + \tan^2\delta)} - 1 \right]}} \qquad (22)$$

This equation shows that the power penetration depth increases with longer wavelengths (lower frequency). At room temperature, the penetration depth in water at 2450 MHz is about 2 cm while at 915 MHz it is about 10 cm. Thus, for large volumes the lower frequency is desirable and 915 MHz is used for industrial applications, where larger volumes are processed. For domestic cooking and especially small laboratory samples 2450 MHz has sufficient penetration. The penetration depth is also affected by the $\tan\delta$ value of the material, which also changes with temperature. The penetration depth variation with temperature and frequency is shown for water in Figure 1.16.

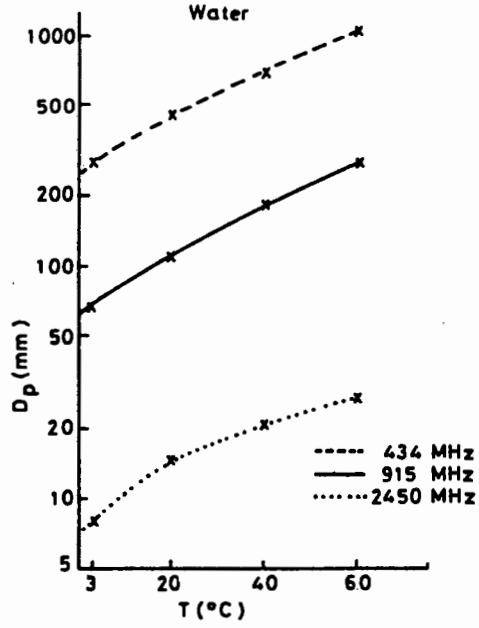


Figure 1.16 Penetration depth in water as a function of temperature and frequency [MET88].

The average power converted into heat for a unit volume is given by:

$$P_{av} = 2\pi f E^2 \epsilon_0 \epsilon_r \tan\delta \qquad (23)$$

The power absorbed by the material can be measured by using the thermodynamic relationship:

$$\text{Power} = m\, C_p\, (T_f - T_i) / t \qquad (24)$$

where m is the mass of the material, C_p is the specific heat, T_f and T_i are the final and initial temperatures of the material, respectively, and t is the time of heating. This equation however ignores any temperature distribution and is limited to small temperature increases since the specific heat also changes with temperature.

The variation of power-absorbed with temperature and as the electrical properties of the material change has very practical implications in many applications. Many ceramics, for example, have a very low microwave absorption (low $\tan\delta$) at room temperature and their absorption of power rises slowly with temperature. However, at some critical temperature the power absorption increases very fast with temperature and causes a condition of thermal runaway. Thus, it is important to control the process very carefully if excessive temperatures are to be avoided [ROU87]. The change of the loss tangent with temperature for water is shown in Figure 1.17. This is characteristic of other liquids as well. With high-boiling-point mineral acids such as sulfuric acid, the power absorbed is drastically reduced at high temperatures, and so the power has to be increased to obtain good rates of heating.

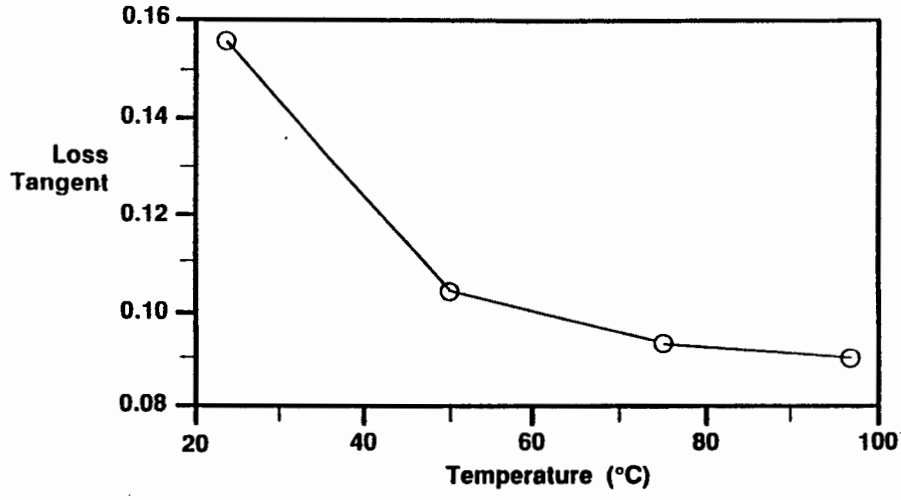


Figure 1.17 Typical loss tangent *versus* temperature curve for water at 2.58 GHz [NEA92].

From the above heating equations, it is clear that if all the parameters (f, E, ϵ_0, $\epsilon_r \tan\delta$) at a given frequency and temperature are known, the heating characteristics of materials can be modelled if the heat losses are also known (especially at high temperatures). However, data for complex liquid and solid mixtures are generally not readily available. In practice, the heating characteristics are usually measured and the power requirements adjusted for the particular process. Thus, microwave heating technology tends to be a very practical field involving much laboratory experimentation and design of the equipment for each process.

1.2 Applications of microwave heating in the chemical laboratory

An early laboratory application of microwave frequencies was microwave spectroscopy which is an important analytical tool and is still widely used nowadays for studying molecules in the gas phase [SUG65]. As mentioned above, microwave cavities have been used to excite discharges for spectroscopy and to generate gaseous species such as H and the excited singlet oxygen used in synthetic chemistry [MUR69,SCH70,GLE70,SCH76,WAS79], as well as for the low temperature ashing of materials [BOC79,AND87]. Microwave discharges have also been used for gas phase decomposition/cracking reactions [SEC69,LIU69,LIU71]. Microwave induced plasmas are used as a source for emission spectroscopy [RUN67,LIC72,LIC73].

While the domestic microwave oven has been available since about 1956, it is only in the last 18 years or so that this equipment has been used to process materials in chemical laboratories. The large number of publications, conference proceedings and patents in the literature is an indication of the importance, usefulness and many percieved advantages of using microwave heating, as well as documenting the successes achieved in numerous fields of chemistry using microwaves. The organization of the First World Congress on Microwave Chemistry by the International Microwave Power Institute, in Breukelen, The Netherlands in 1992, further confirms the serious international interest in this technology.

The various laboratory applications are discussed under separate headings below. It is beyond the scope of this work to review comprensively each application in detail. Emphasis is placed on the equipment that is used for the various purposes.

1.2.1 Drying, ashing and fusion of laboratory samples

Microwave drying has been applied in industry for about thirty years. Particularly, it has been used extensively in food processing where great energy efficiency and throughput can be achieved. The applications of microwaves in freeze-drying for industrial processes have been discussed by Copson [COP62] and by Ma and Peltre [MA75].

The drying characteristics of microwaves have been discussed in details by Perkin [PER83] and thus a qualitative description follows. When microwaves penetrate the material to be dried, they are absorbed by water or other polar solvents. Heating occurs throughout the material and the solid is typically heated to the vaporization temperature of the solvent. Attenuation occurs as the microwaves pass through the material. However, the surface is generally cooler than the interior of the material even though it receives the most energy. This is due to evaporative cooling and the rate of energy input to the interior, which is usually greater than the rate of heat transfer to the outside surface for dissipation. This results in a positive vapour pressure gradient from the interior to the surface which accelerates the moisture transfer.

In almost all laboratory manipulations drying is an essential operation which often hinders the overall task as it is a slow process by traditional means (the drying electrical resistance oven). It thus appears that the most basic application of microwave ovens in the chemical laboratory is for sample drying.

One of the first applications to sample drying in a laboratory was reported in 1973 by Takiyama *et al.* who used a microwave oven to dry precipitates for gravimetric analyses [TAK73]. Hesek and Wilson used a 550 W oven to dry a variety of salts including carbonates and sulfates to constant weight [HES74]. It was realised that great savings in time compared with traditional methods could be achieved. For example, a 20 g barium carbonate sample could be dried in 15 minutes compared with 3 hours in a drying oven at 105°C. Microwave drying of biological tissues for trace element analysis was described by Koh [KOH80]. Much faster weight loss than traditional drying was recorded. Since these early publications, there have been many reported investigations on the uses of microwaves for sample drying. These include the drying of salts and precipitates [TAK73,HES74,MEL81,AND84,TAD90], sludges [BID76,VER81,CAM82,LUM87], plant materials [STE75,SMI80,BAT90,ELI91], coal and coke [SUM84,JAC84,HEI89], foods [NAK86,DRA89,FER92], soils [THI78,NET92], ores [STE78], clays [MCC86] and slurries [KUE86]. Alcohol was removed from hydrogels by

microwave heating [SUW76]. It is also common practice in many chemical laboratories to dry silica gel and molecular sieve in a microwave oven.

Nakaoka *et al.* have described a microwave dehydration apparatus to dry relatively large food samples rapidly (vegetables, milk, fish, and seaweed) for the determination of radionuclides [NAK86]. The system is shown in Figure 1.18.

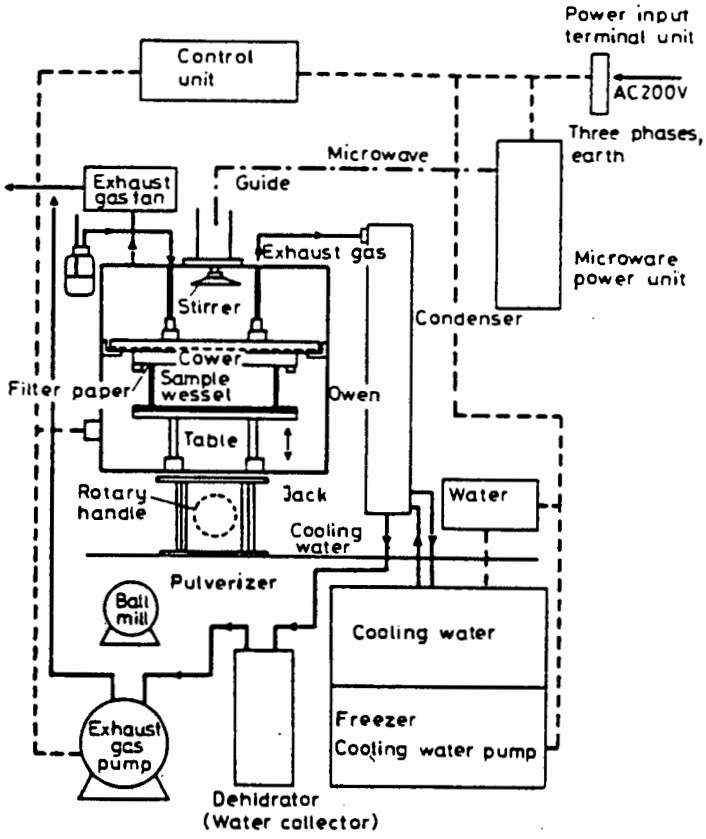


Figure 1.18 Microwave dehydrating apparatus [NAK86].

Bachmann from Bergbau-Forschung GmbH reported on a computer-controlled microwave oven incorporating an electronic balance that was developed to dry samples of up to 1.2 kg quickly [BAC89].

A microwave vacuum oven for quickly removing volatile material from laboratory samples is described in the Canadian patent from Domtar Inc. [HAR86]. The equipment is shown in Figure 1.19. It consists of an oven with a vacuum chamber and a vacuum system and means to monitor the rate of volatilization that can be used in turn to control the microwave power. A balance placed outside the oven can also be used to monitor the rate of volatilization.

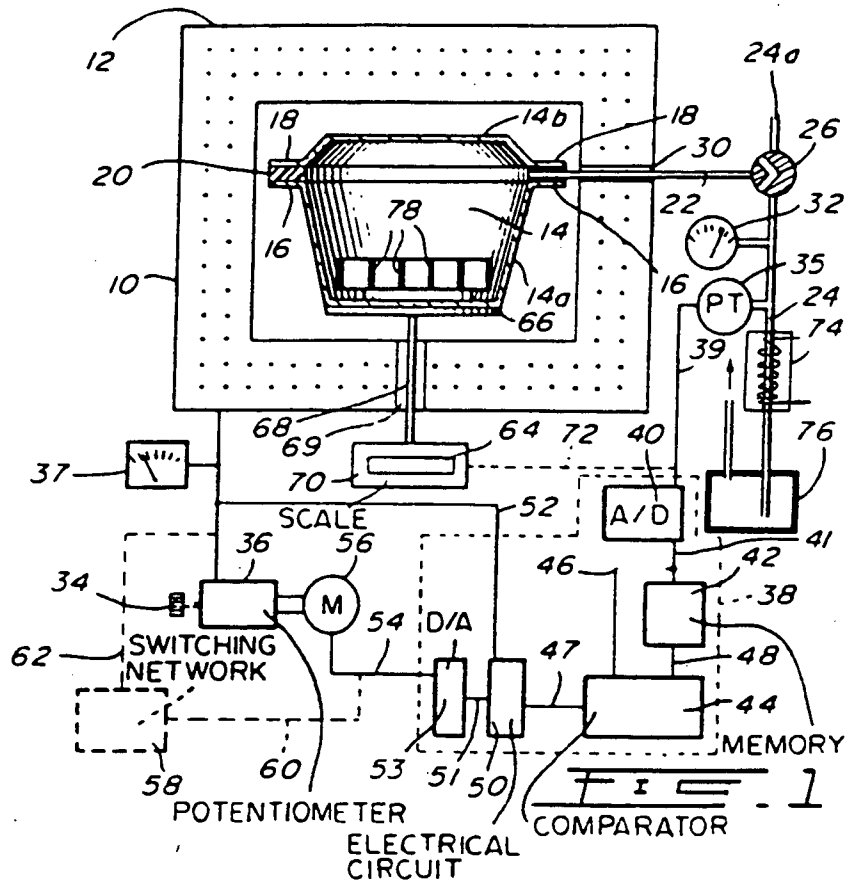


Figure 1.19 Microwave vacuum system [HAR86].

A moisture analyser, the AVC-80 (now upgraded to the model LabWave 9000), has been commercially available from CEM Corporation, USA, for many years. It consists of an oven with built-in electronic balance and a microprocessor which automatically monitors sample drying and determines the moisture content. Similar instruments are available from Questron Corporation, USA (the QMAS 1700 and 1750). Other ovens combine microwaves and convection for general laboratory drying of samples, for example a combination air circulation / microwave oven is offered by Heraeus Instrument GmbH.

Microwave drying may not be suitable for all samples. Materials containing non-polar solvents are not effectively dried by microwaves. Further, certain materials such as oxides can couple strongly with the microwave field and reach very high temperatures and thus the composition of the material can be changed. For example, some zeolite materials have been found to melt under microwave irradiation [KOM86]. If the material's structure needs to be analysed after the drying step (e.g., by infrared spectroscopy or X-ray diffraction

spectroscopy), it is important that no change in the structure occurs. Also, at certain temperatures elemental losses could occur. In the heating of coal at higher-than-normal drying temperatures, sulfur can be lost during irradiation. Steger *et al.* have reported on the oxidation of sulfide-bearing materials during drying in the microwave oven [STE78] and Thien *et al.* discussed the anomalous chemical results that were obtained for soil dried by microwaves [THI78]. Beary has also warned against the use of microwaves for drying of certified reference materials [BEA88]. Although microwave drying in laboratories has become very popular, it is important that care be taken to investigate the feasibility of the microwave drying method for each particular application.

Certain ferrite materials experience a large change in microwave absorption when they reach a certain temperature, the Curie Point. Below this temperature they have a high energy loss, while above it they have a low loss. Ceramics containing such materials can be manufactured according to the temperature limits required. Objects placed on these materials under irradiation are primarily heated by conduction. The applications of such devices (thermopads) for drying laboratory samples have been reported by Beary [BEA88].

The use of the above technique means that non-polar solvents can be evaporated from materials by using microwaves and this could be useful for many applications. Milestone, Italy, manufactures a PTFE-carbon material (Weflon) which can be used for indirect heating of samples [LAU90].

The ashing of samples is a popular technique used to remove the organic bulk (matrix) of a material so that only the inorganic constituents remain and can thus be determined. The process is also used for removing an organic phase which could interfere with the sample preparation procedure, and for concentrating the analytes to increase the sensitivity of certain analytical procedures. Traditional methods make use of muffle furnaces which consume large amounts of energy and make the technique relatively slow.

The CEM patent [COL86] describes an "ashing block" made of silicon carbide (strongly absorbing material) which is placed inside a microwave oven and can attain temperatures of 400 to 1000°C. The material to be ashed is placed between pads of fused glass fibre or in suitable crucibles which are in contact with the ashing block. The latter is supported by a non-absorbing material such as firebrick which also provides insulation.

Another application of this technique is for sample fusion. The fusion technique is widely used for refractory (highly stable, hard-to-dissolve) materials and involves the reaction between a suitable flux (inorganic salt/mixture) and the sample (e.g., rock and mineral) in a

crucible (ceramic, gold or platinum alloy) at high temperatures either over a flame or in a muffle furnace. The latter also consumes large amounts of energy.

A microwave muffle furnace, the MAS-300, is available from CEM and a similar instrument, the QASH-1100, from Questron. The furnace chambers reach temperatures of up to 1200°C and have temperature control. These are useful for drying, ashing, fusion, loss-on-ignition tests and heat-treating processes. Matthes has discussed some applications of the microwave muffle furnace [MAT88]. Morales-Rubio *et al.* used the muffle furnace to ash vegetable samples [MOR92].

1.2.2 Sample digestion

For most routine determinations of metals by spectroscopic techniques such as atomic absorption spectroscopy (AAS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), as well as others such as ion chromatography and electrochemical methods, it is required that the samples be in the form of a solution. This involves time-consuming sample preparation procedures for dissolving solid materials in mineral acids. While the modern instruments can perform analyses very fast and automatically, the limiting factor is often the time taken to prepare the samples. Thus in industry, where process control can benefit from the ability to perform analyses rapidly, improvements in sample preparation techniques are highly desirable. Such improvements involving the use of microwave energy have been demonstrated over the past 17 years. Today it is well-accepted that the introduction of microwave heating to the dissolution (digestion) of samples is one of the most important breakthroughs in sample preparation techniques. The number of research papers published in this field (including a few commercial patents) and general articles illustrate the tremendous interest and successes of this approach (Figure 1.20, data from Chemical Abstract listings). The first book on this subject was published by Kingston and Jassie in 1988 [KIN88]. This field was reviewed by Matusiewicz and Sturgeon in 1989 [MAT89] and this review includes 72 references and a tabulation of digestion methods for different sample types.

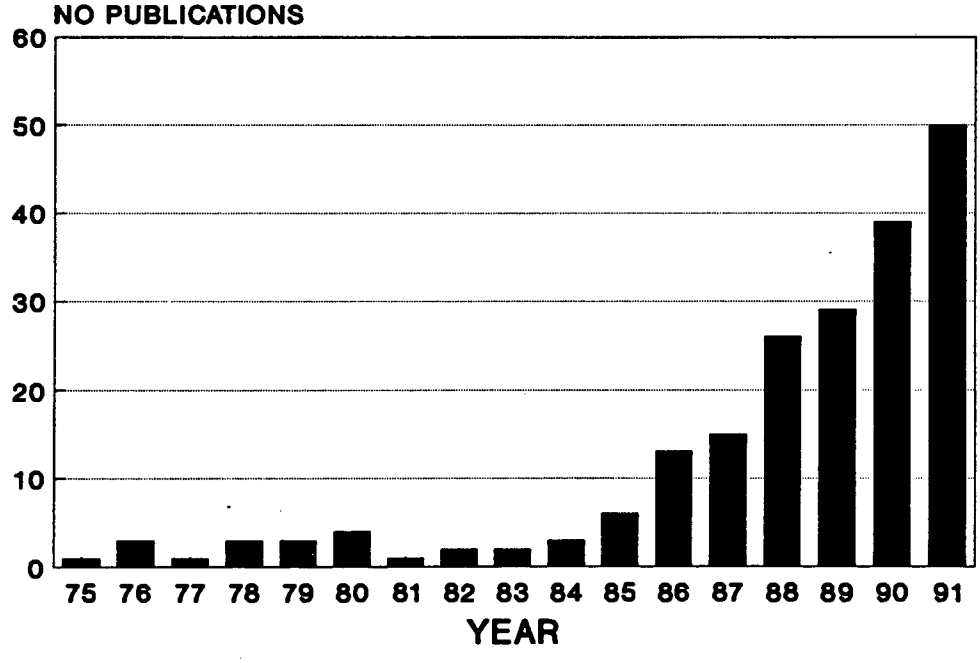


Figure 1.20 Growth of the published literature on microwave sample digestion.

The first report on the use of a microwave oven for sample digestion was by Abu-Samra *et al.* in 1975 [ABU75]. A 600 W commercial microwave oven was used with the modifications outlined below. Digestion of biological materials was performed using a mixture of nitric and perchloric acids in Erlenmeyer flasks. The flasks were placed in a Plexiglas (Acrylic) box inside the oven. A hole was drilled through the side of the oven to accommodate a glass exhaust port connected to the Plexiglas box in order to evacuate the acid fumes from the latter. Various means of evacuation of the acid fumes were investigated and included a water aspirator, a drum fan and a small vacuum cleaner. Traps to remove acid fumes from the exhaust gases prior to venting included the use of CaO, $CaCO_3$, and NaOH solutions and a water spray. Not surprisingly, the small vacuum cleaner was found to be unsuitable. However, successful digestions of the biological materials (liver and leaves) were achieved in about 10% of the time required for traditional procedures.

It is surprising that such a new idea for sample preparation did not attract more attention. During the years that followed, and up to about 1982, no major developments of this idea occurred. However, there were some interesting publications about the use of commercial ovens and some problems were identified. Mainly, it was the corrosion of the ovens and many modifications were tested to protect the implements that had not been designed for laboratory uses.

A patent was filed by Mitsubishi (Japan) in 1982 on the development of a wet-sample decomposing apparatus [KAW82]. Some details of the apparatus are shown in Figure 1.21. It consisted of a microwave cavity with a door, a controller for the power supply and an extraction system to which a variety of vessels could be attached from the inside of the cavity. Sensors placed at the exhaust side could be used to monitor temperature and evolution rates of generated gases.

In 1983 a report from the Bureau of Mines, USA, by Matthes *et al.* [MAT83] brought some new developments in the microwave digestion technique. The major difference between the latter work and previously published procedures was that instead of using open vessels (e.g., flasks and beakers) in enclosed, vented containers, samples were digested in sealed plastic containers. Metallic and mineral samples were dissolved using mixtures of hydrochloric, hydrofluoric and nitric acids in 250 ml polycarbonate bottles. Twelve such containers could be heated in the oven, and after digestion the vessels were cooled with a stream of carbon dioxide. Complete dissolution of the materials was achieved in approximately 5 minutes.

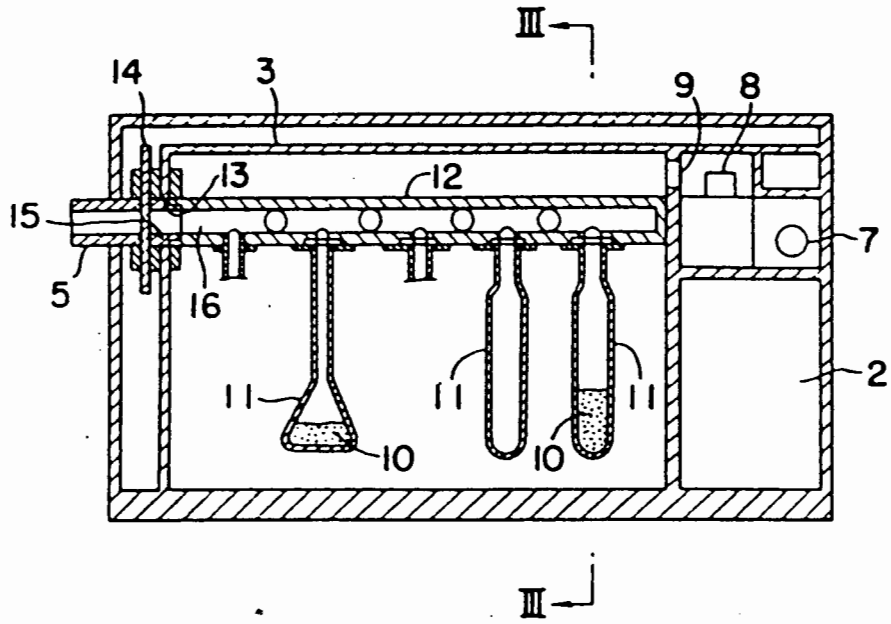


Figure 1.21 Wet sample decomposing apparatus [KAW82]. The vessels (11) are connected to a manifold (12) inside the cavity (3) with an outlet (5) through the walls of the oven.

The applications of pressure vessels or so called "digestion bombs" have been known to analytical chemists for a long time. They are powerful tools for the dissolution of materials such as alloys, minerals and ceramics which are difficult to dissolve at low temperatures. These digestion bombs consist of steel containers lined with PTFE into which the material to be dissolved and the acid(s) are placed (Figure 1.22). A normal oven is used to heat them.

The rate of reaction and efficiency of acid decomposition increase dramatically with temperature. Thus, numerous substances which fail to react with nitric and hydrofluoric acids (as well as others) at their boiling points can be decomposed at elevated temperatures and pressures in closed reaction vessels. Because of the high rates of reaction, the time required for complete dissolution is usually short. With microwaves this time is further reduced due to the rapid temperature rise compared with traditional heating of the vessels in an oven or in a heated jacket, where a long time is necessary for isothermal conditions to be reached. There are other advantages to using closed vessels for these laboratory applications. Since the reactions are more efficient, smaller acid to sample ratios can be used. This leads to lower reagent blanks (wit less contamination from reagents) and savings in the expensive high-purity reagents. Closed systems maintain the integrity of the materials, i.e., contamination from the environment is avoided, and thus very low levels can be measured (at the ppm and ppb levels). Furthermore, the determination of volatile analytes is possible.

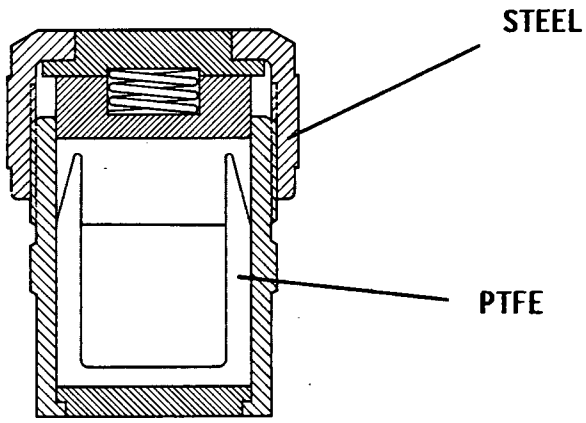


Figure 1.22 Design of a traditional digestion pressure vessel from Parr Instrument Company, USA.

Further developments in microwave digestion technology were brought about by the work of Kingston and Jassie [KIN86] from the National Bureau of Standards in 1986. In collaboration with a manufacturer of microwave equipment (CEM Corporation, USA), they developed a system to monitor the temperature and pressure during digestions inside pressure vessels made of Teflon. Initially, thermocouples were used to measure the temperature and later fibre-optics manufactured by Luxtron Corporation, USA were introduced. The pressure was monitored by a pressure line and a transducer outside the oven. This work was important since it provided some insight into the behaviour of acids and acid/sample mixtures when heated by microwaves in closed vessels. Such information is useful in developing the digestion procedures as well as designing the pressure vessels and their safe operation.

Progress in microwave digestion techniques has advanced tremendously in recent years due to the introduction of especially-designed apparatus for sample preparation. At present nine manufacturers offer microwave equipment for sample dissolution. These include Anton Parr, Austria; CEM Corporation, USA; Cober Electronics, USA; Floyd Associate, USA; Milestone, Italy; Microwave Materials Technologies Inc., USA; North Atlantic Equipment Sales, Inc., USA; Prolabo, France; and Questron Corporation, USA. Several other companies offer pressure vessels designed for use in microwave ovens. Included are Savillex Corporation, USA; Berghof GmbH, Germany; GEC Alsthom International, Belgium; Lorran International, Canada; and Atomic Energy Corporation, South Africa.

A discussion on the development of the equipment follows.

The CEM system (the MDS-81D) was the first to become available commercially. It featured a microwave oven of 600 W fitted with an isolator and a microprocessor to control time and power. The cavity was PTFE-coated and an extraction system was used to evacuate acid fumes from the former. A turntable and a vessel rack were provided for the twelve vessels made of moulded PFA (perfluoroalkoyl). The vessels (either 60 or 120 ml) were rated at 100 psi (6.9 bar) and were fitted with relief valves to prevent excessive pressure buildup (Figure 1.23).

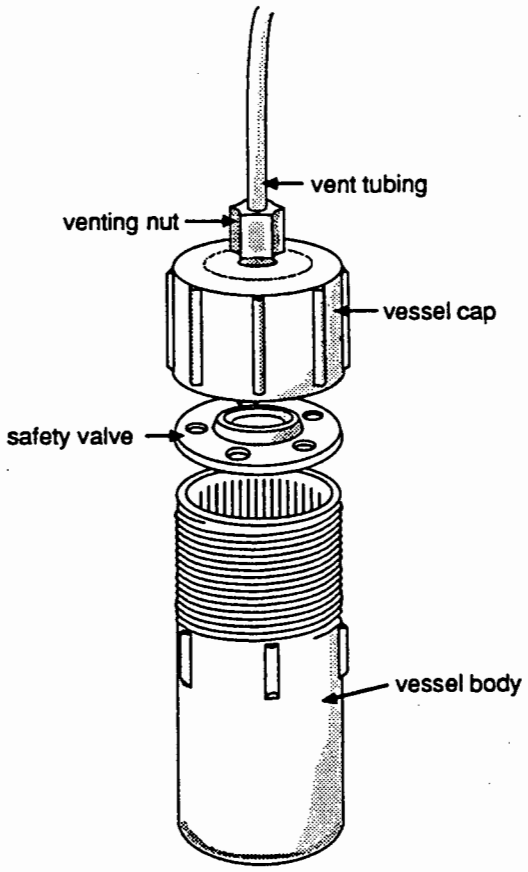


Figure 1.23 PFA digestion vessel (From CEM Corporation).

Today most of the commercial systems incorporate an oven which has been protected by PTFE coating and an extraction system to vent the cavity of any fumes. Pougnet [POU93a] successfully protected the oven's cavity with a polypropylene liner and the extraction was done through a polypropylene-lined metal port. This work is presented in Chapter 3. Some ovens have on-board microprocessors while others are controlled by a Personal Computer. The ovens are generally fitted with a turntable to accommodate the pressure vessels.

The designs of pressure vessels have evolved since the work of Matthes *et al.* [MAT83], who used polycarbonate containers. The latter were found to be not entirely satisfactory since they developed discolouration and cracking after use for several digestions and had a limited life. PTFE has been found to be a superior material to polycarbonate. The PFA polymer was introduced due to the ease of manufacturing by injection moulding compared to PTFE (Teflon), which has to be machined or isostatically sintered. Milestone introduced vessels made of TFM (Tetrafluoromethaxil) polymer manufactured by Hoechst, which is claimed to have better properties than the standard PTFE due to a more compact structure. This reduces the possibility of analyte migration into the body of the vessel under high pressure conditions, which would lead to low recoveries and subsequent contamination. The advantages of this vessel were reported by Noltner *et al.*[NOL90]. Some properties of polymeric materials used for digestion vessels appear in reference [KIN88].

Initially, the digestion vessels were of single-wall fabrication. Most vessels available presently are double wall designs. The inner wall is made of either PTFE, PFA or TFM and the outer wall is made of a strong polymeric (or ceramic) material to give the strength required. All pressurised vessels must incorporate some form of safety feature. Deformable discs have been used by CEM and Savillex (safety valve in Figure 1.23) and rupture discs made of PTFE or other materials have also been used by other manufacturers. The Parr vessel makes use of a compressible silicone disc (equivalent to a spring in the traditional vessels) and an O-ring system for over-pressure protection (Figure 1.24).

In recent years, temperature and pressure control of the digestions has become an important issue, presumably because of the proposal and adoption of the microwave digestion of environmental samples by the Environmental Protection Agency, USA (Methods 3050 and 3051) [BIN90,EPA91,BIN91,EPA92,BIN92]. This is an important development in microwave digestion since the adoption of this technique by an important organization like the EPA confirms the advantages of the technique and displays its maturity and wide acceptance. The need for temperature control stems from the fact that the digestion conditions have to be reproducible in order to obtain reproducible results for a given sample type with a certain acid (or mixture). This as lead to the implementation of temperature and pressure control by the manufacturers of microwave digestion systems. Thus experimental conditions can be transferred from one system to another. The limitations of both the temperature control and the pressure control are dependant on the actual technique used (*e.g.*, thermocouple or fibre-optics, pressure transducer, or an indirect method such as the Anton-Parr system, see below) and the designs of the pressure vessels (*i.e.*, their temperature and pressure ratings). The best and fastest results will be achieved with higher temperatures and pressures, but the need to monitor can limit the temperatures and pressures that can be tolerated in a pressure vessel.

This issue is open to much debate. It must also be said that the implementation of temperature and/or pressure controls makes the instrumentation more complex and more expensive.

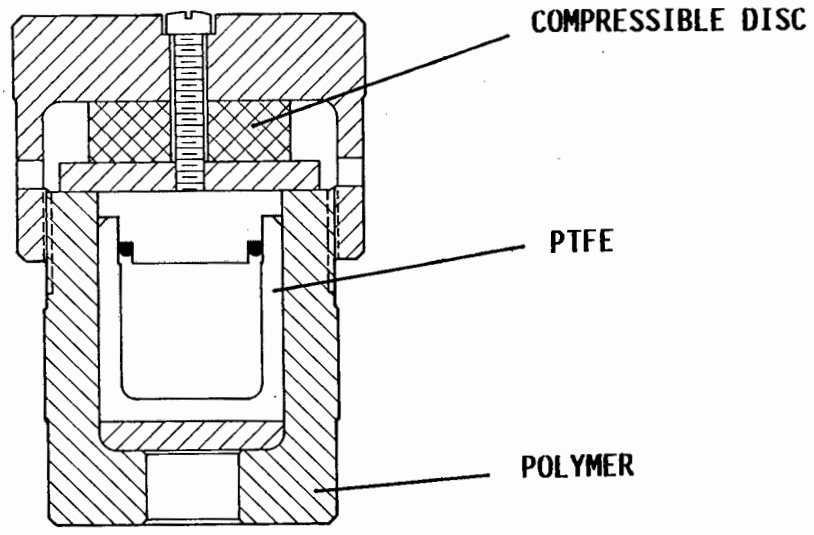


Figure 1.24 The Parr microwave digestion vessel.

The Anton-Parr system includes an oven and vessels that are pressure-controlled to 80 bar. In this original design, the pressure is monitored indirectly by an optical sensor which tracks the movement of the sealing plug as pressure is increased (Figure 1.25). When approximately 80 bar is attained, the microwave power is switched off. Quartz vessels are used for high temperature digestions and PFA is used when hydrofluoric acid is a necessary reagent.

As with most modern developments in instrumental analytical techniques, automation of the microwave digestion system has been accomplished. Labrecque has described the automation of pressure digestion using a CEM MDS 81-D unit and a Zymate II robot system (Zymark Corporation) [LAB88]. Walter *et al.* have also described a similar system [WAL91]. Norris *et al.* reported on an automatic system that was developed to dissolve titanium dioxide samples [NOR92]. The system was built from a Peerless System robot, a CEM MDS 81D microwave oven and Milestone pressure vessels. In all these developments, reliable operation, good accuracy and reproducibility have been achieved.

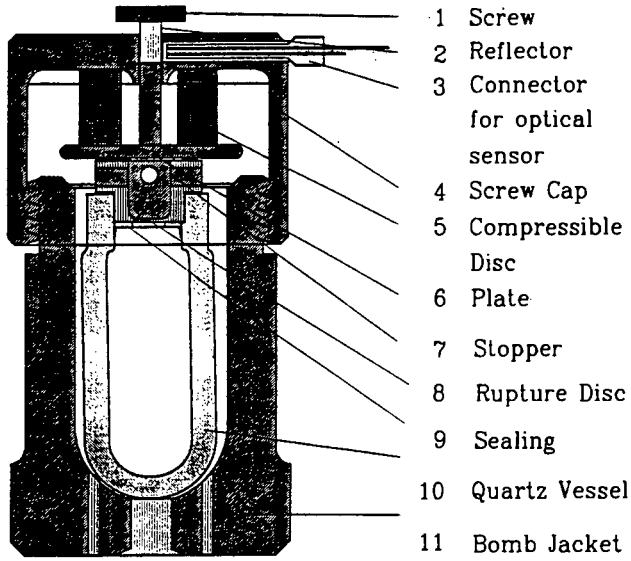


Figure 1.25 The Anton-Parr vessel.

In 1985, a patent was filed by the French company Rhone Poulenc Recherches [COM85]. A different approach to microwave sample digestion was adopted, viz. using "focussed microwave technology". The instrument consists of a waveguide in which energy from the magnetron is focussed directly into the sample, and a port to introduce the sample vessel (Figure 1.26), while a water load is placed at the end of the waveguide to absorb excess power. Digestions are performed in glass or PTFE containers with the mineral acids under reflux at atmospheric pressure. An extraction system pumps the acid fumes out of the vessel. Prolabo (now Merck-Clevenot) manufactures equipment based on this principle. In the model Maxidigest MX 350 acid can be added using a peristaltic pump during irradiation, and sample sizes of up to 10 g can be processed. The model A301 allows automatic treatment of up to 16 samples. A computer and robotics are used for addition of acids to the sample and each sample can be processed differently. This equipment is useful for the automatic digestion of a wide range of samples and, in particular, the digestion of organic materials for nitrogen determination. The operation and applications of this instrumentation have been described in the literature [DID90,MAT91a,MAT91b,FEI91]. The Prolabo waveguide system was adapted for pressure digestion using quartz tubes as pressure vessels by Anton Parr (the Superdigest System). Welz *et al.* also adapted this waveguide for on-line digestion [WEL92] (see below).

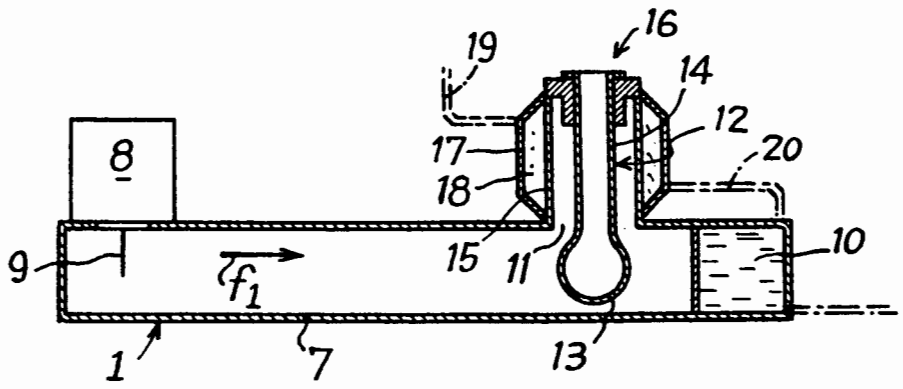


Figure 1.26 The Prolabo patent [COM85]. 7: waveguide, 8: magnetron, 9: antenna, 10: water load, 14: sample container.

Pougnet et al. [POU91] have discussed the design of a computer-controlled waveguide system with temperature control for laboratory applications. A design for a pressure vessel for waveguide applications was also presented. This work is presented in chapter 4.

An interesting comment was made by Matusiewicz and Sturgeon in 1989 in their *Suggestions for Further Studies*, concluding their review on microwave digestion [MAT89] :

Microwave digestion systems could also be designed specifically for use with steel-jacketed Teflon bombs utilizing a waveguide cavity design rather than an oven. This approach (energy from the magnetron focussed through a waveguide directly into the sample) should attain much faster heating and higher pressures. Additionally, this should result in higher precision and sample-to-sample reproducibility compared to microwave oven digestions.

The above idea was pursued by Pougnet *et al.* and a provisional patent was filed in South Africa in 1991 [PAT91]. The design has been published recently [POU93]. The work is described in chapter 7.

The Kjeldahl method of analysis for organic nitrogen determination is a well-established procedure which is extensively used to determine protein in food products as well as the nitrogen content of environmental samples. It involves the conversion of the nitrogen to an ammonium salt by digestion with concentrated sulfuric acid and other chemicals such as oxidants, catalysts and a salt to increase the boiling point. Traditionally the reactions are carried out in glass flasks (Kjeldahl flasks) or tubes over flames, heating mantles or heating

blocks. Temperatures of 400°C are normally reached and the total digestion time can be up to 1.5 hours. The disadvantage of traditional heating methods is the slow heat transfer and thus the long time necessary to reach the high temperature necessary for the oxidation to take place. The Kjeldahl digestion has been subject to much research in attempts to speed it up, both by modifying the traditional chemistry and by using microwaves. The most important modification to the chemistry has been in the use of hydrogen peroxide for the oxidation step [LOW80,HAC85,WAT87,HAC87,CHR89]. A mixture of sulfuric acid and hydrogen peroxide to form peroxymonosulfuric acid (Caro's acid), which is a powerful oxidant, is added to the reaction mixture. Hach *et al.* [HAC87] obtained very fast, efficient reactions by adding the hydrogen peroxide dropwise during the oxidation. The reactions were done on an electrical heater and reaction times were of the order of ten minutes.

Alvarado *et al.* carried out Kjeldahl digestion (using the traditional reagent mixture) in pyrex tubes inside a closed plastic container that was placed in a microwave oven [ALV88]. The latter was used to prevent corrosion of the oven. He *et al.* [HE90] also used the CEM MDS-81D microwave oven to digest several samples, stoppering the digestion flasks with ground glass adapters filled with glass beads to control the excessive fuming and large release of acids in the cavity.

Two microwave systems specifically designed for Kjeldahl digestion have become commercially available. The CEM Corporation has patented a modified oven designed for processing one sample at a time [NEA87]. The equipment (shown in Figure 1.27) also includes a pumping and dispensing system for addition of the Caro's acid and a scrubber to deal with the acid fumes. The application of this equipment has been described by Neas and Zakaria-Meehan [NEA88]. Prolabo make use of their waveguide (the Maxidigest MX 350) to carry out the digestion with continuous addition of hydrogen peroxide. Bermond and Ducauze have discussed its application to the digestion of meat products [BER91].

The advantage of microwave Kjeldahl digestion in reducing preparation times is well established and the technique is being used in many laboratories. However, the large amount of acid fumes which are released has prevented systems being developed for fast processing of many samples at a time, since it is difficult to deal with the fumes inside a microwave oven. In many laboratories processing one sample at a time is not sufficient and thus there is a need for microwave equipment to carry out this task.

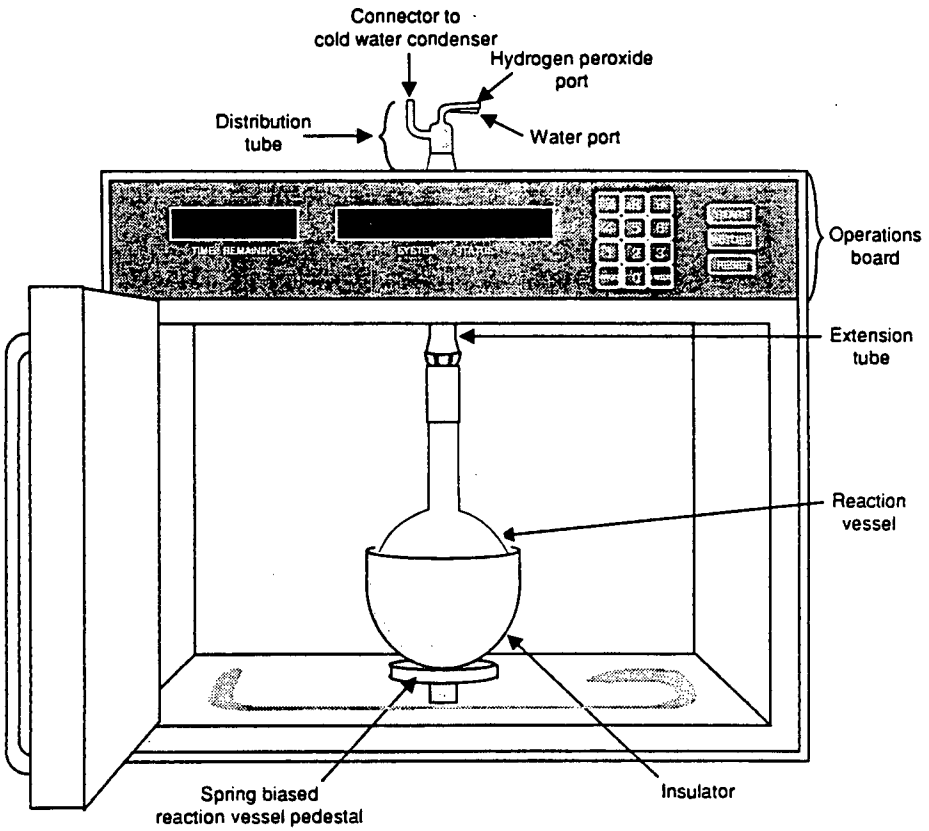


Figure 1.27 The CEM microwave system for Kjeldahl digestion.

One of the interesting developments in microwave digestion is the on-line preparation of samples. The on-line (or continuous) heating of fluids by microwaves is not new and has been used previously for industrial applications [FOR91]. The principle is simple and involves microwave irradiation of a flowing fluid inside a microwave-transparent container (usually a tube) positioned in a waveguide system or a multimode cavity.

The first such analytical application was described by Burguera *et al.* who developed a system for the digestion of whole blood followed by analysis by atomic absorption spectroscopy (AAS) [BUR86]. In this system the blood and acid were mixed by flow injection and the mixture passed through a pyrex coil inside a microwave oven. The sample was pumped into the nebulizer of the AA spectrometer and the analytical signal was continuously recorded (Figure 1.28). Carbonell *et al.* described a system for digesting sludge samples in which a PTFE coil was used as a reactor inside the oven [CAR90]. Hinkamp and Schwedt used a continuous microwave digestion system for determining phosphorus in water samples by reaction with potassium peroxodisulfate and an amperometric detection [HIN90]. Karanassios *et al.* described a system for stopped-flow digestion of biological samples [KAR91]. In that

system, a plug of sample/acid slurry was pumped into a coil inside a microwave oven. Sample flow was stopped and the coil closed by two valves. After irradiation for two minutes, the valves were opened and the sample pumped out of the coil. Haswell and Barclay [HAS92] and Carbonell et al. [CAR92] also described on-line digestion procedures for biological samples and sludges respectively. Welz, Tsalev and their co-workers have used the Prolabo waveguide instead of a microwave oven for their on-line digestion procedures of liquid samples [WEL92,TSA92a,TSA92b].

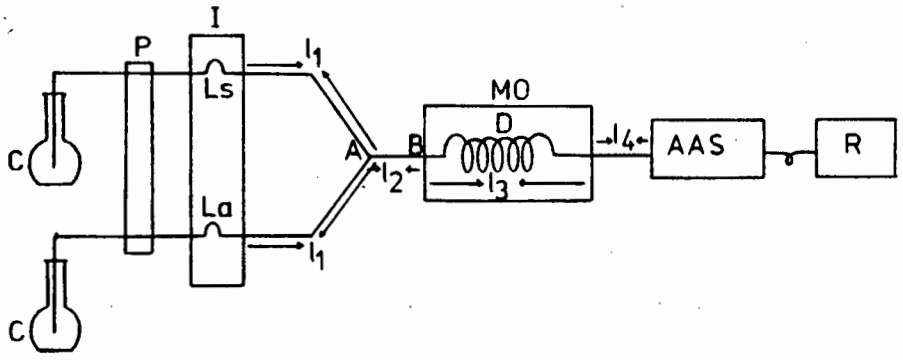


Figure 1.28 On-line digestion system for blood [BUR86]. P: Peristaltic pump, I: Double injector, D: Pyrex coil, MO: Microwave oven, AAS: spectrometer, R: Recorder.

On-line sample pretreatment has been shown to be of great practical value and has the advantage of easy automation. Further developments of this approach to digestion by microwaves are expected to take place.

Finally, there have been several recent reports on the development of computer software and databases aimed at the optimisation of microwave digestion procedures and the development of reliable and reproducible analytical methods [KOK92a,SET92,KOK92b,KIN92,MOH92].

1.2.3 Organic and organometallic syntheses and solid state reactions

As was mentioned earlier, microwaves have been used for a long time in spectroscopy and it was only in 1986 that a chemical synthesis using microwave heating was reported in the literature. Gedye and his co-workers, from the Laurentian University, Ontario, Canada, reported on the use of a PTFE closed vessel (such as those described above for sample digestion) to carry out efficiently several organic reactions in a domestic microwave oven [GED86]. They found considerable rate increases for the reactions studied compared to traditional methods. Independently, Giguere and his co-workers confirmed the dramatic reduction in reaction times when they carried out their reactions in sealed tubes [GIG86]. Since this pioneering work, the applications of microwave heating in chemical laboratories have grown tremendously and a large number of papers has been published in the literature. Other applications have developed, such as specific hydrolysis reactions, solvent extractions, organometallic and solid state systheses, synthesis of labelled compounds for pharmaceutical applications, catalytic reactions and reactions on solid supports. Two relatively recent reviews by Mingos and Baghurst [MIN91] and Abramovitch [ABR91], with each referencing some 95 papers, have covered the literature adequately. Two other more recent articles include those by Mingos and Baghurst [MIN92a] and Mingos [MIN92b].

Compared to sample digestion, where the acids are good microwave absorbers, not all organic solvents absorb microwaves and heat up efficiently since many are non-polar (*e.g.*, carbon tetrachloride). Thus, for a reaction to be successful either it has to be carried out in a suitable solvent or one of the reactants must heat up efficiently. Alternatively, a chemical can be added to provide the coupling with the field if the additive does not affect the reaction and the desired product. This points to the fact that microwave chemistry can be successful under different "chemical conditions" than those traditionally used. The choice of a solvent (or mixture) will affect the temperature and vapour pressure and their rates of increase. These two parameters could in turn affect the reaction and the product yields.

While it is clear that the pressurised reactions in general proceed faster when using microwave heating than when carried out traditionally, and that this can be explained rather easily, the successes of those reactions that were carried at atmospheric pressure have initiated much debate about the exact mechanism and the hunt for a *microwave effect*. Some reactions performed under controlled conditions by both traditional and microwave methods showed no difference in reaction rates, while others behaved differently [ABR91]. Superheating in organic solvents has been measured and a mechanism was proposed by Baghurst and Mingos [BAG92a]. This effect could be responsible for many of the enhanced results.

Most of the pressure work has been carried out in home-made vessels or those used for sample digestion which are commercially available. As with sample digestion it has become necessary to measure the temperature and pressure conditions and to control these parameters. In some cases the unpredictable course of certain reactions and the use of poorly constructed vessels have led to explosions and these have also prompted the need to measure the conditions within the closed vessels.

In earlier work, the temperature was measured by the use of sealed capillaries containing compounds of known melting points that were placed in the reaction container or affixed to it externally [GIG86]. The use of thermochromic temperature-indicating labels which change colour with temperature have also been used to give an estimate of temperature. Infrared techniques are used in many experiments, but mainly for high temperature work with solids. Thermocouples can also be used if the equipment is properly designed. With the development of the equipment for digestion, both fibre-optic sensors and pressure transducers are now being used by chemists to monitor the conditions inside the closed vessels.

One important danger of heating volatile organic solvents in a microwave oven is the potential for an explosion if a spark should occur inside the cavity. Furthermore, the organic vapours can be sucked into the power supply compartment by the fan that is used to cool the magnetron and again a spark (from switches, relays or the power supply) could lead to an explosion. More and more chemists are now using the digestion ovens which have a built in extraction system.

There are a few reports on modifications and the development of specialised equipment to carry out chemical reactions. These are described below.

Perhaps the most original idea for carrying out certain reactions is the continuous-flow reactor (MicroLab), developed by Strauss from the CSIRO, Australia and Industrial Microwave Applications Pty. Ltd., which has been tested for many reactions [PET89,STR90]. Basically the system consists of a microwave oven fitted with a Teflon coil through which the reactants are pumped. A heat exchanger is used to cool the product as it exits the cavity. A microprocessor is used for on-line measurement and control of pressure and temperature. The use of the Teflon tubing allows temperatures of 200 $^{\circ}$C and pressures of up to 1400 kPa. This system offers good control of the reactions and is flexible since the flow rates and the coil length can be varied for different applications. Chen *et al.* have also described the application of a home-made reactor based on the above principle [CHE90]. The very important advantage over the batch method (i.e., the pressure vessel) is that this principle can be extended to larger-scale production and should find practical applications in industry.

Baghurst and Mingos have modified a commercial microwave oven to allow them to carry out organometallic reactions under reflux [BAG90]. The modification is shown in Figure 1.29. The same authors also modified an oven for controlled-pressure reactions using a glass vessel [BAG92]. A pressure tranducer was used to control the power to the oven. The pressure vessel is shown in Figure 1.30.

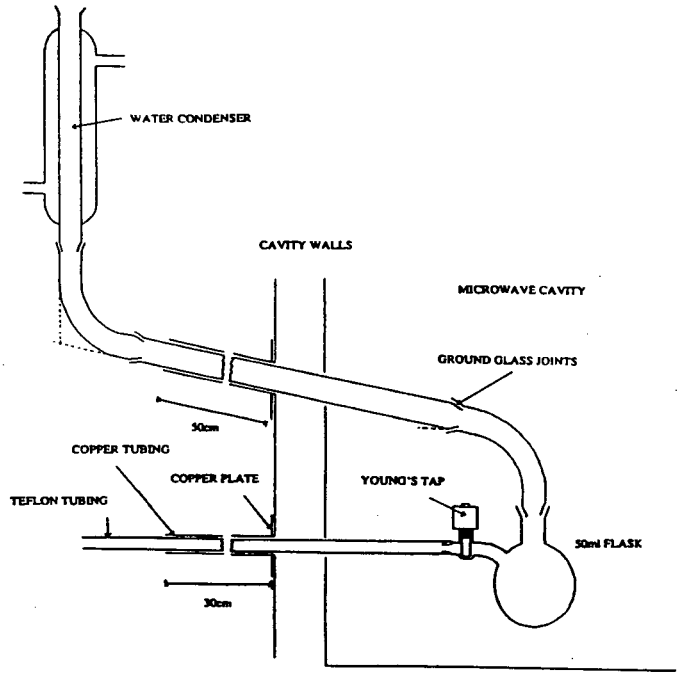


Figure 1.29 Modified microwave oven for reactions under reflux [BAG90].

Constable *et al.* have described a microwave system for pressure reactions with temperature and pressure measurement and facilities for stirring the contents of the reactor [CON92]. The system is shown in Figure 1.31. The 100 ml-capacity reactor was constructed from PFA with a PTFE lid and was designed to operate up to 200 °C and 1000 kPa. A Luxtron fibre-optic system was used for temperature measurement and a gauge for pressure measurement. An additional feature of the system was the use of a variable transformer to control the high voltage to the magnetron so as to achieve continuous power outputs at the required level.

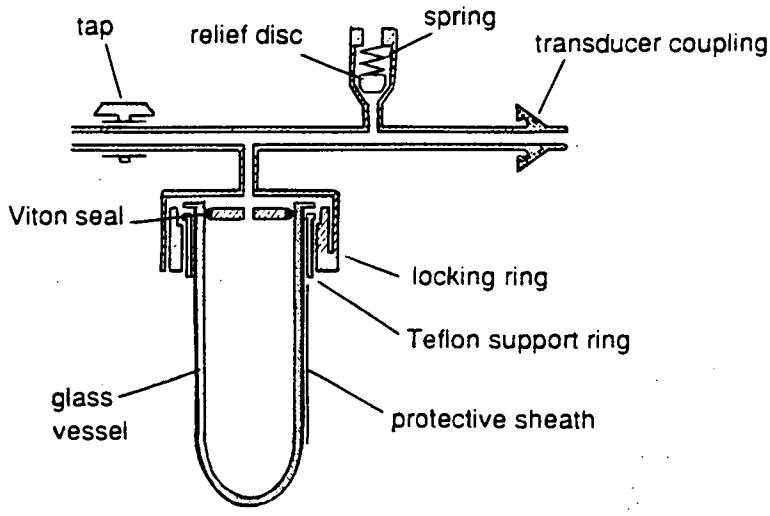


Figure 1.30 Pressure-controlled microwave reactor [BAG92].

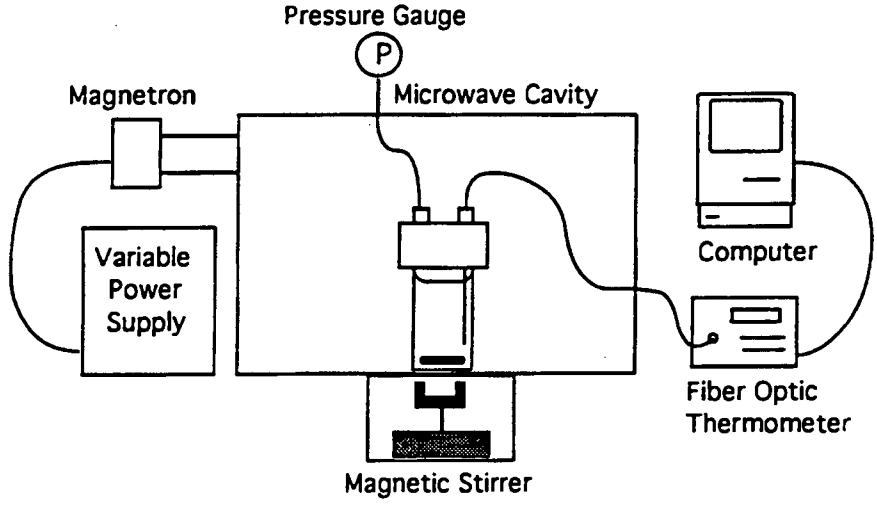


Figure 1.31 Schematic diagram of the microwave reactor [CON92].

An interesting development in the method used to carry out catalytic reactions with gases was reported by Wan and his co-workers [WAN90]. They have described a waveguide system

(Figure 1.32) incorporating a 3 kW magnetron with pulse controller, circulator, power attenuator, and a directional coupler to monitor the incident power amplitude and pulse width. This system allowed the generation of millisecond pulses of microwaves for irradiation of the material in the reactor. The latter consisted of a length of waveguide section with pressure windows on each side and into which was placed a pyrex tube containing the catalyst. A vacuum manifold was used both to introduce the reactant and to sample the product. This system was found to yield highly selective and efficient results for the decomposition of methane on a nickel catalyst and a mechanism was proposed to explain this unusual mode of energy application.

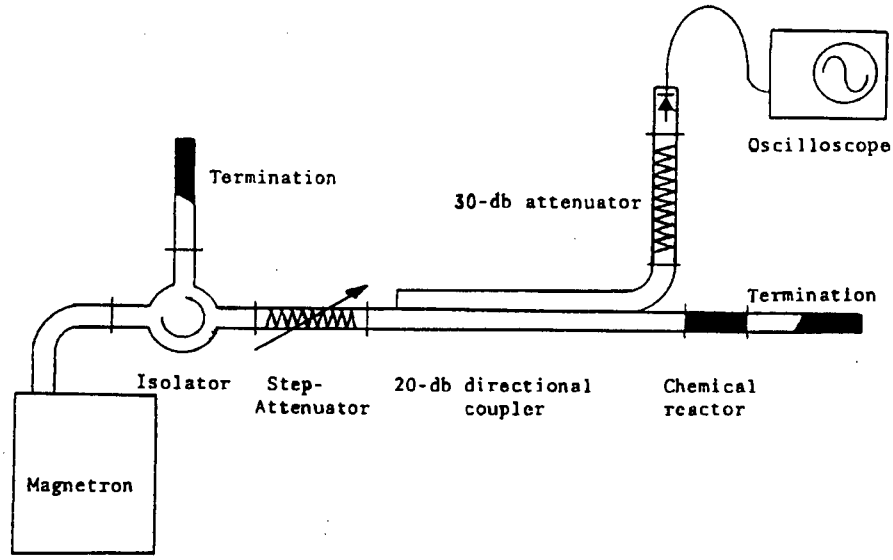


Figure 1.32 Schematic diagram of the pulsed microwave system [WAN90].

Gourari *et al.* have used a waveguide system to study the catalytic oxidation of ethylene in reactor (Figure 1.33) filled with microporous alumina particles impregnated with platinum [GOU92]. The internal temperature of the reactor was measured with a thermocouple inserted through the small side of the waveguide (i.e., perpendicular to the axis of the reactor, not shown in the figure).

Finally, Stone-Elander and co-workers have used a coaxial resonant cavity to carry out the small-scale synthesis of radiolabelled compounds [STO91,THO92]. These low-power cavities, available from Opthos Instruments Inc., USA, are used for microwave discharge studies and are suitable for small samples.

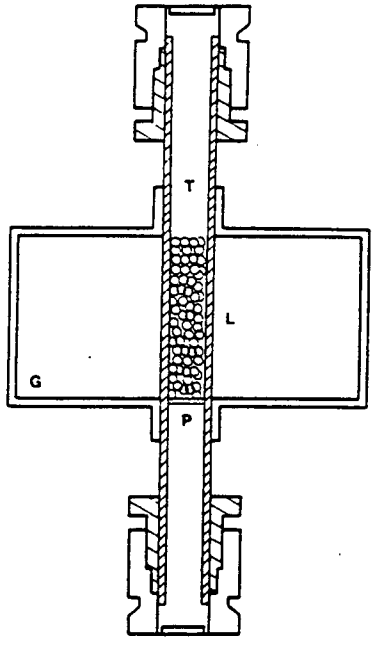


Figure 1.33 Waveguide system for catalytic reactions [GOU92]. G: waveguide, T: silica tube.

1.2.4 Applications in pathology

A large number of publications on the subject of microwave applications in pathology laboratories is to be found in the literature. Microwaves are used for histoprocessing and for staining and fixation in the preparation of biological specimens for microscopy. Boon and Kok, in their "Microwave Cookbook of Pathology", have discussed these applications in detail [BOO88].

A specially-designed microwave oven for pathological laboratories, the H2500, is commercially available from the Bio-Rad company. The instrument is capable of controlling the temperature accurately and an air/nitrogen agitation system is used to avoid local temperature variations.

1.3 Objectives and organisation

It is clear from the substantial experience available in the industrial applications of microwave heating that in order to take full advantage of the technology the applicator has to be carefully designed according to the specific configurations and needs of the material to be heated. Thus, we have the use of travelling-wave applicators, multimode cavities and single-mode resonant cavities, where these designs are best suited for the particular processes. It is felt that the same approach is relevant for laboratory applications, although here the running cost (electricity consumption) is less of a constraint than for large industrial applications. It is also clear that domestic ovens, modified versions or some commercially available items of equipment do not always comprise the ideal applicators for all laboratory applications. It is thus necessary for further development of the technology to research suitable designs of equipment that would be ideally suited for the very varied applications possible in the field of chemistry.

The broad objective of the present work was to design and evaluate suitable equipment for different applications of microwave heating in the laboratory.

The work is presented in seven Chapters. In each of the Chapters 2 to 7, designs of specific items of equipment are presented. Each of these Chapters comprises the objective(s), a description of the equipment, an evaluation, its application and a conclusion.

The design and evaluation of several pressure vessels, and that of a modified microwave oven for sample digestion, are presented in Chapters 2 and 3, respectively.

Computer-controlled microwave applicators with temperature control for general investigations into the laboratory applications of microwave heating are discussed in Chapters 4 and 5.

The development of a suitable microwave applicator with external fume extraction for processing multiple laboratory samples simultaneously is discussed in Chapter 6.

In Chapter 7, several designs of microwave applicators for carrying out pressure reactions in closed vessels are presented.

Chapter 8 describes miscellaneous equipment for microwave applications, some of which are upgrades or improvements to those described in the previous Chapters. Specifically, designs of a modified oven with temperature control, a cylindrical reactor, waveguide systems for on-

line heating, a cavity for gas discharge experiments, and a gas thermometer are described in this Chapter. Additionally, the development and evaluation of a moisture meter for laboratory samples operating at 10 GHz is also presented in this Chapter.

A general conclusion is drawn in Chapter 9.

CHAPTER 2

THE DESIGN AND APPLICATION OF PRESSURE VESSELS FOR MICROWAVE DIGESTION

2.1 Objectives

The aim of this work was to design a general purpose vessel suitable for a wide range of applications which could be easily manufactured from available materials at a reasonable cost while providing the necessary safety features and ease of operation. The design and application of this vessel is discussed in Section 2.2.

The design of a very small capacity vessel for the digestion of biological materials is also discussed in Section 2.3.

2.2 The design and application of an 85 ml PTFE vessel

2.2.1 Construction and features

A schematic diagram of the vessel is shown in Figure 2.1 and the design features can also be seen in Figures 2.2 and 2.3. The 85 ml capacity vessel was constructed entirely from PTFE with a body wall thickness of 12 mm and was machined from solid PTFE cylinders.

Protection shield:

The protection shield was made of 20 mm polypropylene since the temperatures achieved on the outer surface of the PTFE structure during typical digestions are well below the working temperature of polypropylene (100 °C) and the latter retains its mechanical strength during digestions and prevents sideways deformation of the PTFE body. Furthermore, the shield offers an extra safety feature since it prevents the opening of the vessel when still pressurized. Initially the vessel is cooled by partial immersion of the whole assembly in running water. After a few minutes the shield can be removed for further cooling.

Sealing plug:

After investigating several sealing structures, a radius-to-flat contact between the sealing plug and the vessel's body was found to provide the best seal during pressurization [PAT91a]. Two other features were included in this design. Firstly, the tapered structure of the plug (inside the vessel) with a very smooth surface causes the droplets formed during condensation of digestion fumes to drop back into the vessel. Thus a very small amount of condensed material remains on the plug when opening and a minimum amount of water is necessary to

wash out the plug. Secondly, after removing the screw cap, the plug can be easily handled for washing by holding its cylindrical section (containing the bursting-disc holder). This feature allows handling of the plug without the need to wear gloves when corrosive or dangerous acids such as hydrofluoric acid are used and also helps avoid contamination.

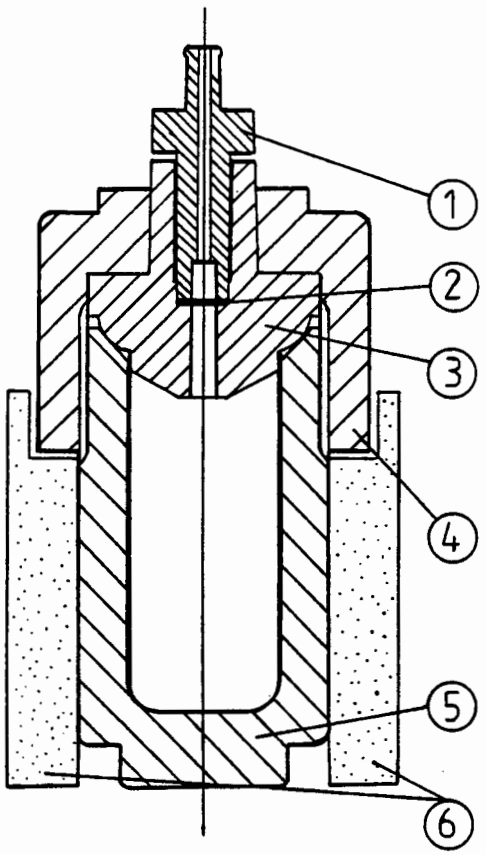


Figure 2.1 The design of the 85 ml digestion vessel.
1. Bursting-disc holder
2. PTFE bursting disc
3. Sealing plug
4. Screw cap
5. Body
6. Polypropylene safety shield

Figure 2.2 The assembled vessel with protection shield.

Pressure relief valve:

The simplest approach for protection against over-pressurization was to incorporate a bursting or rupture disc. The latter consisted of a 0.2 mm thick PTFE disc of 12 mm diameter, which had been irradiated using gamma radiation [PAT91b]. PTFE is a highly elastic material undergoing extensive (400%) elongation before breaking. Thus an untreated PTFE rupture disc would tend to blow up like a balloon. The purpose of the radiation degradation is to eliminate the elasticity and result in a material which breaks shortly after yielding, thus affording a clean, sharp break under predetermined temperature/pressure conditions and using a specific effective surface area (6 mm inside diameter blow hole). The disc was found to rupture reproducibly at a pressure of 10 atm at 110°C. The discs are easily changed from the disc holder when necessary. The bursting-disc holder can be unscrewed to allow controlled depressurization of the vessel after cooling and before opening, when an internal pressure still remains due to the formation of gaseous products.

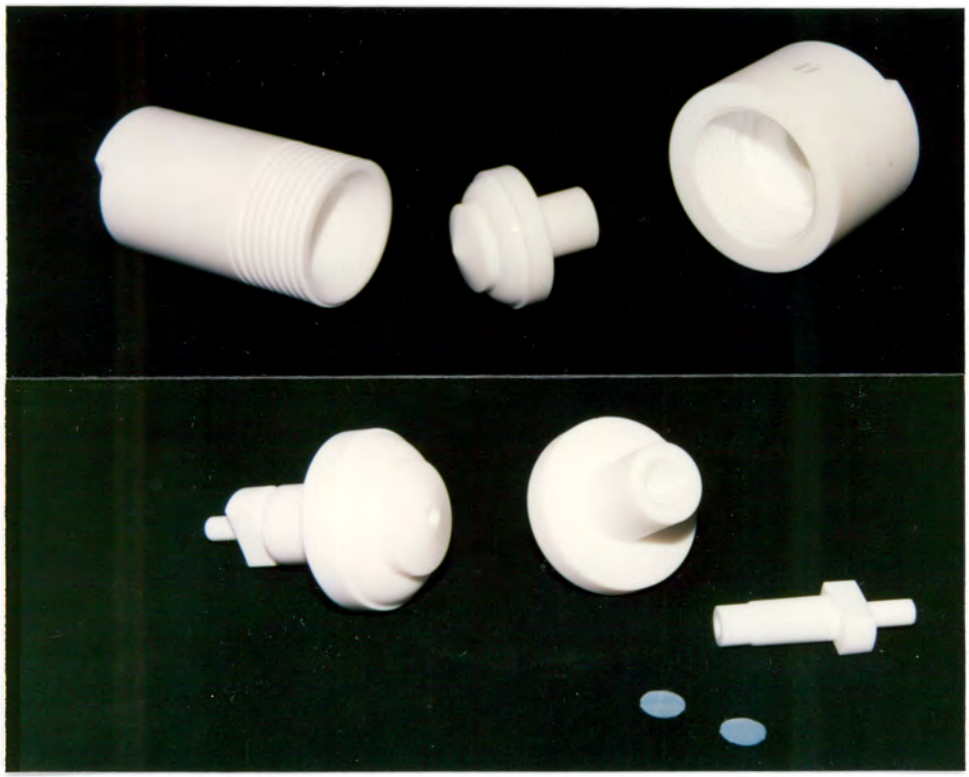


Figure 2.3 View of the dismantled vessel showing the different components.

Vessel closure:

The vessel was closed by using a holder which gripped the lower part of the vessel and a handle which fitted over the screw cap, both made of polypropylene (Figure 2.4). While this method was found to be suitable, a torque wrench set at 15 N m was also used to seal the vessel reproducibly. Use of the torque wrench prevented both over-tightening (which could put strain on the threads) and under-tightening (which could lead to leakages during the digestions).

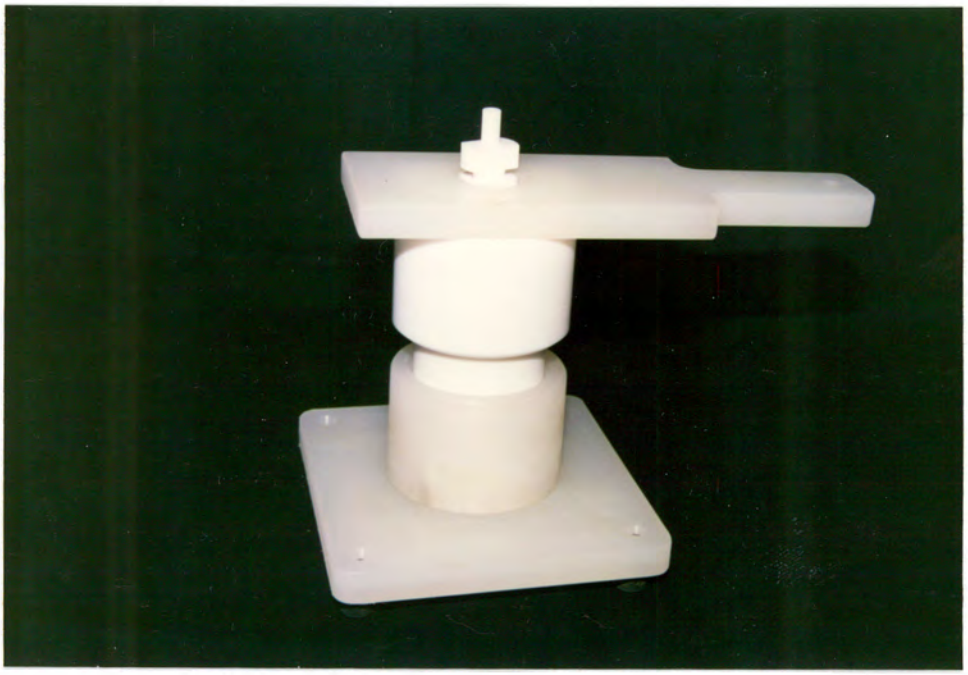


Figure 2.4 Closing and opening device.

2.2.2 Applications

For each type of sample the digestion conditions were investigated and optimized. The governing parameters include the vessel's capacity, the microwave power of the oven and type of control (*i.e.*, pulsed average power or continuous irradiation at different levels), time of irradiation, type of acid and acid mixtures, sample size, sample-to-acid(s) ratio and the number of samples processed simultaneously. This vessel has been subjected to a large variety of sample digestions and the optimum parameters used for several samples and some analytical data are presented below.

(a) Biological samples:

For a large range of biological samples with similar analytical requirements [*i.e.*, major or trace analysis by atomic absorption spectroscopy (AAS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES)], a common set of digestion parameters can be applied effectively. The conditions given below were used for fish meal, soya beans, dried tea leaves, sunflower seeds, corn leaves and crushed kernels, cereals, sludges and the following National Bureau of Standards Standard Reference Materials (NBS-SRM): Bovine Liver 1577, Pine needles 1575, Tomato leaves 1573, Orchard leaves 1571, Spinach 1570, and Oyster tissue 1566.

Microwave oven:	MLS-1200 (Milestone)
Power:	1200 W (25, 50, 75% continuous power)
Sample weight:	0.3 - 0.4 g
Reagents:	5 ml 70% HNO_3
	0.5 ml 30% H_2O_2
Heating:	4 min at 25% power
	1 min at 50% power

For all the materials digested, clear, colourless solutions were obtained. When hydrogen peroxide was not used slightly yellowish solutions were obtained, indicating that the material had not been fully oxidized. The vessels remained pressurized even after extensive cooling for several hours because of the gaseous products formed. The pressure was released by using the safety valve before opening. The mass of sample used and volume of acid were found to be optimum for this vessel. Increasing the mass of biological sample to more than 0.6 g gave pressures that were too high and caused the vessel to vent.

Analytical results for the determination of some elements by ICP-AES in three NBS-SRM digested by the above method appear in Table 2.1. The instrument used and the operating conditions have been reported by Pougnet and Wandt [POU86a]. Each value reported was the mean of three separate digestions. Apart from a few cases : Ca in spinach and bovine liver, Mg in orchard leaves and bovine liver, Fe and K in spinach and orchard leaves where the measured values were lower than certified values, good agreement (within the quoted error on the certified material) with certified values was obtained and the precision of analyses was comparable to that obtained previously [POU86a]. The low recoveries mentioned above could be due to the association of these elements with small ampounts of undissolved residues (not visible after digestions) or small errors (*e.g.*, interferences) associated with the spectroscopic measurements.

In the case of fresh human liver and kidney, a more elaborate digestion procedure was necessary in order to break down the materials completely. This was necessary because of the high moisture content and relatively high fat content. The conditions used were as follows:

Microwave oven:	MLS-1200	
Sample weight:	approx. 1 g wet basis	
Step 1:	reagent:	4 ml HNO_3 and 0.5 ml H_2O_2
	heating:	4 min at 25% power
		1 min at 50% power
Step 2:	evaporate most liquid	
Step 3:	reagent:	1 ml HNO_3 and 0.5 ml H_2O_2
	heating:	4 min at 25% power
		1 min at 50% power

Table 2.1 ICP-AES analysis of NBS-SRM biological materials.[a]

ELEMENTS	SPINACH 1570		ORCHARD LEAVES 1571		BOVINE LIVER 1577	
	FOUND	REPORTED[b]	FOUND	REPORTED	FOUND	REPORTED
Ca	1.31%	1.35 ± 0.03%	2.10%	2.09 ± 0.03%	111	124 ± 6
Mg	0.80%	0.86 ± 0.12%[d]	0.56%	0.62 ± 0.02%	532	604 ± 9
P	0.53%	0.55 ± 0.02%	0.20%	0.21 ± 0.01%	0.96%	(1.1%)[c]
Fe	508	550 ± 20	240	300 ± 20	256	263 ± 8
Mn	159	165 ± 6	83	91 ± 4	10.8	10.3 ± 1.0
Zn	48	50 ± 2	27	25 ± 3	125	130 ± 13
Cu	11.8	12 ± 2	12.8	12 ± 1	198	193 ± 10
Na	1.47%	1.44 ± 0.12%[d]	83	82 ± 6	0.23	0.23% ± 0.013%
K	3.51%	3.56 ± 0.03%	1.35%	1.47 ± 0.03%	0.94%	0.97 ± 0.06%

[a] Concentrations are given in $\mu g\ g^{-1}$ or otherwise as stated.
[b] The reported values are from NBS certificates of analyses.
[c] The value in parenthesis is informational (i.e. not certified) from NBS.
[d] Other data from reference [GLA80].

(b) Coal:

Coal is a difficult material to break down because of its combination of organic and inorganic constituents. The procedure has to be optimized to take care of the two phases. The method outlined below was developed for the determination of rare earth elements by ion chromatography [RID92].

Microwave oven:	MLS-1200	
Sample weight:	0.1 g	
Step 1:	reagent:	3 ml HNO_3 and 1 ml H_2O_2
	heating:	3 min at 25% power
		4 min at 50% power
Step 2:	evaporate to < 1 ml	
Step 3:	reagent:	4 ml 40% HF and 0.25 ml 70% $HClO_4$
	heating:	3 min at 25% power
		4 min at 50% power

With this vessel it was not possible to digest a larger mass of coal powder. Two separate samples were combined for the determinations.

(c) Limestones:

The argillaceous limestone samples were digested as follows:

Microwave oven:	Litton 650 W	
Sample weight:	0.2 g	
Step 1:	reagent:	1 ml water, 2 ml 32% HCl and 5 ml 40% HF
	heating:	6 min at 80% power
Step 2:	cool	
	add 50 ml 6% boric acid solution	
Step 3:	heating:	6 min at 80% power

The samples were analysed by atomic absorption spectrometry. The results are compared with results obtained by using X-ray fluorescence spectrometry (XRF) and are shown in Table 2.2. For all the elements determined good agreement between the two techniques was obtained. Thus complete digestion of the material was achieved and the elements were quantitatively recovered.

Table 2.2 Comparison between microwave digestion/AAS and XRF analyses of South African argillaceous limestone samples.

ELEMENT	CONCENTRATIONS (%)									
	PR1/2		PR1/3		PR1/9		PR2/7		PR2/14	
	XRF	AAS	XRF	AAS	XRF	AAS	XRF	AAS	XRF	AAS
Si	9.29	9.34	8.91	8.93	11.42	11.35	8.89	9.00	7.88	7.88
Al	1.43	1.42	1.29	1.26	1.52	1.49	1.22	1.17	1.23	1.25
Mg	0.90	0.94	0.91	0.87	1.51	1.51	0.89	0.84	0.87	0.90
K	0.24	0.24	0.24	0.25	0.22	0.22	0.24	0.25	0.21	0.21
Na	0.10	0.08	0.07	0.05	0.07	0.04	0.08	0.06	0.08	0.07

(d) Determination of alkalies in limestones :

Only the first step of the above procedure was necessary for these analyses. Sodium and potassium concentrations were determined by AAS. These results (reported as % oxide) are compared with results obtained using XRF in Table 2.3. The simple digestion procedure allows relatively fast quality control of these materials.

(e) Iron ores :

The following procedure was used to digest samples of hematite, magnetite and British Certified Standards materials:

Microwave oven:	Litton 650 W	
Sample weight:	0.3 g	
Step 1:	reagent:	7 ml 32% HCl
	heating:	8 min at 50% power
		2 min at 80% power

The iron content was determined by a standard titration with potassium dichromate. The precision of the procedure was investigated by analysing hematite and magnetite samples and the accuracy of the method was determined from the analyses of the standard reference materials. The results are shown in Table 2.4. Good agreement with certified values were obtained for the reference materials. Precision of better than one percent can be achieved using this method.

Table 2.3 Comparison between microwave digestion/AAS and XRF analyses of Pienaarsriver limestone (South Africa) and control samples.

SAMPLE	CONCENTRATIONS (%)			
	K_2O		Na_2O	
	XRF	AAS	XRF	AAS
PR SP 33	0.46	0.43	0.13	0.10
PR SP 34	0.43	0.41	0.14	0.11
PR SP 35	0.45	0.43	0.11	0.08
PR SP 36	0.48	0.46	0.13	0.08
Control 1432[a]	0.25	0.25	0.08	0.08
Control 1433[a]	0.54	0.51	0.14	0.14

[a] South African samples used as in-house calibration standards.

Table 2.4 Analytical results for iron ores.

SAMPLE	CONCENTRATION (% Fe_2O_3)	
	Found	Certified value
BCS 172/2 NIMBA iron ore	94.2	94.5
BCS 378 iron ore sinter	87.2	88.4
BCS 301/1 Lincolnshire iron ore	34.3	34.0
South African hematite	85.4 ± 0.10 [a]	-
South African magnetite	72.8 ± 0.40 [a]	-

[a] Mean of 4 separate analyses.

2.2.3 The 40 ml digestion vessel

A vessel of 40 ml capacity was constructed for the digestion of smaller masses of material. The design features of the 85 ml vessel were retained and the vessel is shown in Figure 2.5. For applications with about half of the mass of materials used above, this smaller vessel is preferred.

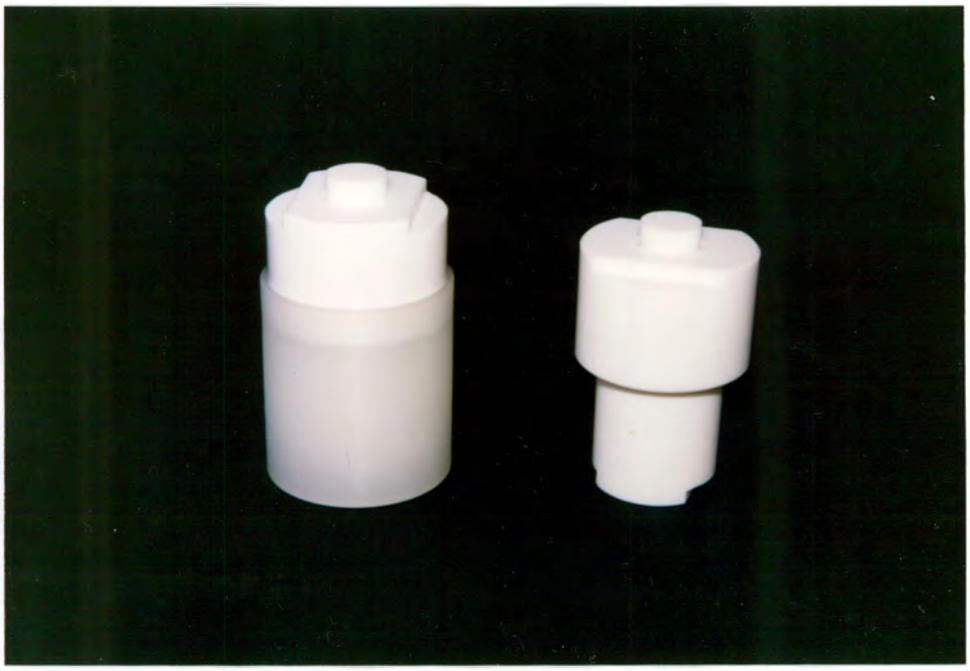


Figure 2.5 The 40 ml capacity vessel with and without the protection shield.

2.3 The design and application of a 10 ml digestion vessel

The vessel described in this section was developed for the digestion of small volumes of whole blood and plasma for metal determination by graphite furnace atomic absorption spectrometry. With sample sizes of typically 0.2 g and volumes of acids of 1 ml or less, the pressures achieved in the larger vessels were not high enough to yield adequate digestions in a short time.

A 10 ml capacity vessel was constructed from PTFE and polypropylene as shown in Figures 2.6 and 2.7. The polypropylene screw plug and body hold the PTFE vessel and sealing plug. The vessel is tightened by hand and a good seal is obtained. No safety valve was incorporated due to the small dimensions of the vessel.

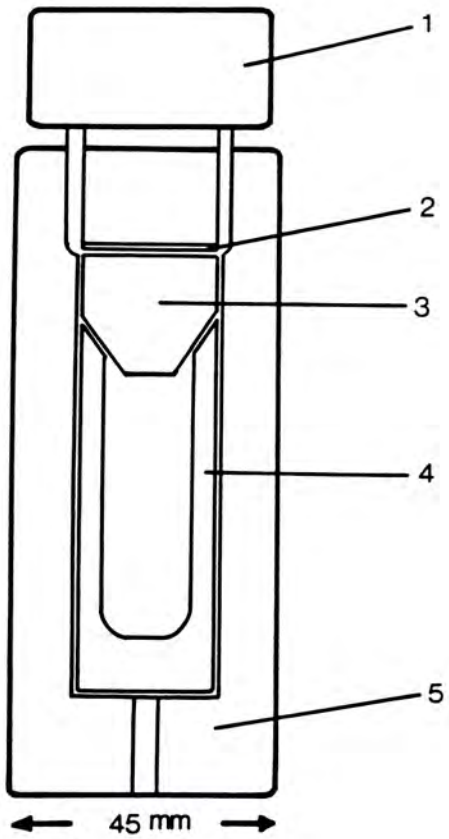


Figure 2.6 Design of the 10 ml capacity vessel.
1. Polypropylene screw plug
2. PTFE washer
3. PTFE sealing plug
4. PTFE vessel
5. Polypropylene body

Figure 2.7 The 10 ml capacity vessel.

With this vessel, about 0.2 g of whole blood were suitably digested with 0.5 ml nitric acid in 5 minutes (3 min at 600 W followed by 2 min at 400 W) using the Sharp microwave oven (see Chapter 3). After cooling in a water bath for about 10 minutes, the vessel was opened and dilution was made in the PTFE cups by addition of 5 ml of water. Aliquots of this sample were transferred directly into the containers of the graphite furnace autosampler for analysis.

Up to twelve such vessels in a specially made rack can be accommodated in the oven. However, due to the very light load in the oven, a dummy load of 100 ml water is placed at the centre of the rotating table.

2.4 Discussion and conclusions

The 85 ml microwave digestion vessel has been found to be versatile for many types of materials from biological to geological, and even for difficult samples such as coal. After optimization of the digestion conditions, the analytical results obtained for the different materials show that accurate and precise determinations can be achieved with relatively fast sample preparation using microwave digestion. In the case of coal, although precise-enough results were obtained for the rare earth elements by combination of two digests, the very small mass processed can be a problem if the material is not extremely well homogenized. A sample mass of 0.25 g is normally recommended for reference materials, but to digest such a mass of coal a vessel with more than twice the pressure rating of the present vessel would have to be used. However, for the many materials investigated so far the vessel has been found to be adequate. These have been in operation in several laboratories for over a year and are now being applied routinely in quality control. Some of the simple but successful design features include the sealing structure, which after very many digestions has not deteriorated; the safety valve, which offers protection against over-pressurization, is also useful to release the pressure after cooling and before opening the vessel (this was found to prevent loss of digest material which condenses in the sealing area); and the use of the polypropylene shield to increase the strength of the vessel and prevent sideways deformation. The shield also prevents opening of the vessel whilst still hot and adds to the safety features.

The design features has been extended to smaller capacity vessels (*e.g.*, 40 ml) and the advantage of this design compared to others that are presently available, is the ease of manufacturing and the use of readily available engineering materials for the construction, which results in relatively low-cost vessels.

The design of the 10 ml vessel was found to be excellent for the digestion of blood and serum. The chances of contamination are diminished since the material is weighed directly in the PTFE cups where the dilution is also carried out. The samples could also be stored in the vessel for further use. Thus a large number of the PTFE inserts were fabricated for twelve polypropylene assemblies. The construction is relatively simple and cheap compared to a vessel entirely made of PTFE. This system is being used routinely for the determination of metals in blood.

CHAPTER 3

MODIFICATION OF A COMMERCIAL MICROWAVE OVEN FOR APPLICATION IN THE LABORATORY

3.1 Objectives

The objective of this work was to investigate a simple and cost-effective design for the modification of commercially available ovens that would offer the necessary protection against corrosion and allow the use of volatile organic solvents.

3.2 The Sharp microwave oven

After investigating the suitability of several available microwave ovens for modification, the SHARP model R-10R50 INVERTER oven was chosen. This oven was selected for the following characteristics:

Construction:
It is robust and has a stainless steel cavity and rubber sealing on the door perimeter.

Size:
It has a relatively large cavity size (385×375×270 mm) to accommodate the lining (see below) and a large enough turntable to hold a wide variety of available pressure vessels.

Cooling and overheating protection:
It has efficient ducting for cooling of the magnetrons and adequate over-heating protection (both on the magnetrons and the cavity).

Power and control:
It provides easy programming of several heating steps (power/time), and there is excellent power control through the use of two 500 W magnetrons (total available power of 1 kW) and a state-of-the-art INVERTER circuit which allows power levels to be adjusted in 10 % increments. The desired power is set in watts and is continuous at the different levels, in contrast to the pulsed operation of the magnetron found in most commercial ovens. In this system, only one of the magnetrons is used for power settings of less than 500 W and the power delivered by this magnetron is controlled by the inverter circuit. For higher power settings, the latter is controlled and the second magnetron operates at full power. The output power calibration of the oven is shown in Figure 3.1. Excellent linear and reproducible calibration was obtained for 1 l and 2 l water load tests (using Equation 24 in Chapter 1). The advantage of this system for laboratory applications, where small loads are normally

used, is that lower power levels can be used, which minimizes the amount of reflected power reaching the magnetrons. The results of power tests carried out on five ovens are shown in Table 3.1. The power output of the ovens were found to be reproducible and stable. This is important if heating conditions have to be repeated in another oven.

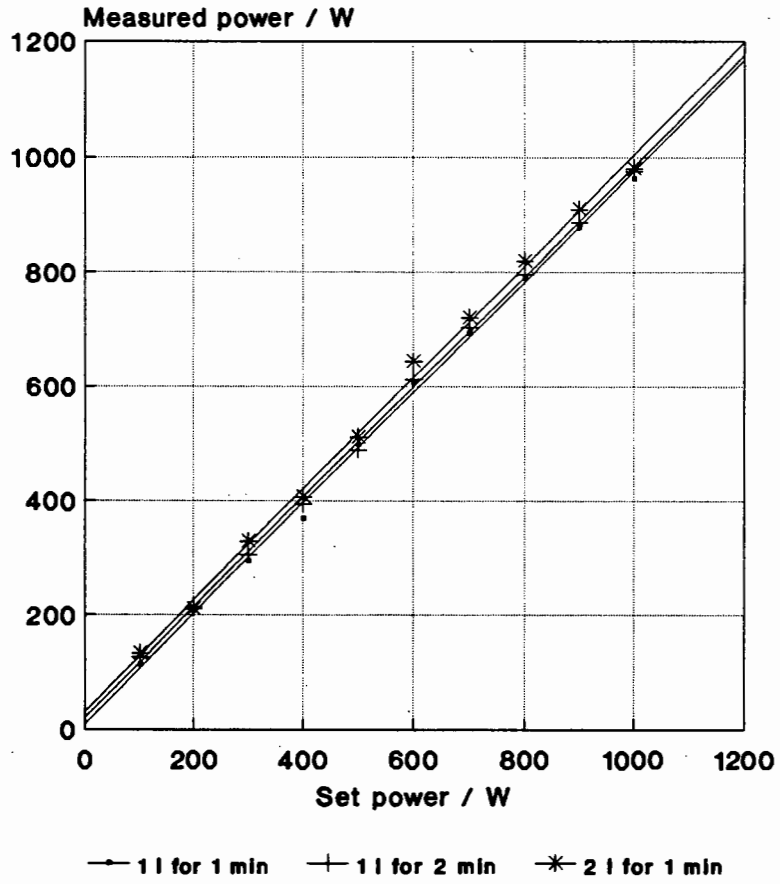


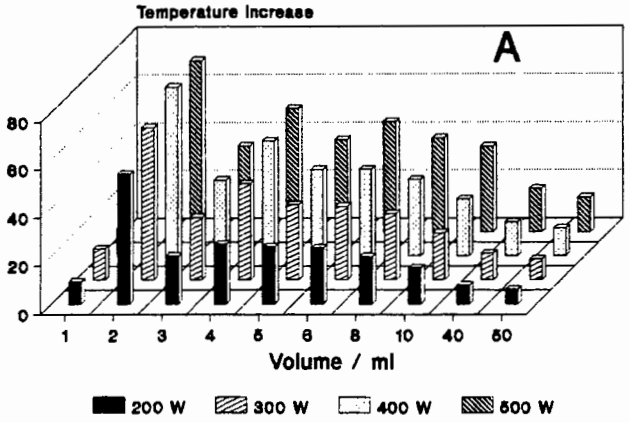
Figure 3.1 Output power calibration.

Table 3.1 Output power test for five ovens.

	Measured power[a] / W				
Set power	1	2	3	4	5
500 W	497	486	508	488	483
1000 W	980	994	1003	995	986

[a] Mean of two measurements for loads of 1 l water heated for 1 minute.

The results obtained for heating small volumes of water at different power levels are shown in Figure 3.2. A dummy load of 100 ml of water was placed in the cavity during the tests and the positions of the test loads were kept as constant as possible. The apparent absorption of power for the different loads (reproducible to within a few percent) in Figure 3.2 (B) shows the "antenna" effect, which is related to the shape and size of the absorbing object in relation to the electromagnetic field in the cavity. Adequate heating rates were achieved for small loads of water, mineral acids of relatively low boiling point, and polar organic solvents. Because of the small volumes of solvents normally used in laboratory applications, a dummy load (*ca.* 100 ml water) was normally placed in the cavity. This was not found to affect the reproducibility of heating of the samples provided the relative positions of the loads were kept constant.



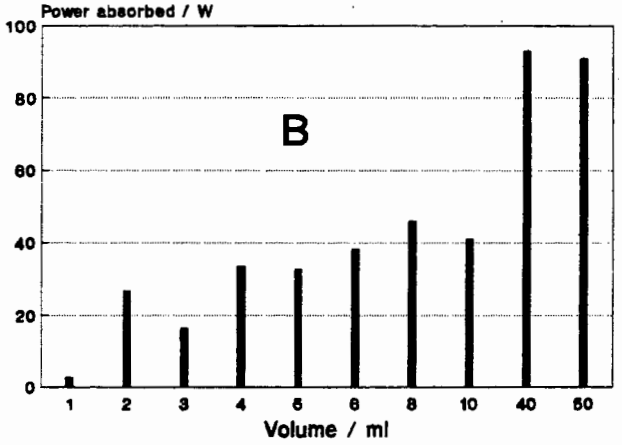


Figure 3.2 (A) Temperature increase for 20 s irradiation of water loads.
(B) Calculated power absorbed for 20 s irradiation of water loads at 300 W.

3.3 Modifications

The oven as purchased was fitted with grill, convection and rotisserie facilities. These components were removed and their electrical connections terminated. The cavity lamp was removed.

The modified oven and its extraction system are shown in Figures 3.3 to 3.7.

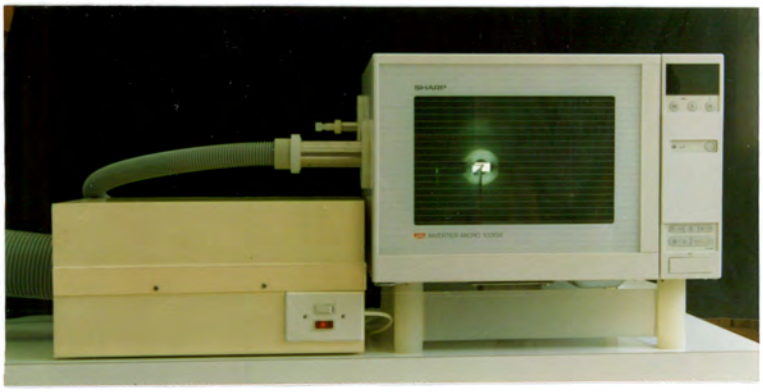


Figure 3.3 The modified oven and the extraction system.

Figure 3.4 The cavity lined with polypropylene, the turntable, and the fluorescent tube.

A polypropylene lining was fabricated by welding 10 mm thick sections and was fitted inside the cavity (Figure 3.4). The indented sections visible in the figure at the top right and back of the cavity lining allow the normal flow of air from the cooling of the magnetrons to the air outlet of the oven. The front of the lining was sealed to the cavity with silicone compound and the stainless steel front of the cavity was treated with several layers of PTFE coating (No. 438, A.W. Chersterton Co., USA).

The standard turntable motor was replaced with a stronger, geared motor capable of turning a load of 8 kg at 5 rpm. To accommodate the larger motor, the legs of the oven were raised by 10 cm.

The standard turntable was replaced by a 15 mm thick polypropylene one fitted with wheels (Figure 3.4). This turns on the polypropylene base of the cavity lining. Thus the mass of the relatively heavy pressure vessels does not rest on the gearbox of the motor.

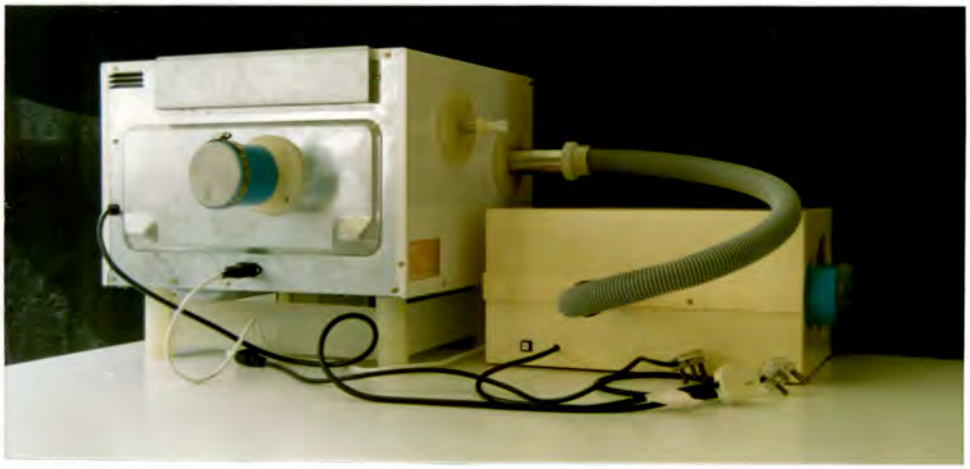


Figure 3.5 Inlet port and filter at the back of the oven and the outlet port connected to the extraction system. A small port is also visible on the side of the oven.

Two stainless steel ports (41.3 mm internal diameter, 130 mm long) were fitted to the cavity (visible in Figure 3.5) by bolted double flanges. One at the back of the cavity serves as an air inlet and one on the LHS as the outlet. The ports were lined with polypropylene and provided a completely plastic connection between the lining and the extraction system (see below). This design was used to offer a free flow system, thus preventing changes of velocity and avoiding condensation, which often occurs with perforated ports. A filter was fitted to the air

inlet port. The extraction system was connected to the outlet port through a flexible 32 mm PVC hose.

The extraction system was built from PVC sections and contained a high speed fan (Figure 3.6). It operated by the venturi effect (Figure 3.7), so that no corrosive fumes could reach the fan. This system provided a high extraction rate of greater than five cavity volume changes per minute and was completely demountable for cleaning. The outlet of the extraction system was led outside the laboratory or to a laboratory fume hood.

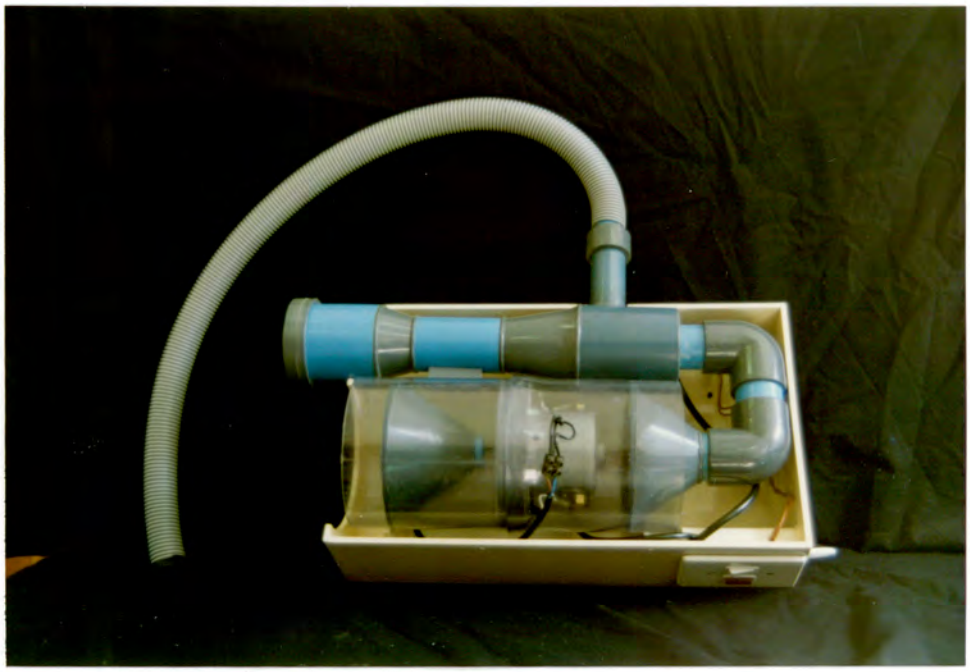


Figure 3.6 The PVC extraction system.

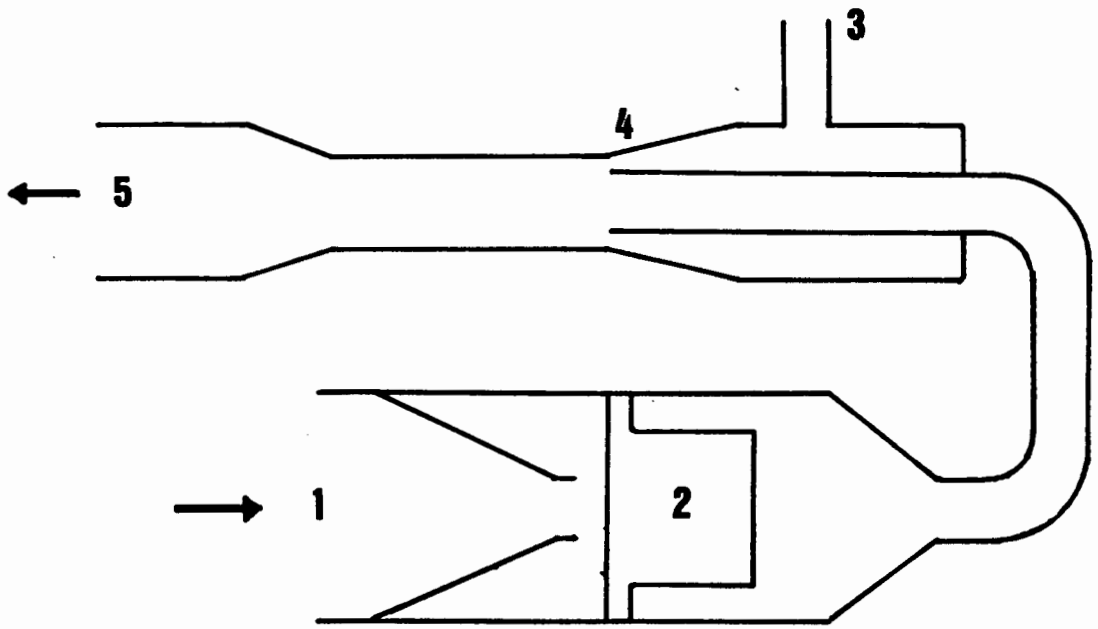


Figure 3.7 Design of the extraction system. 1: air inlet, 2: motor/impeller, 3: connection to oven, 4: venturi nozzle, 5: air outlet.

A small stainless steel port lined with polypropylene (15.8 mm inside diameter, 80 mm long) was fitted for using fibre-optic temperature measurement devices, pressure lines, for flushing gases through the cavity, or for special extraction purposes.

The standard lamp was ineffective through the thick polypropylene lining. A small fluorescent tube as is used for caravan lighting (12 V, 130 mm long) was used instead (Figure 3.4). Direct ionization of the gas in the tube was achieved even at low powers. The problem of using such tubes is that they get very hot, especially at the metal caps, and cracking of the glass occurs. This problem was dealt with by inserting the two ends of the tube in stainless steel tubes, exposing only about 30 mm of the tube's centre portion, and placing this in front of the inlet port where the flow of air kept the tube cool. This device was simple, offered a bright light, and could be inserted when visual observation was required. However, in routine work using pressure vessels, it is not necessary to observe the interior of the cavity.

By means of current-sensing circuitry in the extraction-fan motor and a relay placed in the oven's power input line, the operation of the oven was not possible without proper functioning of the extraction system. This precaution was deemed necessary for complete protection in laboratory applications.

3.4 Discussion

The modified oven was tested for microwave leakages. Levels were below 1 mW cm^{-2} at a distance of 5 cm. The polypropylene lining structure showed slight deformation after several weeks of intensive use but the basic shape and functioning was not affected. The extraction system was found to provide sufficient flow to deal with the acid fumes released from venting valves of pressure vessels and with the boiling-off of organics. No condensation was noted within the cavity or in the extraction system. The system has been used extensively for sample digestion using a wide range of pressure vessels and mineral acids, for drying of samples, and for reactivation of silica gel and molecular sieve containing organic solvents.

The use of the metal ports and the polypropylene lining has also been incorporated in other custom-built or modified ovens and an example of a temperature-controlled microwave oven for general laboratory application is presented in Chapter 8.

CHAPTER 4

DEVELOPMENT OF A COMPUTER-CONTROLLED WAVEGUIDE SYSTEM FOR LABORATORY APPLICATIONS

4.1 Introduction

Waveguide applicators can offer several advantages over the most commonly used multimode cavities. Especially for laboratory work in which the samples are small, and where heating reproducibilities and the ability to monitor temperature are of importance, these applicators are well-suited.

The objective of this study was to develop a simple computer-controlled waveguide applicator where temperature could be accurately monitored.

The design of the unit is presented below together with several examples of its application.

4.2 Construction

4.2.1 The waveguide

The instrument is shown schematically in Figure 4.1 and the different components can be seen in Figures 4.2 - 4.4. It consists of a launch waveguide upon which the 500 W magnetron (2.45 GHz) was mounted. A quarter-wavelength matching transformer section (dimensions 8 cm $\times$ 1.4 cm $\times$ 4.7 cm) was used to transfer power optimally to the main waveguide. The waveguide (dimensions 8 cm $\times$ 7 cm $\times$ 38 cm) contained a sample introduction port, tuning screws to match the power to the load and an observation port with a light source to aid visual inspection of the sample during irradiation. A shielded load with flowing water inside a pyrex glass container terminated the waveguide and absorbed excess power delivered to the waveguide. This proved to be more reliable than directing all of the microwave power to the sample and controlling the output power of the magnetron. The unit was constructed from brass sheeting.

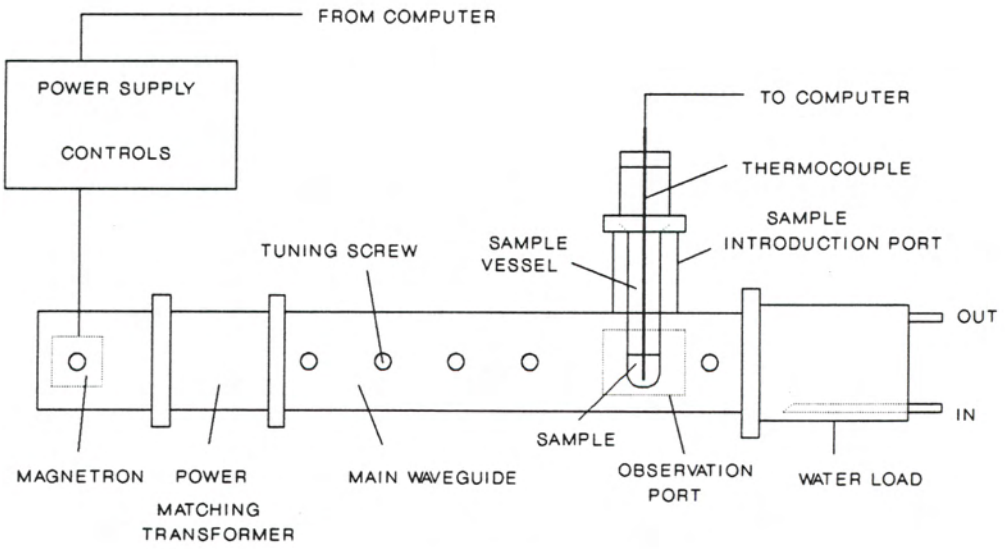


Figure 4.1 Schematic diagram of the waveguide.

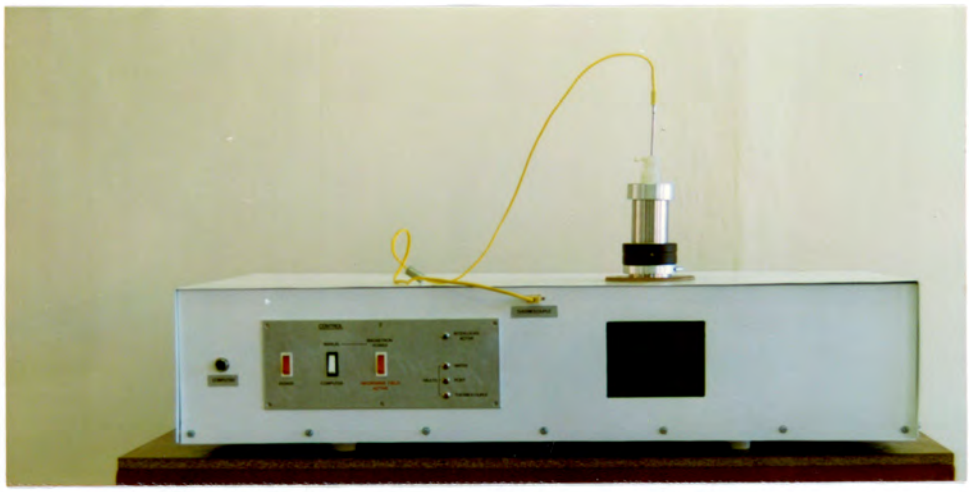
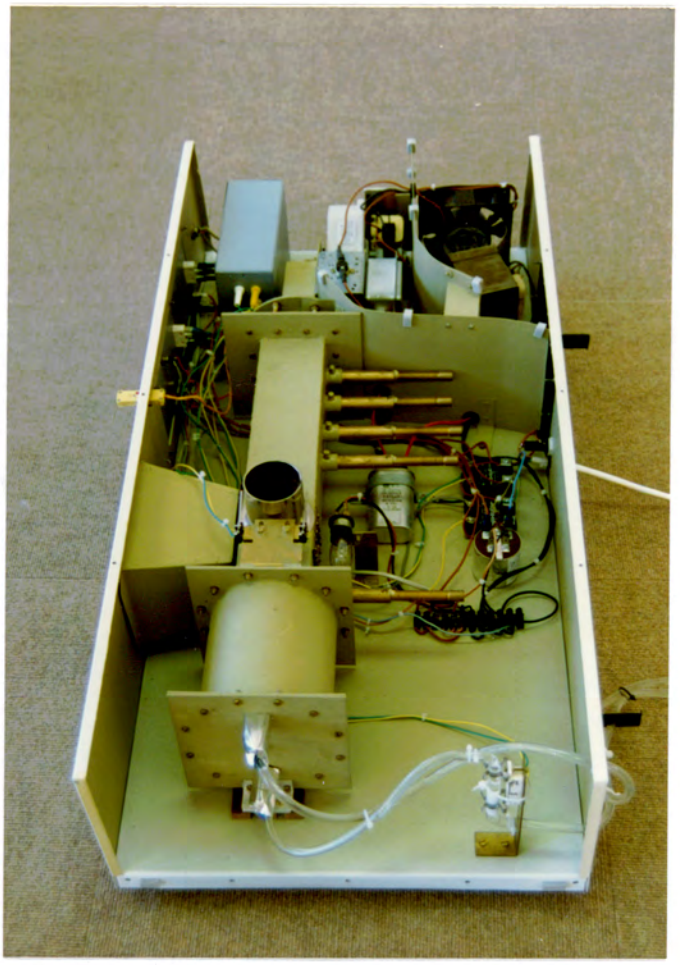


Figure 4.2 The instrument with the thermocouple installed.

Figure 4.3 The control panel. The instrument can be run manually or by computer.



Figuire 4.4 An inside view of the instrument showing the various components.

The dimensions of the waveguide were such that only the fundamental mode (TE_{10}) would propagate. The sample introduction port consisted of a cylindrical section of 55 mm internal diameter and was 70 mm high. These dimensions prevented propagation of the radiation and radiation levels were below 1 mW cm^{-2} at a distance of 5 cm. Two microswitches monitored that the vessel holder adapter was properly located on the port and were used as safety interlocks. A flow switch interlock was also used to ensure that water was flowing in the water load. Another interlock was a thermal switch on the magnetron. A separate filament transformer was used so that only the high voltage supply was switched off during pulsing of the magnetron (*i.e.*, for feed back temperature control).

An HP model 8410C Network Analyser was used to study the power transfer characteristics of the unit. By using the tuning screws, fine tuning of power matching with various loads was possible in order to obtain minimal reflected power. For example, with a 25 ml water sample the level of reflected power was -10 dB (10%). Similar levels were obtained for other liquids such as acids and organics. With solid samples, no problems of high reflected power were encountered. With a 25 ml water load heated at full power, the power absorbed calculated from a temperature increase curve (*e.g.*, Figure 4.12; T = 69.5 °C in 40 seconds) was approximately 182 W.

4.2.2 Temperature measurement

Since the direction of the electric field component of the microwave was plane-polarized and perpendicular to the sample port, standard thermocouples could be used without them self-heating (*i.e.*, they did not interact with the field). K-Type stainless steel shielded ungrounded thermocouple probes of 3 mm diameter or narrower were used for all temperature measurements. For measurements in corrosive substances such as mineral acids, a thin PTFE sleeve was inserted over the probe. The presence of the PTFE shield did not affect the time response of the thermocouple in any significant way but limited measurements to about 350 °C. A commercial analog-to-digital integrated circuit (AD 595, from Analog Devices) and the necessary circuitry provided linearization and a suitable output voltage for the interface card to the PC. The accuracy of the temperature measurement was better than 0.5 °C.

Small microwave leakages through the thermocouple probe holder were found to affect temperature measurements. The problem was solved by using a quarter-wavelength low impedance transmission line choke. The choke consisted of an aluminium cylinder with a hole to accommodate the probe, which was electrically insulated from the aluminium by a Teflon (PTFE) sleeve [see Figure 4.9(A)]. Using the above design, no temperature increase was detected when the waveguide was operated at full power with no sample present.

4.2.3 Computer control

A computer program written in TURBO PASCAL V5.0 was developed to control the microwave equipment. The program was menu-driven (Figure 4.5) and offered flexibility, *e.g.*, for heating with a choice of percent power (through pulsing of the magnetron), and temperature, pressure or other signal monitoring and display (Figure 4.6). Feed-back control was used to maintain a set temperature. Experimental parameters (*i.e.*, step, time, power, and maximum temperature) could be programmed (Figure 4.7). The readings were displayed on the monitor (Figure 4.8) and the data were stored in files for further use. Signals were read by means of the computer through a PC-26 analog-to-digital card and a 8255 card was used for controlling the unit.

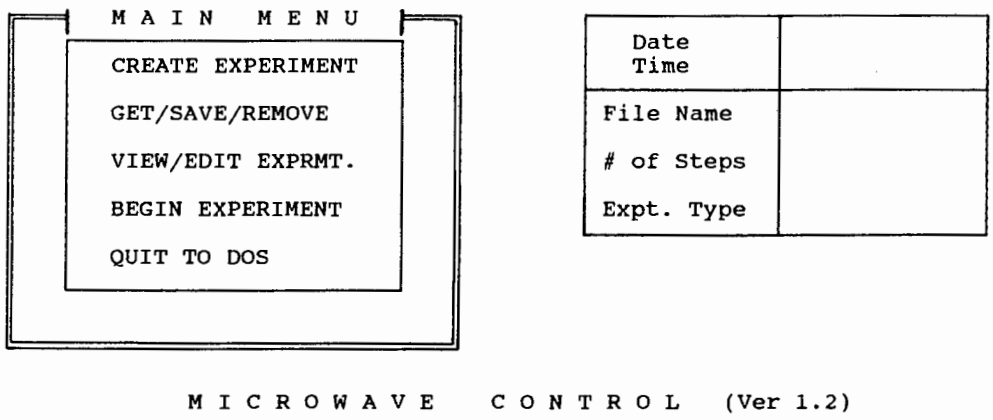


Figure 4.5 Main menu.

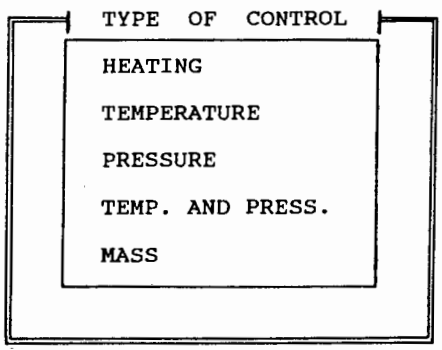


Figure 4.6 Type of control required.

STEP	TIME (s)	POWER (%)	TEMP (°C)
1	20	100	30
2	50	80	50
3	200	50	120

Figure 4.7 Programming each step for time, power and temperature maximum.

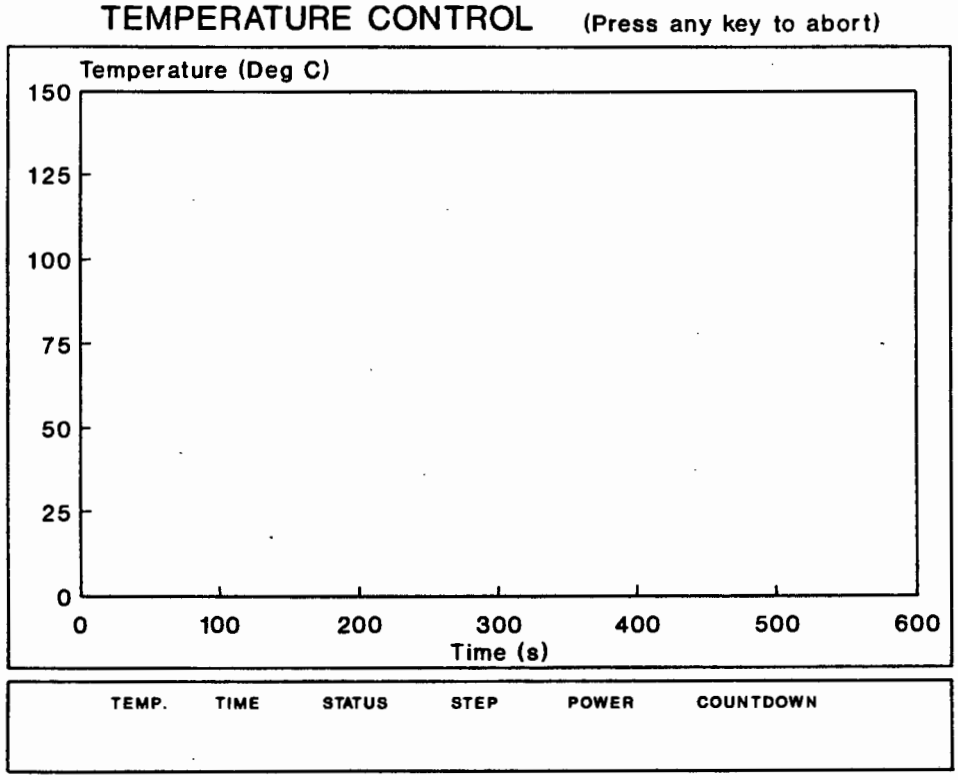


Figure 4.8 Graphic display during operation.

4.2.4 Sample containers and pressure vessel

Several types of vessel could be introduced through the sample introduction port. For solid materials, small silica or other microwave-transparent crucibles were mounted on a length of silica tubing or on other insulating materials (Figure 4.9(A)). For heating liquids and for many reactions, digestions and extractions, pyrex or quartz tubes or round bottom flasks (50 ml capacity) were found to be suitable. Different types of adaptors were used to hold the vessels in the waveguide. Ground-glass joints were used in the vessels so that extension tubes or condensers could be used when reflux was necessary or for extraction of fumes. An arrangement for Kjeldahl digestion using a continuous feed of Caro's acid during the digestion is shown in Figure 4.9(B). A scrubber was used to neutralize acid fumes. For reactions with hydrofluoric acid (*e.g.*, dissolution or leaching of minerals) specially machined PTFE tubes (30 cm long × 3.5 cm diameter) were used.

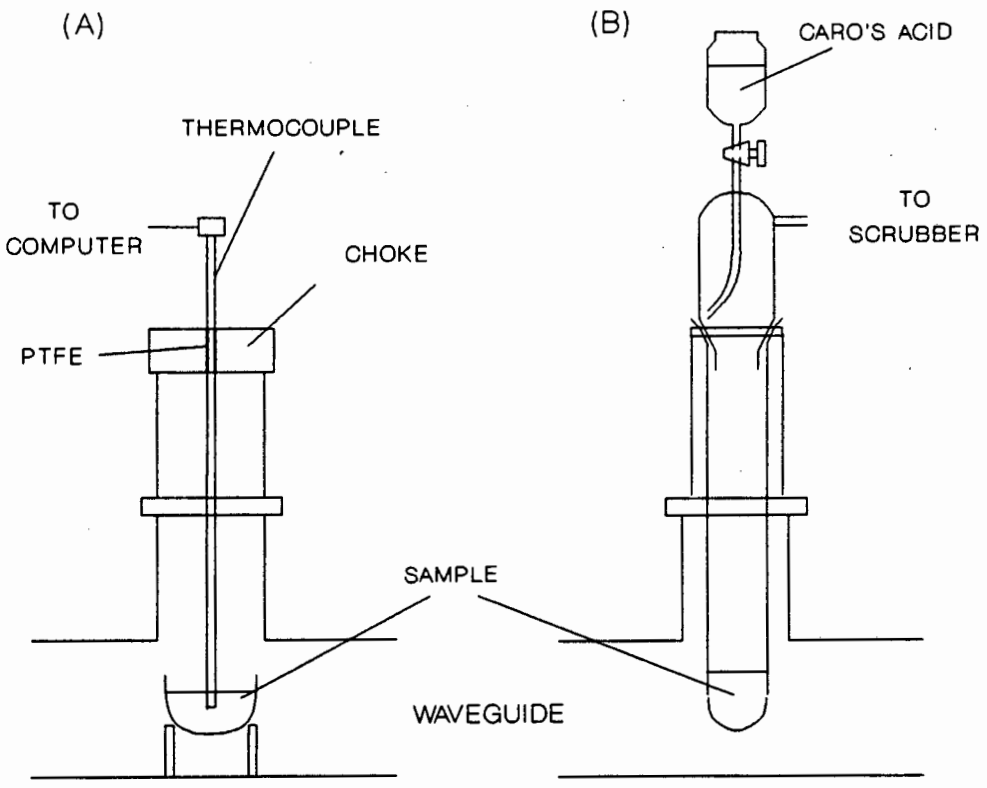


Figure 4.9 (A) Arrangement for heating solid materials.
(B) Glassware for Kjeldahl and other chemical reactions.

A pressure vessel is illustrated in Figure 4.10. The vessel was constructed from PTFE with a wall thickness of 12 mm. A stainless steel casing supported the vessel over the introduction port. A flat brass nut compressed the PTFE plug, which provided a tight seal. In experiments where no corrosive fumes were generated, a simple pressure gauge was used to monitor pressure increase, and a relief valve was implemented to provide additional safety. Alternatively a pressure transducer (Wika, type 891.14.525, 2500 kPa) and a chemical seal was also used to send signals to the computer for pressure monitoring and control. The chemical seal prevented contact of hot corrosive vapours with the transducer. It comprised a PTFE-coated stainless steel diaphragm which transmitted the pressure to the transducer through silicone fluid. The chemical seal was connected to the pressure vessel with thick wall PFA tubing of 3 mm internal diameter. The transducer, mounted on the chemical seal, is shown in Figure 4.11.

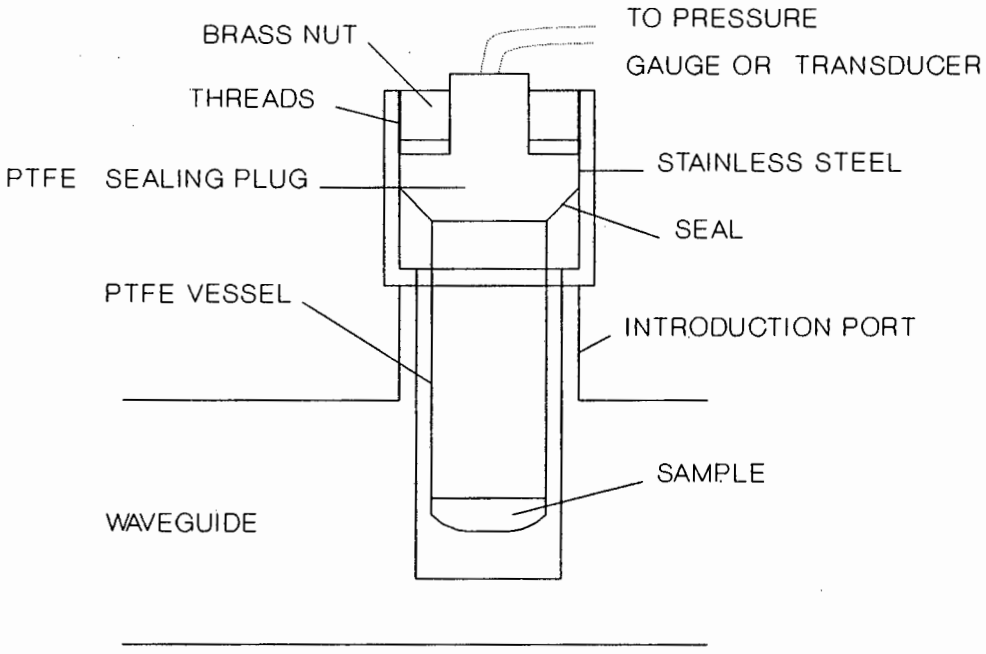


Figure 4.10 Pressure vessel for the waveguide.

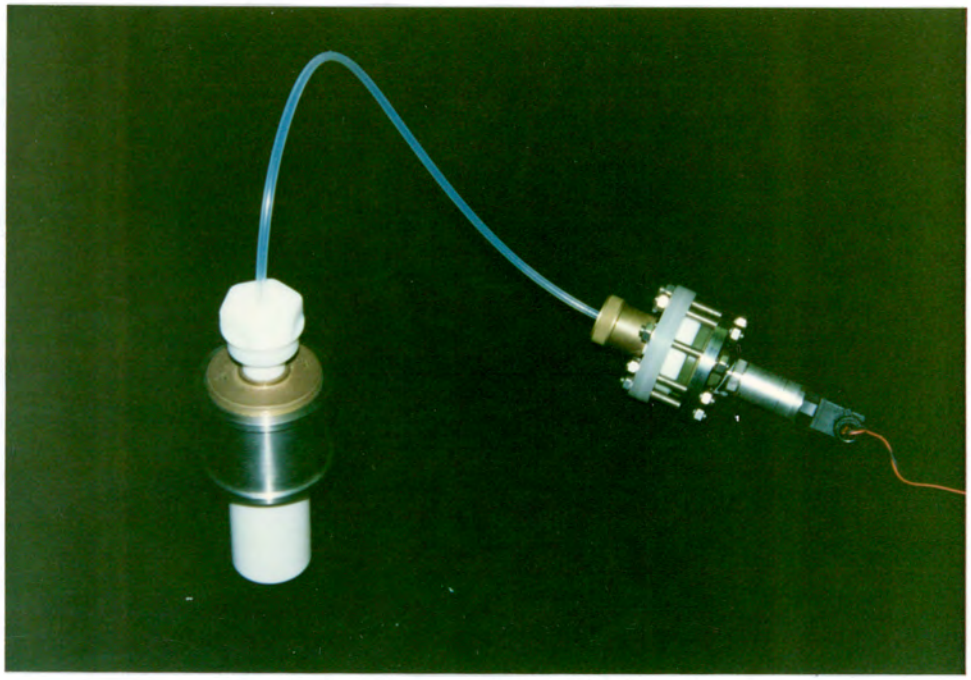


Figure 4.11 Pressure transducer and chemical seal connected to pressure vessel.

4.3 Results and discussion

The performance and applicability of the waveguide in terms of sample heating and temperature measurement were studied through numerous investigations. Some examples follow.

The instrument was found to offer excellent reproducibility for heating materials. However, heating was affected by sample geometry and position within the waveguide. These had to be kept constant. The reproducibilities of the heating curves for liquids and solids are illustrated in Figure 4.12 for 25 ml of water and in Figure 4.13 for 30 g of magnetite powder (< 300 mesh), respectively. Superheating of about 5 °C for the water was noticed (see section 4.3.2 below).

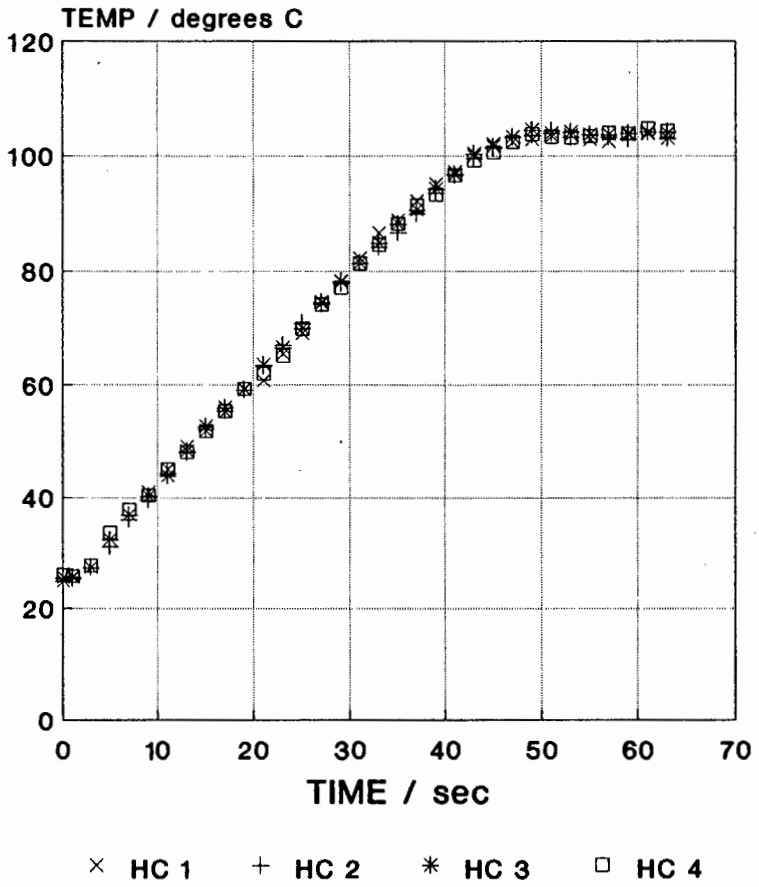


Figure 4.12 Replicate heating curves (HC) for four × 25 ml of water.

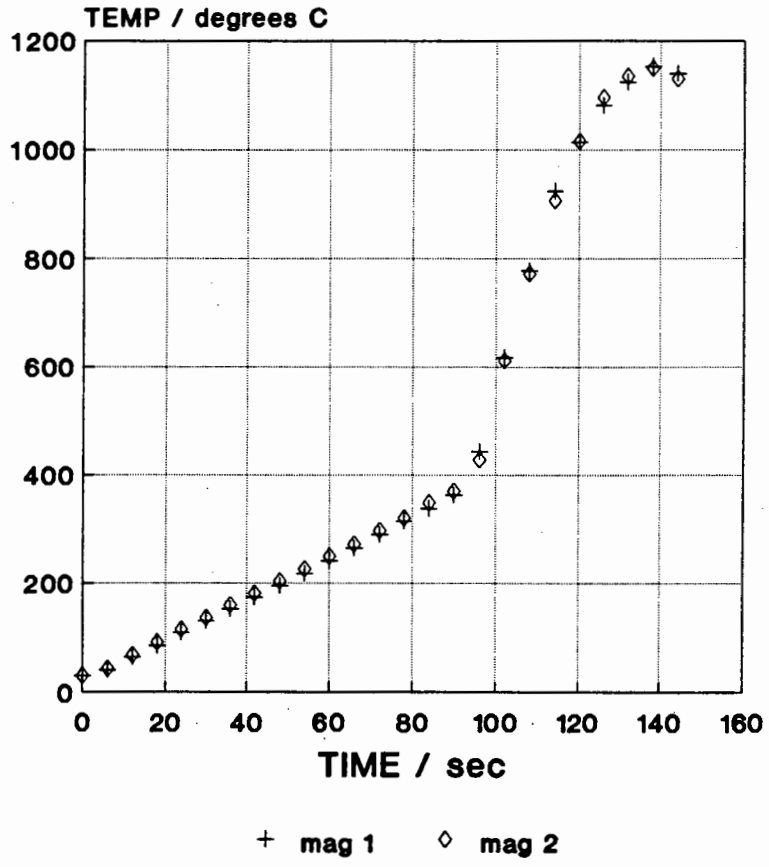


Figure 4.13 Duplicate heating for 30 g of magnetite powder.

The ability to maintain a set temperature using feed-back control of the microwave irradiation is illustrated in Figure 4.14 for a 27 ml sample of water controlled at 80 °C , 25 ml of glycerol at 150 °C and 30 g of ilmenite mineral at 500 °C. The temperature of the mineral was maintained to within 4 °C.

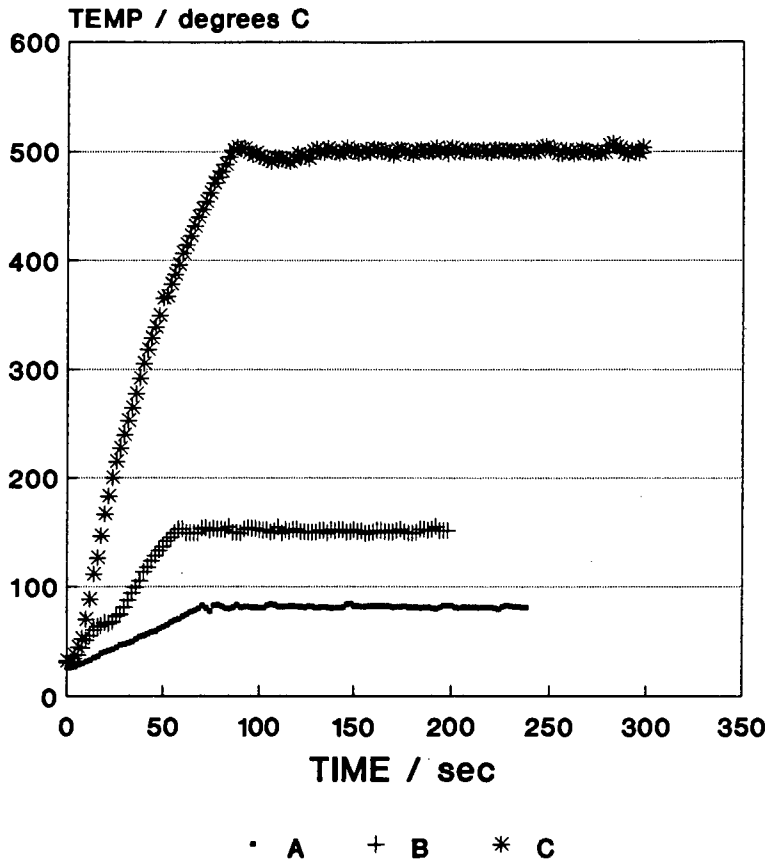


Figure 4.14 Feed-back control of temperature of:

A: 27 ml water at 80 °C

B: 25 ml glycerol at 150 °C

C: 30 g ilmenite at 500 °C

A large number of materials has been processed in the waveguide and some examples are given below.

4.3.1 Mineral acids

Most commonly used mineral acids which are used for sample preparation are good microwave absorbers. Heating curves for 25 ml of concentrated nitric, hydrochloric, sulfuric and phosphoric acids are shown in Figure 4.15. The curved temperature profiles indicate the change of microwave absorption with temperature increase. This is very significant for the high boiling acids. In practice, much smaller volumes were used and the temperature increased much faster.

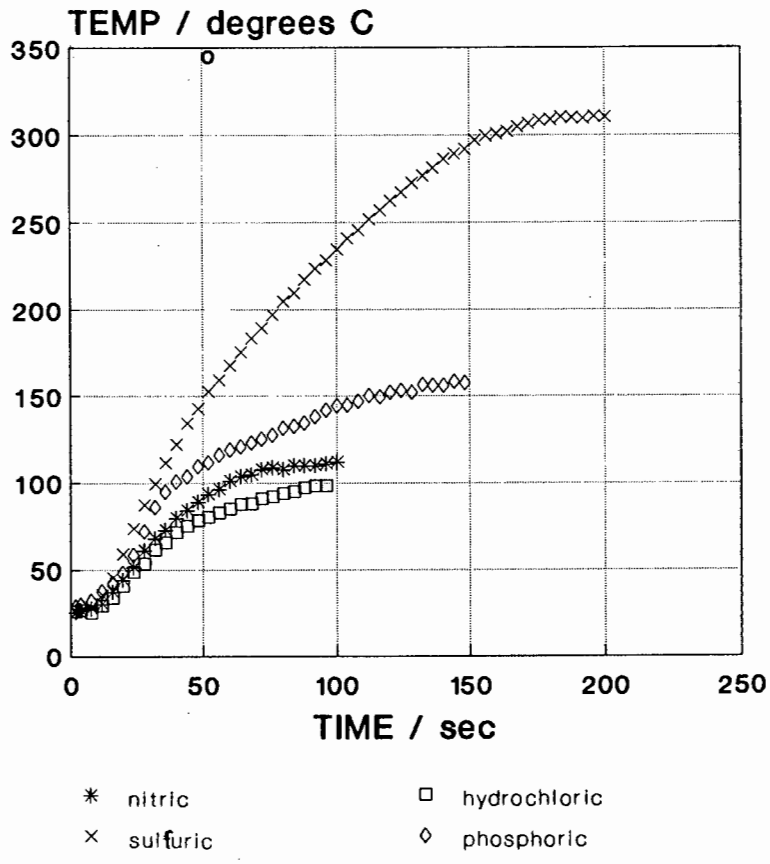


Figure 4.15 Temperature profiles for 25 ml of mineral acids.

4.3.2 Organic solvents

A comparison of the heating curves for several organic solvents of varying polarities appears in Figure 4.16. The chemicals were of analytical grade or better and were dried with molecular sieves prior to the measurements. Strongly polar solvents such as ethylene glycol and dimethylformamide are seen to exhibit superior rates of heating compared with water, while carbon tetrachloride does not couple well with the microwave field. Heating rates for several solvents are compared in Table 4.1. The heating rates were calculated from the gradients of the heating curves, although sometimes these were not linear. The normal boiling points are compared with the maximum temperatures achieved during microwave heating. Data for the dielectric constants of the solvents are also included.

The overshoot of temperature above the normal boiling point for methanol is clearly seen in Figure 4.16. This behaviour has been reported and discussed by Baghurst and Mingos [BAG92a]. Although the objective of this work was not to investigate in details the behaviour of solvent heating by microwaves, the results obtained for the superheating of water and the

organic solvents are in agreement with those obtained by other researchers [Bag92a,NEA92]. The 5 °C superheating of water is confirmed by Neas [NEA92] where the measurements were carried out in a microwave oven with fibre-optic probes. Similarly superheating of the pure organic solvents are confirmed by the other authors but the magnitude of the superheating were found to be lower than those reported by Neas. For example Neas reported superheating of 20, 19, 33, 21, 25, 25, 28 °C for ethylene glycol, methanol, acetone, 1-butanol, ethyl acetate, diethyl ether, and chloroform respectively. In this work the following values were measured for the same solvents: 6, 12, 12, 18, 8, 4, 5 °C. The reason for these differences is not clear but could be related to the experimental set up (*e.g.*, the size of the sample and penetration of microwaves, the presence of the steel thermocouple) but it is noted that in the present case the increases of temperature above the boiling point measured were not due to the presence of the thermocouple (self-heating). Baghurst and Mingos [BAG92a] have proposed a mechanism for the superheating effect and claimed that the extent of superheating is greatly affected by the wetting properties of the solvents. It is thus possible that the differences observed here could be related to the surface of the container used (pyrex glass) and the stainless steel thermocouple probe.

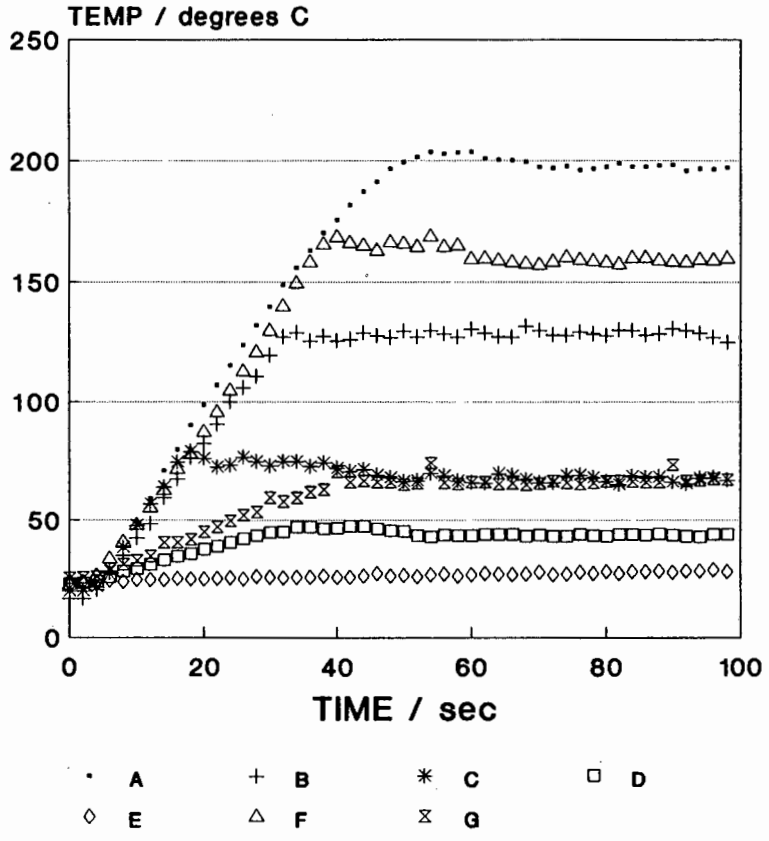


Figure 4.16 Temperature profiles for some organic solvents. A: ethylene glycol, B: acetic acid, C: methanol, D: dichloromethane, E: carbon tetrachloride, F: dimethylformamide, G: chloroform.

Table 4.1 Rate of heating of solvents.

Solvent	Boiling point °C	Maximum temperature °C	Dielectric constant	Rate of heating °C s^{-1}
water	100	105	78.5	2.0
glycerol	290	-[a]	42.5	3.5
ethylene glycol	198	204	37.7	3.6
methanol	65	77	32.6	3.8
ethanol	78	90	24.3	3.5
acetone	56	68	20.7	3.5
1-propanol	97	110	20.1	4.5
1-butanol	117	135	17.1	5.7
acetic acid	118	130	6.2	4.0
ethyl acetate	77	85	6.0	0.9
diethyl ether	35	39	5.2	0.3
dichloromethane	40	47	5.0	0.8
chloroform	62	67	4.8	1.0
carbon tetrachloride	77	28[b]	2.2	0.04
1,4-dioxane	101	29[b]	2.2	0.05
cyclohexane	81	27[b]	2.0	0.05
hexane	68	26[b]	1.9	0.03

[a] Not heated to boiling point.

[b] For a time of 100 seconds.

In experiments with flammable solvents, the vapours are extracted from the containers or are condensed to reduce the fire hazard.

4.3.3 Minerals

Several studies on mineral processing using microwaves have been reported in the literature. One of the main interests is possibly to reduce the laborious leaching processes of certain ores by microwave "roasting" of the minerals prior to leaching. Chen *et al.* [CHE84] studied the

heating of minerals in a waveguide system and Walkiewicz *et al.* [WAL88] have compared heating rates of a number of compounds and minerals in a microwave oven. It was also reported that microcracks could be observed in minerals composed predominantly of a poorly absorbing silicate phase containing strongly absorbing mineral grains when irradiated with microwaves. The formation of these microcracks could allow more efficient chemical reactions to take place in the leaching processes. Other interests in microwave processing of solids are the solid-state reactions and syntheses of oxides and ceramics. Examples of microwave heating of solids using the present waveguide are discussed below.

The heating profiles for three minerals appear in Figure 4.17. Magnetite (Fe_3O_4) was initially, up to 400 °C, found to heat up about twice as fast as ilmenite ($FeTiO_3$) and red oxide (92% Fe_2O_3). The sharp increase in heating rates around 250-400 °C indicates that the dielectric properties of the materials are changing drastically and this can possibly be associated with chemical conversions or phase changes. The sharp transition is well defined and reproducible, as was illustrated by duplicating the magnetite heating experiment. After heating, the material was examined for magnetic properties and in the case of red oxide (non-magnetic) a magnetic substance was formed (magnetite or Fe metal), and the reverse occurred for magnetite. Results obtained from similar experiments have been discussed by Standish *et al.*, who used microwave ovens rather than a waveguide [STA90].

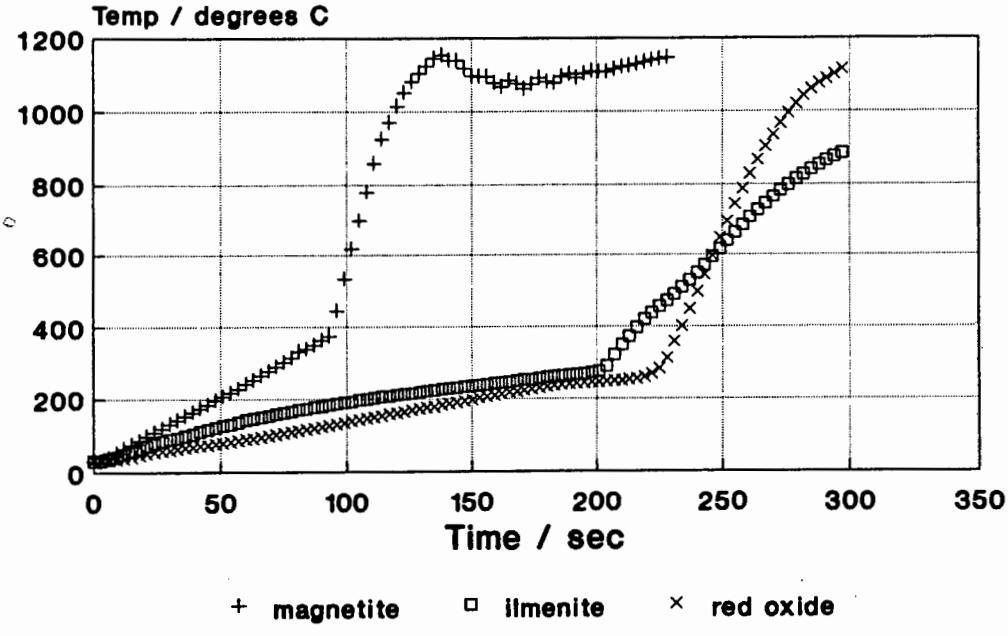


Figure 4.17 Temperature profiles for minerals.

It was found that the temperature profiles were different when measured at the centre of the sample or at a distance from the centre (Figure 4.18). For example, no sharp transition occurred when the temperature was measured on the side of the sample under the present conditions. The samples were heated in silica crucibles that were not insulated, and thus a higher temperature could be expected in the centre due to the insulation provided by the outer layer. The heating losses from the surface of the material are also greater at higher temperatures. The temperature decrease from the centre to the surface has also been measured in pellets heated by microwaves by Standish *et al.* [STAN90]. An interesting observation was that of the effect of particle size on the heating rates of some minerals. This is illustrated for magnetite and ilmenite in Figures 4.19 and 4.20, respectively. The volumes in all cases were kept constant. For magnetite, the middle size particles (1-2 mm) had a higher rate of heating while for ilmenite the larger fraction heated faster but did not display the sharp transition shown for the smaller particles. The sample size was also found to affect the heating rates. While reproducible results could be obtained if the parameters were kept constant, the actual heating rates achieved and the occurrence of a sharp transition was shown to be dependent on the size of the sample and the particle size.

Several factors are likely to affect the behaviour of these minerals and their geometry when irradiated by microwaves. The size of the sample obviously affect the penetration depth and therefore the temperature profile within the sample. Grain size (and therefore the void fraction) is an important parameter regarding the heat conduction and thus the insulation properties of the material. Penetration depth is a function of the dielectric properties which is temperature dependent, the occurrence of an exothermic or endothermic reaction, and diffusion of gases in and out of the sample, further complicates the behaviour in the microwave field. In the decomposition of these oxides, the oxygen environment can be expected to be critical. The diffusion of the oxygen would be affected by the void fraction. The different thermal (and chemical) behaviours for the samples consisting of different grain size is therefore expected. Finally consideration must also be given to the measurement technique. Accurate local measurement of temperature is dependent on the actual contact between the thermocouple probe tip and the material. With granular materials the contact is poor and in the case where microwaves directly couples with the particles, there could be a sustantial error between the particle temperature and the measured temperature. This could not be evaluated and therefore the extent of the effect contributing to the observed differences in behaviour is not known. In general the best rates of heating were achieved when the materials were insulated using high temperature insulating materials such as fire bricks or silica wool.

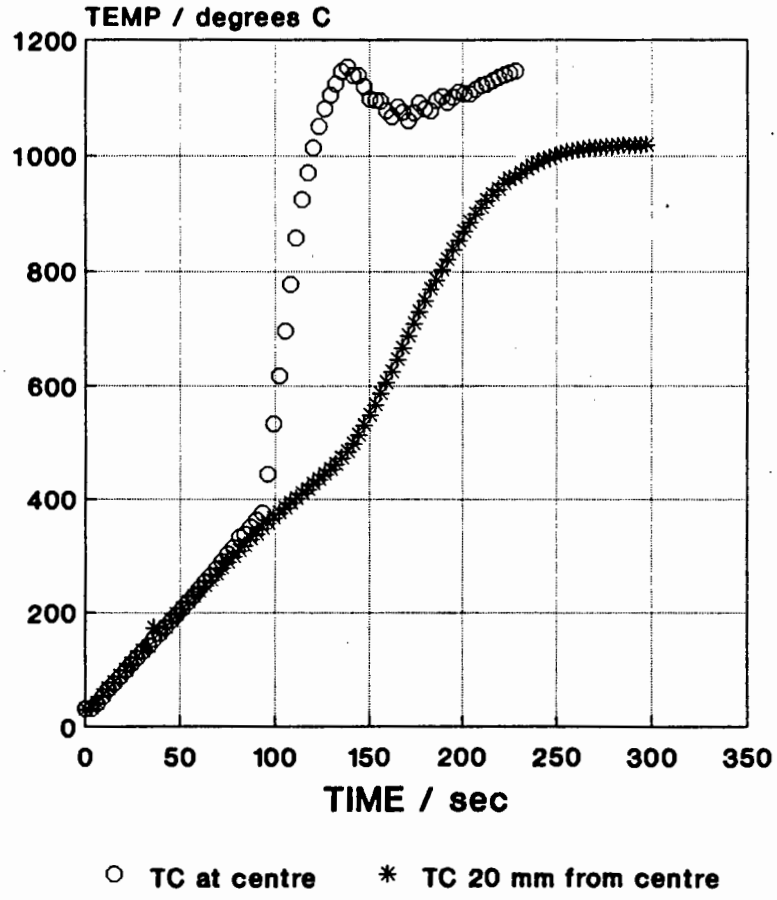


Figure 4.18 Temperature profiles for 30 g of <300 mesh magnetite with the thermocouple tip placed at two different positions in the sample.

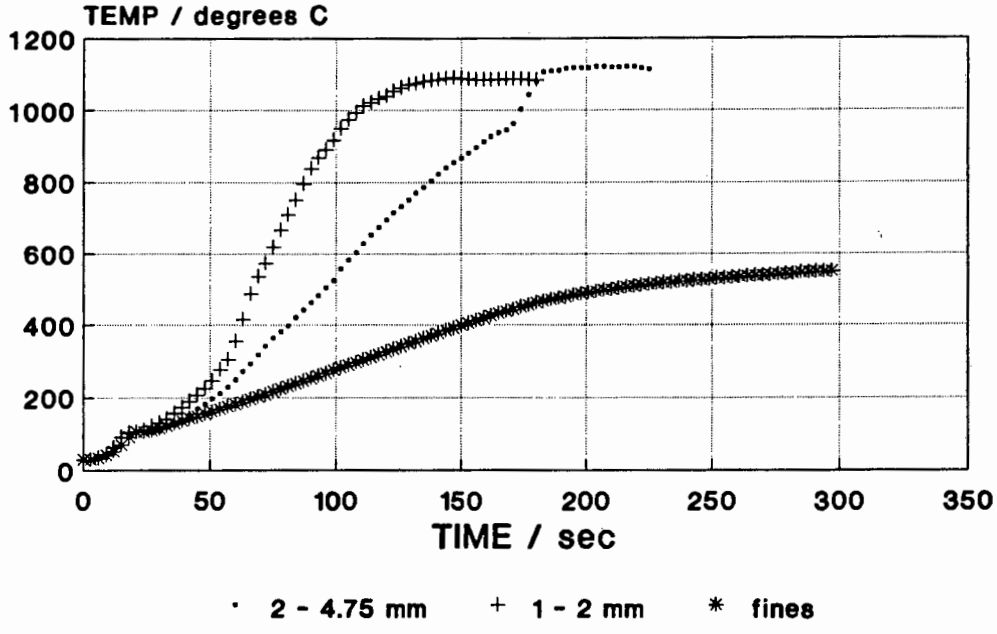


Figure 4.19 Temperature profiles for magnetite samples of different particle sizes.

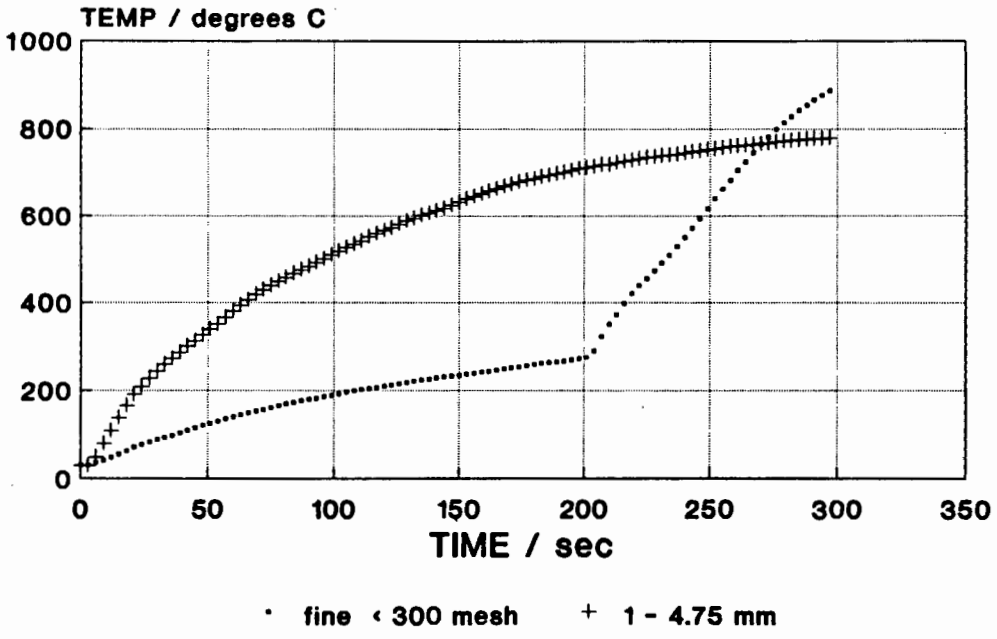


Figure 4.20 Temperature profiles for ilmenite samples of different particle sizes.

The waveguide was used to investigate the application of microwaves in making superconducting ceramics [ROW92]. In these experiments, pellets of the mixed oxides were heated in fire brick insulation and the thermocouple tip was positioned about 1 mm from the surface of the pellets. Although the temperature measurement was not accurate, this was done to prevent any reaction between the material and the stainless steel shield of the thermocouple. The necessary oxygen environment during the reaction was obtained by flushing the waveguide with pure oxygen. Using computer control it was possible to maintain the temperatures at the different required levels over a total period of 3.5 h, and in this way the superconducting $YBa_2Cu_3O_{7-x}$ pellets were successfully prepared.

4.3.4 Carbon fibre-PTFE

In order to heat materials indirectly using microwaves, several material compositions can be used. The use of a composite material made from carbon fibre and PTFE was investigated here. Test pieces of different carbon fibre contents were made by homogenizing the PTFE resin and the carbon fibre prior to pressing and sintering in the traditional manner used to prepare PTFE billets. The microwave heating characteristics of these materials were tested in microwave ovens and in the waveguide. Test pieces of different sizes and shapes were machined and irradiated. The waveguide experiments were carried out using pellets of 30

mm diameter and 10 mm thickness, in which a hole had been drilled to accomoddate the thermocouple probe. Temperature curves for five pellets appear in Figure 4.21. It can be seen that the carbon content dramatically affects the rate of heating of the material, with a content of 2.5% providing almost no coupling with the field. The rates of heating were not found to be proportional to the carbon content and the materials decomposed above a temperature of 350 °C. Provided the temperatures were limited to below 350 °C, containers of various shapes could be made for the heating of poorly coupling materials in the microwave field. For example, shallow dishes were used to remove moisture from oil and for drying samples. A small pellet of the material can be used to initiate boiling in non-polar organic solvents. The material is readily machined and has a good resistance to chemicals. It has also been found useful as a shielding material against low levels of microwaves, the effectiveness being dependent on the carbon content and thickness of the material.

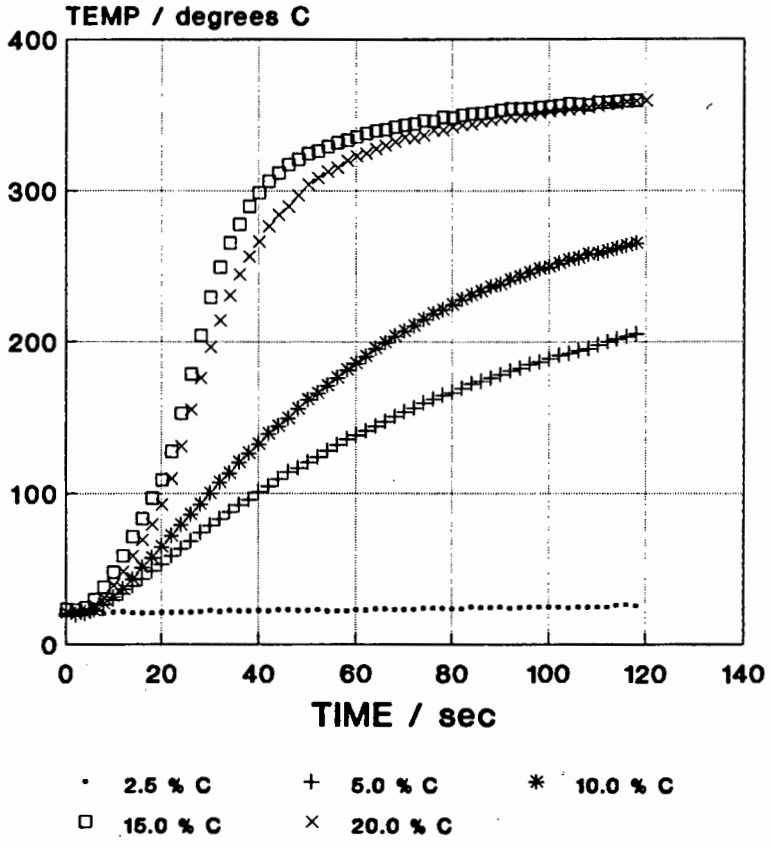


Figure 4.21 Heating profiles of carbon fibre-PTFE pellets.

In several solid processing experiments, it was found desirable to rotate the sample during irradiation so that better uniformity of heating throughout the material could be achieved. A small geared motor and a platform were incorporated in the bottom of the waveguide,

centered with the sample introduction port. However, it was not possible then to measure the temperature using a thermocouple. An infrared system (which was not available) could be used for these experiments, although this technique can only measure surface temperature which can be quite different from the internal temperatures, as illustrated above.

4.3.5 Kjeldahl digestion

One useful analytical application of the waveguide is in sample digestion. The set-up as in Figure 4.9(B), or incorporating a Vigreux column (see below), was used for the microwave digestions. Two dissolution procedures for organic materials were compared with a standard Kjeldahl digestion procedure (Table 4.2). Experimental details follow:

(a) Standard Kjeldahl:
About 0.5 g of sample was digested with 10 ml of conc. H_2SO_4, 3.5 g of K_2SO_4 and 0.35 g of $CuSO_4$ (catalyst). The digestions were carried out using micro Kjeldahl flasks on a heating mantle in the traditional manner.

(b) Microwave digestion (1):
The same amounts of sample and reagents as in (a) above were used.

(c) Microwave digestion (2):
The samples (*ca.* 0.5 g) were firstly charred with conc. H_2SO_4 (4 ml) for 3 minutes. This was followed by further heating with continuous addition of Caro's acid (1 vol. conc. H_2SO_4 : 4 vol. 50% H_2O_2) using the dropping funnel.

The times reported in Table 4.2 are those used to obtain a perfectly clear solution. For all the samples investigated, the time taken for the microwave digestion using standard Kjeldahl reagents was greatly reduced. Still better efficiencies were achieved through the use of continuous feed of Caro's acid or neat hydrogen peroxide after the initial (charring) reaction with sulfuric acid (Chapter 1.2.2).

Several factors affected the speed of the reaction. These included the sample type and size, the moisture content of the sample, the amount of reagent used and the microwave power. Additionally, with microwave heating the reactions were very vigorous and physical losses of sample could occur through the scrubbing outlet. This resulted in low recoveries in the nitrogen determination. These losses could be avoided by using tall enough tubes, by keeping the top of the tube relatively cool so that a reflux action was achieved and by the use of a Vigreux column, which was efficient at trapping volatilised material and causing a refluxing action.

Table 4.2 Kjeldahl Digestion.

Sample	Digestion times/min		
	Standard	Microwave	
		(1)	(2)
Wheat flour	30	10	5
Corn kernels	40	16	7
Powdered milk	60	16	6
Corn leaves	30	11	-
Tea leaves	40	15	-
Mussel tissue	53	16	-
Russian sausage	65	16	-

(1) Standard Kjeldahl (2) Using Caro's acid

It was found more advantageous to char the sample with sulfuric acid only, followed by the addition of hydrogen peroxide dropwise over a period of time. However, it was also found that if the hydrogen peroxide was added immediately after the charring reaction with the power on, a larger volume of hydrogen peroxide was necessary for complete reaction. This occurred because if the sulfuric acid vapour was not allowed to settle and the temperature was too high, most of the hydrogen peroxide was decomposed and lost before entering the charred solution. It was then better to switch the power off after the charring time and allow the solution to cool for about two min before the addition of the hydrogen peroxide (*ca.* 5 ml) with the power off over a period of one min. This was followed by one to two min irradiation at full power. For the most difficult samples, a time of up to 10 min was necessary for complete charring of 1 g of sample with 10 ml sulfuric acid alone and the optimum times varied greatly with the different materials. The above procedure was found to be adequate for all samples tested so far. These included wheat flour, corn kernels, powdered milk, corn and other leaves, tea, mussel tissue, sausage, coffee, baby cereal, coffee creamer, a meat-pasta mixture, soya, fishmeal, soil, and nicotinic acid (which is used as a standard reference material). Soil samples were not completely digested and were filtered before analysis.

One particular advantage of microwaves for these applications is the excellent control of heating which can be achieved. Many samples tend to foam excessively during the initial reaction with sulfuric acid, especially so for some fruit materials. The potential for boiling over and mechanical loss is therefore serious. In traditional processing, the reaction vessel

has to be very large or has to be manually moved away from the heating element, since little temperature control can be achieved with a flame or a heating block. With microwave heating, a very much more controlled reaction can be achieved by pulsing the power. This is easily achieved using computer control. It was thus possible to digest pulped, unmatured, green apples which was very difficult using the standard Kjeldahl apparatus.

4.4 Conclusion

The waveguide described above is a simple instrument which has been found to be extremely versatile and has been used for many investigations in this laboratory. Two such instruments were built and have been in use for several years. Another version of this design was constructed and tested and is shown in Figure 4.22. The main difference is the presence of a tapered transformer section between the launching and the main waveguides and the use of a tapered water load made from polypropylene. The use of the tapered load provided a better match than the flat water load used for the previous waveguide system. Two ports (top and bottom) were available in this version so that a product could be moved through the cavity during irradiation and for on-line heating of liquids in a small coil placed in the cavity (see also Chapter 8). This design was found to perform as well as the original design.

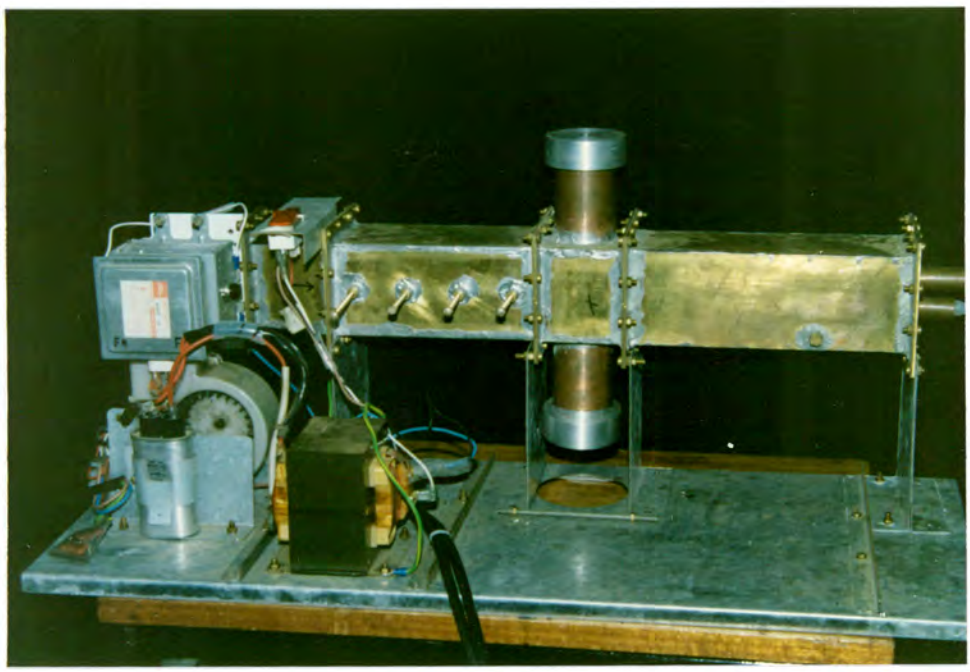


Figure 4.22 Another version of the waveguide applicator.

The major drawback of the above designs is that a fixed matching was usually kept for the different applications. Better-optimized conditions could only be achieved if the waveguide was matched for a particular application using the network analyser. This could be done at low temperatures only and was a laborious procedure. On-line tuning is desirable for a multipurpose instrument. A directional coupler could be incorporated to measure the reflected power and thus provide a means to tuning using the stub tuners. A variable power generator with a circulator and means to measure reflected power, was consequently used for experimental work and is described in Appendix 1. Several examples of the waveguide applicators are discussed in Chapters 7 and 8.

CHAPTER 5

CONSTRUCTION OF A CYLINDRICAL WAVEGUIDE APPLICATOR

5.1 Introduction

The use of a waveguide for heating small laboratory samples (liquids ≤ *ca.* 30 ml) has been shown to be advantageous (Chapter 4). For larger scale processes involving liquid volumes of a few hundred millilitres, an alternative applicator is desirable.

The objective of this work was to design a suitable cavity to process volumes of liquid of up to 1 litre with temperature measurement and control as well as some facilities to configure reactors for different applications. The design of a cylindrical applicator is described and some applications are outlined.

5.2 Design of the applicator

The application of a cylindrical waveguide has recently been described for the sterilization of breast milk to eliminate the HIV virus [DOW91]. This type of applicator was choosen since it could contain a relatively large volume of liquid (2 litres) and it was relatively easy to construct. The cylindrical section was fabricated from a stainless steel tube of 122 mm internal diameter. The tube diameter was chosen to ensure that only the fundamental or dominant mode would propagate and not the higher order modes. The cutoff frequencies for various modes are shown in Table 5.1. For a magnetron frequency of 2.45 GHz, it is evident from the table that only three modes could propagate. These are the TE_{11} (dominant), TM_{01} and TE_{21} modes. Higher order modes can propagate when the cavity is filled with a liquid since the relative permittivity would then generally be much higher than for air. The cutoff frequencies for the propagating modes decrease when the cavity is filled with a dielectric.

The TE_{11} mode was generated in the cylindrical waveguide. This was achieved by first launching the fundamental TE_{10} mode in a rectangular waveguide. A horn taper was used as a transition between the rectangular and cylindrical waveguides (Figure 5.1). Four stub tuners were used to match the impedance discontinuity between the liquid in the sample container and the air in the waveguide. Matching for various loads was achieved by replacing the launching guide with a standard coaxial-to-waveguide transformer and measuring the reflected power from these loads using a HP model 8410C Network Analyser. For a variety of liquids such as water, aqueous solutions and the commonly used mineral acids, matching was considered adequate when the return loss was less than 10 dB (at ambient temperature). This corresponds to at least 90 % of the power generated being absorbed by the load.

Table 5.1 Cutoff frequencies for different modes.

Mode	$\lambda_c/\pi a$ [a]	f_c(GHz) [b]
TE_{11}	0.543	1.44
TM_{01}	0.416	1.88
TE_{21}	0.327	2.46
TE_{01}	0.261	3.00
TM_{11}	0.261	3.00
TE_{12}	0.188	4.16
TM_{02}	0.181	4.33

a λ_c = cutoff wavelength, a = 122 mm

b f_c = cutoff frequency

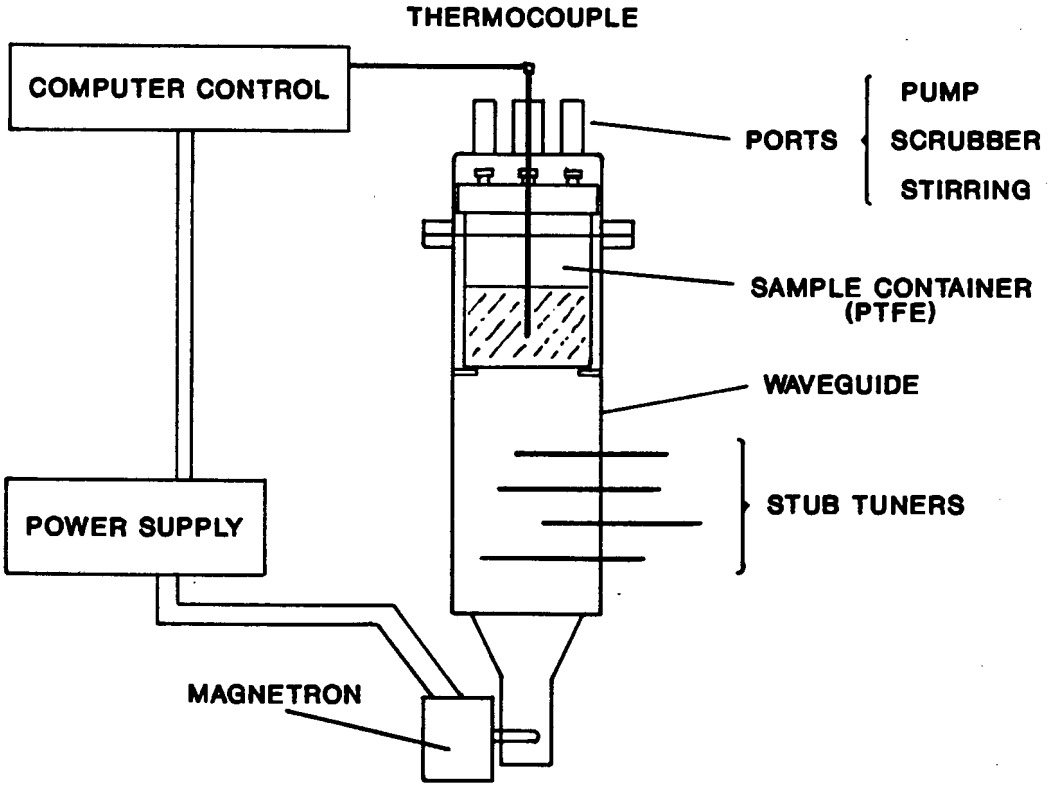


Figure 5.1 Schematic diagram of the cylindrical applicator.

The instrument is shown in Figure 5.2. A Toshiba 2M172AH magnetron capable of delivering 500 W was used. The power supply was standard except for a separate filament transformer that was used to allow fast response of the magnetron when operating in the pulsed mode. Control could be manual (*i.e.*, ON/OFF) or computerized (Chapter 4). The waveguide cover (or lid) was electrically earthed to the main waveguide using beryllium-copper slotted shielding (Instrument Specialities Co., Inc.), which effectively prevented microwave leakages. The cover activated two independent micro-switches which prevented powering of the magnetron if the cavity was open. Three ports of 22 mm internal diameters were available in the cover for measuring temperature, stirring of the reactor contents, pumping in and out of the reaction vessel, and for connecting fume extraction tubes or other components such as reflux condensers. A small, perforated steel window in the side of the cavity in line with the load and an electric bulb on the opposite side allowed visual observation of the load when transparent containers were used. To prevent accidental leakage of fluids onto the magnetron antenna at the bottom of the applicator, a 1 mm thick PTFE sheet was placed at the interface of the tapered and the cylindrical waveguides. Depending on the application, different vessels such as pyrex glass, PFA or PTFE were used. These were suported by four PTFE pins in the wall of the cylindrical waveguide.

Figure 5.2 The cylindrical waveguide applicator. A one litre PFA vessel is seen on the left hand side of the waveguide.

The K-type stainless steel shielded thermocouple (as in Chapter 4) was placed through the centre port. To prevent small radiation leakages past the thermocouple holder that could affect the performance of the electronics, a choke device similar to that used previously in the computer-controlled waveguide was used (Chapter 4). The computer software used to acquire temperature data was also the same as that used previously.

5.3 Performance of the applicator

The heating rates were found to be very reproducible and temperature feedback could be used to control the temperature of a load to within a few degrees (Figure 5.3). Temperature profiles for 100 to 500 ml of water in a PFA container are shown in Figure 5.4. In these examples the thermocouple (TC) tip was positioned at the centre of the loads.

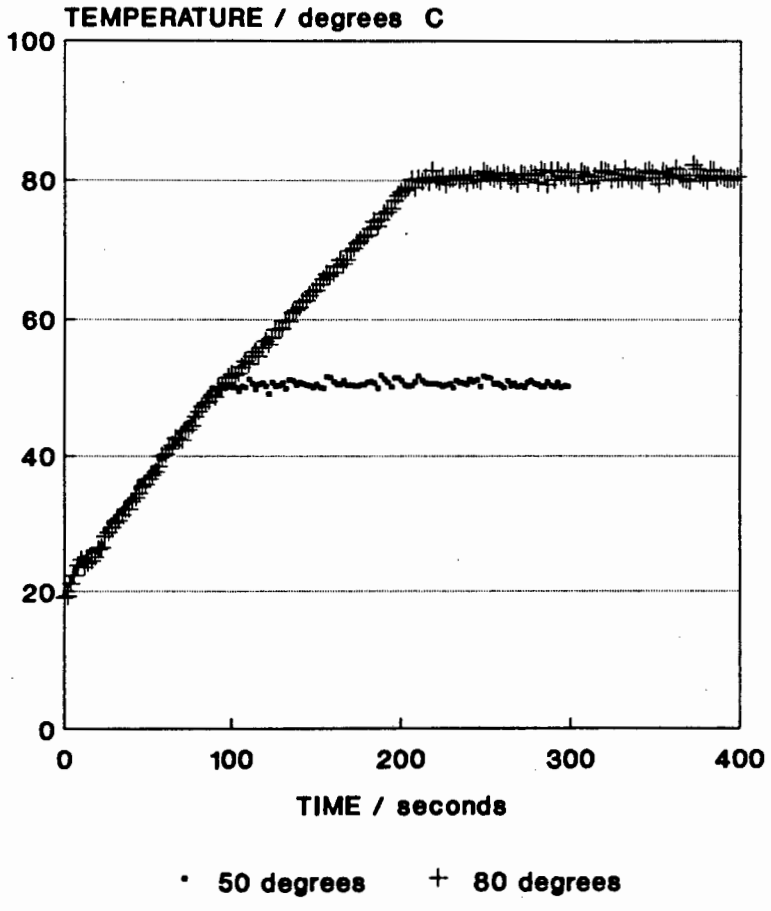


Figure 5.3 Control of temperature at 50 and 80 °C for a 250 ml load of water.

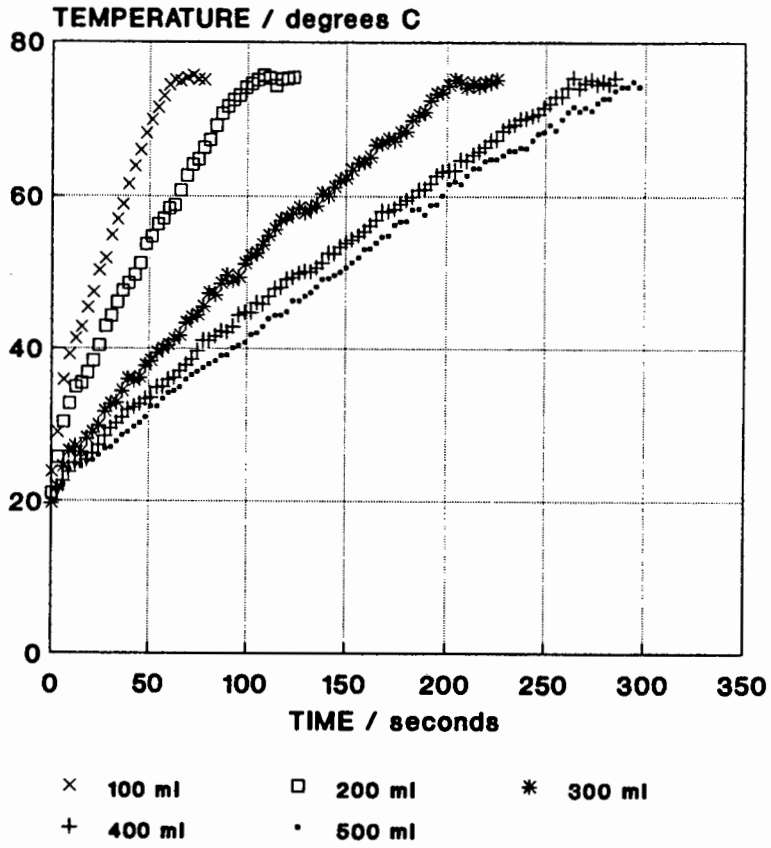


Figure 5.4 Heating rates of different volumes of water with the thermocouple tip placed in the centre of the load.

The effect of the TC position in the load was investigated. The tip was positioned at various heights in the liquid and the temperature was monitored during irradiation. The results for a 500 ml water load being heated between 20 and 80 °C with the TC tip at 10 and 50 mm from the bottom of the load are shown in Figure 5.5. Measured temperature differences of up to 5 °C were observed between the lowest and highest positions. The presence of the 3 mm diameter stainless steel shielded TC did not appreciably affect the temperature measurements. The TC was normally well shielded by the liquid from the microwaves (except when placed a few mm from the bottom of the container and within the penetration distance of the microwaves) and the fluid also dissipated the heat effectively. Self-heating would have caused higher temperatures to be monitored (in the lowest positions) which was clearly not the case when placed 10 mm from the bottom of the load (Figure 5.5), where the lowest temperatures were measured. The temperature differences were also checked by immersing the TC at the

various heights after heating for a length of time with the TC out of the load during irradiation. Similar differences were noted. Several factors affect the temperature and heating rates of a load in the applicator, namely the heat transfer properties of the load (specific heat and viscosity, which affect natural convection and changes with temperature), and microwave absorption and penetration which are also dependent on temperature. The experiments were repeated with ethylene glycol and glycerol, having higher viscosities than water (viscosities at 20°C : water, 10.1; ethylene glycol, 199; and glycerol, 8500 millipoises). Similar results were obtained for ethylene glycol and glycerol with a larger effect being noted for the higher viscosity glycerol (Figure 5.6).

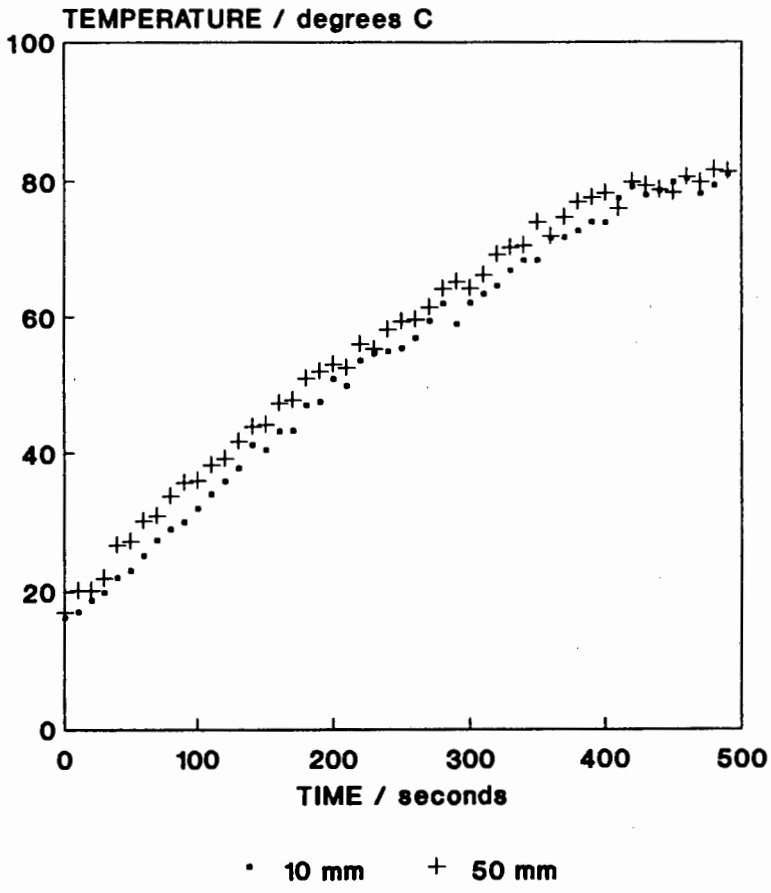


Figure 5.5 Heating rates of 500 ml of water with the thermocouple tip placed at depths of 10 and 50 mm.

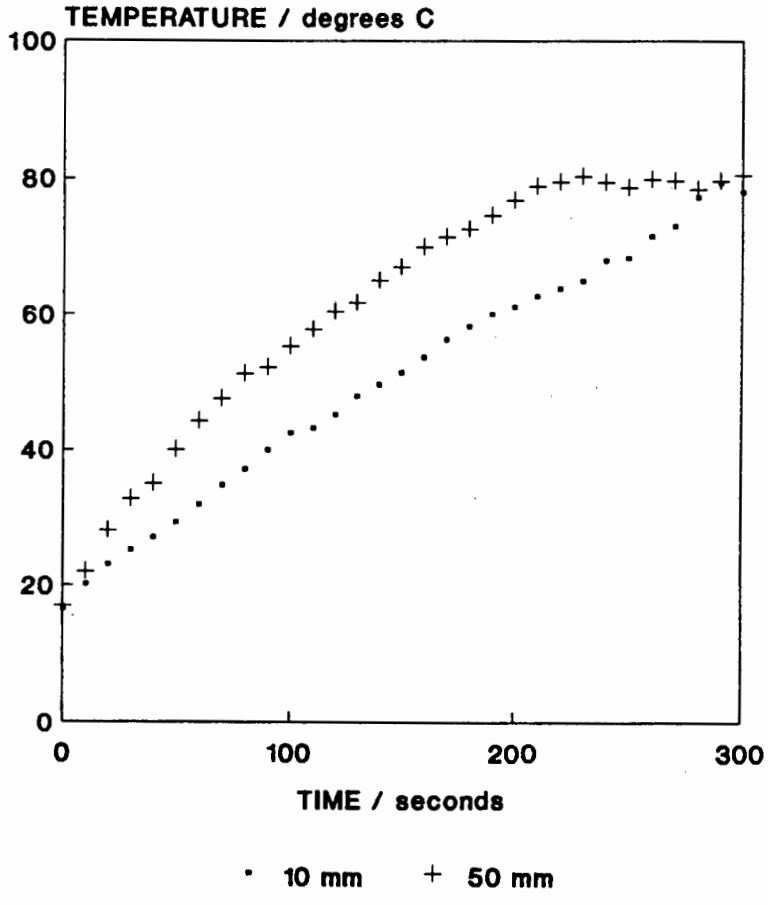


Figure 5.6 Heating rates of 500 ml glycerol with the thermocouple tip placed at depths of 10 and 50 mm.

In the above experiments the PFA container used was only 100 mm in internal diameter and an annular section of the waveguide around the container was not loaded. Therefore it was likely that energy propagated through the unloaded section and heated the liquids from above as well. This would explain the temperature differences noted above. This hypothesis was tested by placing a load of water (at room temperature) in the same container as above. A polystyrene plate was then positioned a few centimeters from the surface of the water and another small load of water in a plastic container was positioned on top of the polystyrene plate. The thermocouple was placed in the small load. The temperature of the latter was found to increase and the energy could not have been transferred by the large load due to the good thermal insulation provided by the polystyrene. It was thus established that energy

could be transferred past the load in the cavity and that the amount transferred was dependent on the size of the load.

Experiments were also done with a container of 1.5 mm wall thickness which fitted tightly in the waveguide. The temperatures at different levels were measured. No temperature gradient was observed for water or low viscosity liquids. With glycerol the liquid was slightly cooler on top when large loads (*e.g.*, 1 litre) was processed. The effect is particularly worst at low temperatures and can be attributed to poor natural convection in the viscous liquid.

In practice, for narrow containers where the temperature of the liquid has to be uniform throughout, stirring can be implemented through one of the ports. Difficulties arise when having to stir in sealed containers housing corrosive acids or volatile organics. Special seals have to be used that allows the stirring shaft to be rotated and prevent the vapours from escaping. Agitation by a stream of gas through a tube in one of the ports was found adequate in many cases.

5.4 Applications

Several laboratory applications have been found for the cylindrical applicator. One general use is as a laboratory "microwave kettle" with the possibility of heating at a predetermined rate (which is difficult when using Bunsen burners and hot plates). Other examples of specific applications are briefly discussed below.

Mineral processing

Microwaves have been widely used for the dissolution of minerals and other small laboratory samples. The technique normally involves the use of less than 1 g of powdered material. For larger scale investigations in chemical processes to either extract (leach) metals from ores or completely dissolve the ores for other processes, small samples are unsuitable because of the large particle sizes and the inhomogeneity of the materials. An amount of 50 g or more of the material is then required to obtain meaningful data, for example on dissolution kinetics.

In studying the kinetics of dissolution of pure minerals or ores, the following parameters are generally investigated: temperature, particle size, nature of acids (or mixtures), acid to mineral ratios and time of reaction. At the end of a reaction, a small amount of the liquid is retained for the analytical work. The number of experiments is normally large and the

manipulation of these solutions containing dangerous acids is hazardous. Any system that can minimize the number of operations would be very desirable. In a typical experiment here, the weighed mineral was placed in a 1 litre PFA container (visible in Figure 5.2), which was placed in the cavity with a sealed lid and the TC (with PTFE shielding) in place. The container had two ports (see Figure 5.2) and two lengths of PFA tubing were sealed in the lid and exited through the two ports of the applicator. The acid at room temperature was pumped into the reactor through one of the tubing, using a peristaltic pump. One of the tubes could be used to pump air through for agitation while the other one served as a breather and was connected to a water pump and a scrubber. The material was heated to a predetermined temperature (or to boiling point where the TC was not required) and the temperature maintained for a predetermined time. At the end of the cycle, a neutralizing liquid (*e.g.*, a boric acid solution or lime water) was pumped into the reactor. The neutralization and cooling allowed the safe transfer of the spent acid from the reactor using the peristaltic pump. A small portion was sampled for further analytical work. Undissolved residues could be further processed by adding fresh reagents or different reagents to deal specifically with resistant residues. When several reactions on a particular material were required (as is often the case for rocks containing several minerals which must be dissolved by different acids or mixtures) the applicator was found to be most useful since it was not necessary to open the reactor after each step.

An example of the above approach was the study of the dissolution kinetics of garnets (general formula $A_3B_2(SiO_4)_3$) at 90 °C. The results are shown in Figure 5.7. The effect of two reagent mixtures [hydrofluoric acid(HF) and water and HF and hydrochloric acid(HCl)] were compared in this study. 50 g samples were treated with 375 ml of reagents in the PFA container. After every hour, heating was stopped briefly and a small amount of liquid was removed with the pump. These samples were diluted and their Si contents determined by standard ICP-AES. Based on these determinations, the percentage garnet dissolved was calculated after each period of time. The results in Figure 5.7 showed that the garnet dissolved more rapidly in the mixture of acids, however a difference of only about 10% in the total dissolution was found after 5 hours of reaction time. Hydrochloric acid is known to catalyze the reaction between hydrofluoric acid and the minerals. The ratio of the two acids and the dilution factor affect the dissolution kinetics. While the results for only two mixtures are shown here for illustration purposes, in the complete investigation, the ratio is varied and a three dimensional picture for the dissolution kinetics is obtained. This types of investigation is required when evaluating industrial processes. In the present case, the cost of the hydrochloric acid, storage, handling etc. must be weighed against the process time cost.

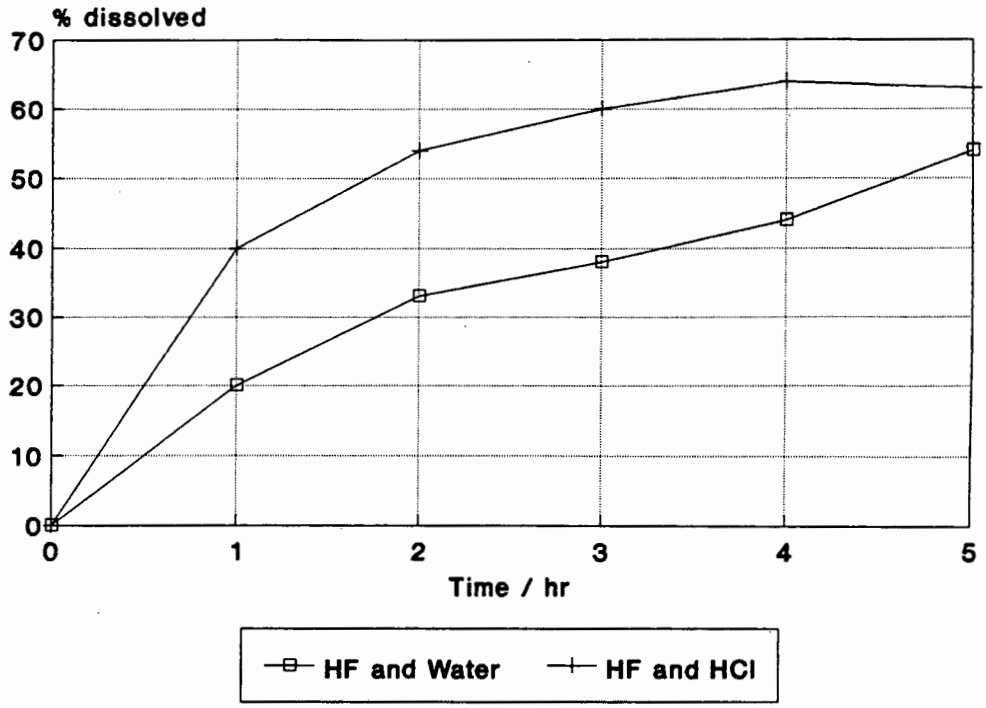


Figure 5.7 Dissolution rate of garnet at 90 °C.

Availability of boron from soils and power station ashes

Boron is an essential element for plant life, although excessive concentrations can be detrimental to certain species. Thus, knowledge of the boron availability from a soil is important for the design of a fertilization programme. A standard procedure for the determination of the total boron availability of a soil is based on extraction by boiling water or other extractants [DAV80]. After filtering, the amount of boron in the extract can be determined by a spectroscopic technique [POU86]. The soil sample is normally dried to constant weight before weighing an aliquot for the extraction. Whereas for very finely grained soils a small sample of a few grams might be adequate to obtain reproducible results, some inhomogeneous soils require a much larger sample. The cylindrical applicator was successfully used for sample sizes of more than 50 g.

In an investigation where the boron availability in power station ash was determined, tests were conducted at different temperatures for various periods of time to determine the leaching kinetics. A small aliquot for analysis was removed from the reactor periodically by pumping.

Some of the results obtained for the leaching characteristics of boron from two power stations (Matla and Lethabo, South Africa) fly ashes are shown in Figures 5.8 and 5.9. The temperature was maintained at about 40 °C. Five samples were removed during the 10 hr experiments for the determination of boron. The total volume of water was 200 ml and various ash to water ratios were compared (1,2,5,10,20 %). These results have allowed the comparison of the boron availability from ashes generated by the burning of different coals in the different power stations in South Africa.

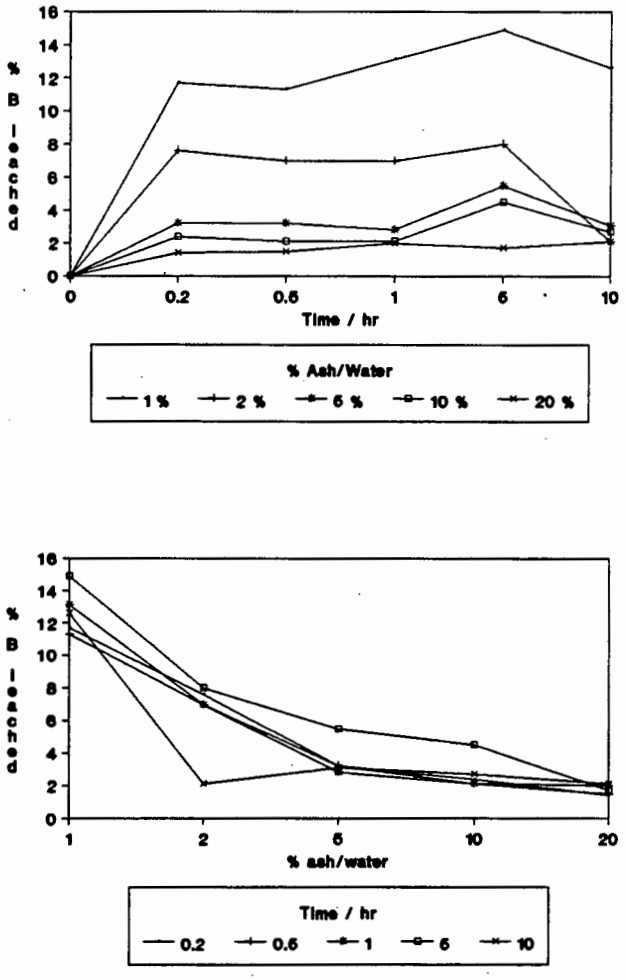


Figure 5.8 Leaching of boron from Matla power station.

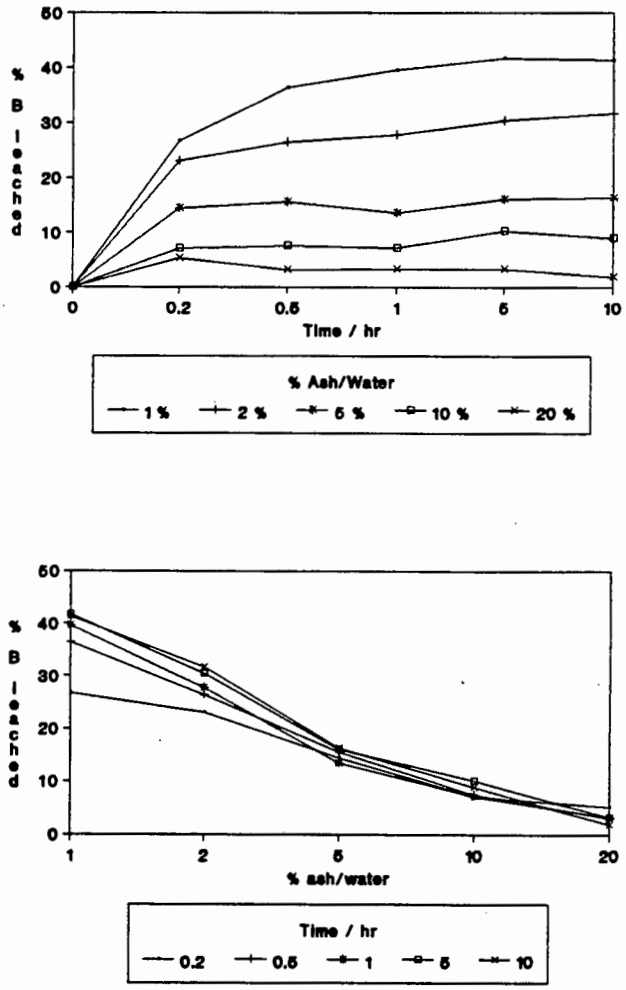


Figure 5.9 Leaching of boron from Lethabo power station.

Determination of free lime from cement and power station ashes

A procedure for the determination the free lime (calcium oxide) in the ingredients for cement and related products is to treat the material with ethylene glycol in a ratio of approximately 1 g sample to 50 ml glycol at 60 to 70 °C for a period of 30 min [JAV82]. The solution is then filtered and the filtrate is analysed for calcium content by AAS or other wet chemical methods. In an investigation of a similar procedure to measure the free lime content of power station fly ash, temperature/time studies were conducted on 5 g samples using the cylindrical applicator. Small aliquots were removed periodically after irradiation for different times and at different temperatures.

The result for the Ca leached from an ash sample is shown in Figure 5.10. A 5 g sample was treated with 250 ml of ethylene glycol over a period of 50 min. The available Ca was completely extracted after about 40 min.

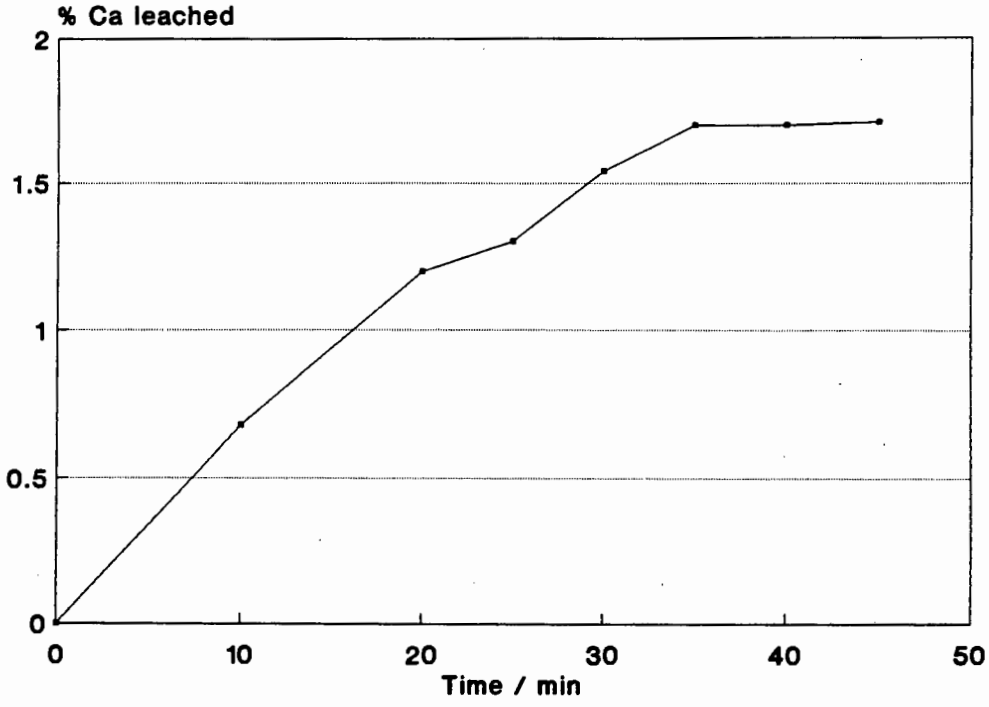


Figure 5.10 Free lime determination of power station fly ash.

Distillation and controlled chemical reactions

The cylindrical applicator is easily adapted for distillation and for conducting reactions under reflux by the construction of a Pyrex glass reactor (Figure 5.11). Temperature measurement of the material and/or of the vapour ensured good control of the process. The Pyrex glass reactor was suitable for the use of acids with high boiling points (*e.g.*, sulphuric and phosphoric acids) which softened the PFA vessel.

This reactor was used for the synthesis of zeolites from power station fly ash. A method for the synthesis has been described by Henmi [HEN87]. The fly ash (20 g) and 3.5 M NaOH (160 ml) are heated to 80-90 °C from 3 to 24 h on a hot plate. In this study, several methods for the synthesis were compared. The five methods were temperature controlled (*e.g.*, 80 °C), boiling under reflux on a hot plate, boiling under reflux with microwaves, pressure

reactions in PTFE lined steel vessels in the standard oven, and pressure reactions in PTFE vessels using the microwave oven. The cylindrical applicator was used for the temperature controlled experiments using a 40 g fly ash sample and 200 ml of saturated NaOH solution. The temperature was controlled for various lengths of time. In these investigations, X-ray powder diffraction spectrometry (XRD) and electron microscopy are used to examine the products. The results obtained by the microwave method compared favourably to those obtained by the other methods listed above [GIF92]. Since the analytical methods used are only qualitative, it was not possible to compare directly the merits of all the investigated method. However the use of microwaves for the temperature controlled experiments are advantageous compared to other heating modes. Firstly, the control of the temperature is far superior to that of a heating mantle since there is no heat inertia in the microwave reactor. Secondly, to achieve the same level of temperature control in the laboratory, a water or oil bath must be used, the final temperature is reached very slowly compared to using microwaves. In general the whole process is more efficient with microwaves.

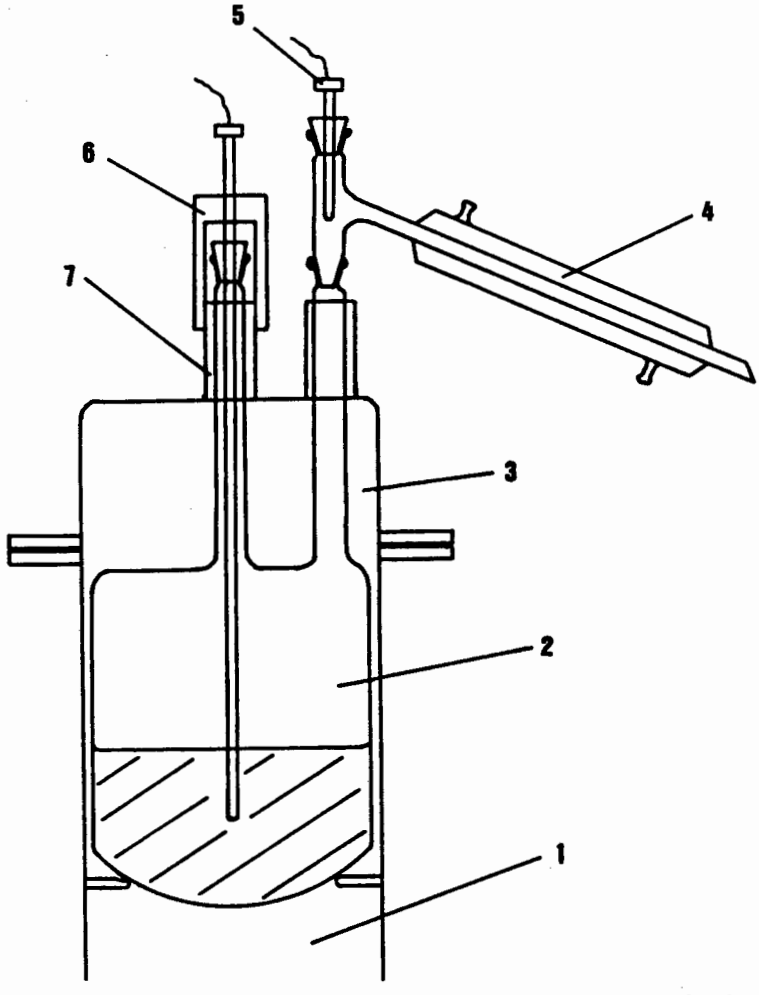


Figure 5.11 Pyrex glass reactor for chemical reactions and distillation. 1: Cylindrical waveguide, 2: Glass container, 3: Waveguide lid, 4: Water-cooled condenser, 5: Thermocouple probe, 6: Choke for thermocouple, 7: Metal port.

Heating of massecuites

Massecuite is a mixture of sugar crystals and mother liquor. In the factory, the massecuite is first cooled to encourage crystallization but it has to be reheated to reduce the viscosity so that crystals and mother liquor can be separated by centrifuge. A temperature increase from 45 to 60 °C is normally used. This study investigated the possibility of using microwaves for such a process. Small-scale microwave heating experiments were performed. Temperature profiles of the 250 ml samples are shown in Figure 5.12. The position of the TC tip was varied between 10 and 50 mm from the bottom of the load. A heating curve for a geometrically identical load of water measured with the TC at 30 mm is shown for comparison.

Several observations are noteworthy: If wat 30 and mas 30 (Figure 5.12) are compared (position of TC tip at approximately half the height of the load), the massecuite achieved a heating rate of 2 °C s^{-1}, while the water heated up at about 0.5 °C s^{-1}. The reason for the high absorption of microwaves by the massecuite is not clear but its relatively high content of ions could explain the efficient coupling of the power. The chemical composition of molasses, which is the mother liquor in which sugar crystals (about 25%) are suspended to make up the massecuite, is shown in Table 5.2. The presence of other polar components in the solution (*e.g.*, ethers) might add to the coupling efficiency.

The heating rates recorded were extremely dependent on the position of the TC and the highest heating rates were recorded at low positions. In these experiments the glass container was also smaller in diameter (100 mm) than the waveguide but the results were opposite to those obtained for water above. This may be explained by assuming that the dielectric parameters of the massecuite resulted in a low penetration depth for efficient absorption of the energy, and that very little energy was transmitted between the waveguide and the material and into the upper part of the waveguide. In addition, the extremely high viscosity of the material did not provide good heat transfer through convection. It was also noted that overshoot of temperature occurred (the microwaves were shut off at exactly 60 °C). It appears that the material was unevenly heated across and slow convection occurred after power was removed. The temperature difference with cross section was not studied but it seems that the material was hotter off-centre and thus caused the convection after heating had stopped. For non-viscous liquids stirring was sufficient for evening the temperature throughout the material. However, with massecuite, the viscosity of the material at the start of the process limited the fluid flow rate required in order to generate a uniform temperature distribution.

Further work that was carried out in a multimode cavity also showed a high coupling with the microwaves and similar problems with the evenness of heating were experienced.

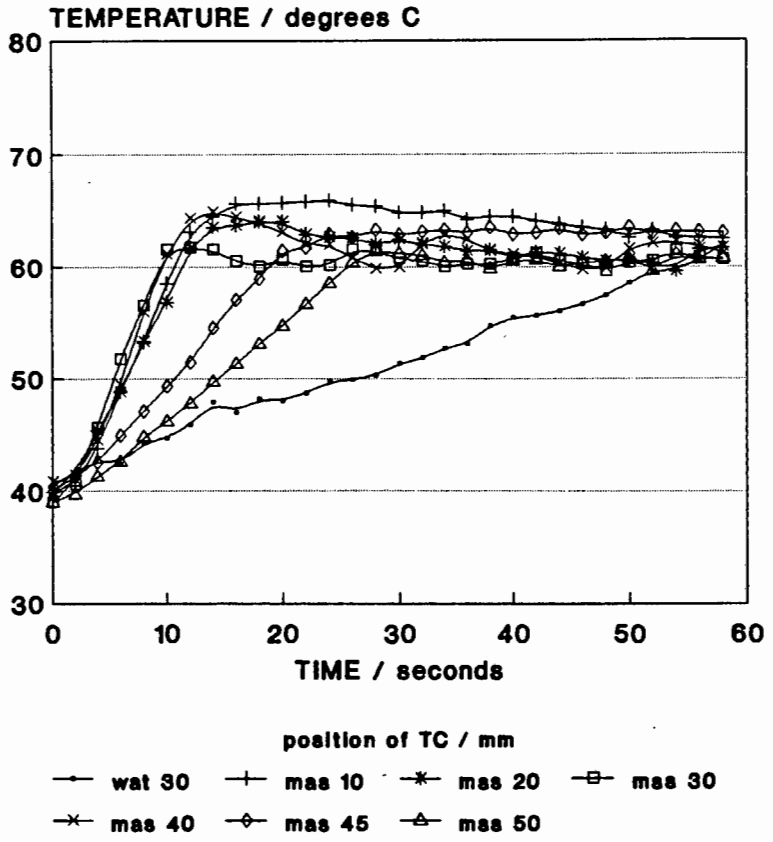


Figure 5.12 Heating of 250 ml massecuite (mas) with the thermocouple placed at different depths (position given as height from the bottom of the load). A heating curve for an identical load of water (wat) is shown for comparison.

Table 5.2 The average proximate chemical composition of standard molasses (average of 19 South African Sugar Mills).

Component	75% DM basis
	($g\ kg^{-1}$)
Moisture	250.0
Crude protein	50.0
Ether extract	1.0
Total ash	115.0
Nitrogen-free extract	584.0
Sucrose	332.0
Total sugars	467.0
Gum	25.5
Wax	4.7
Starch	1.7
Calcium	8.8
Phosphorus	0.7
Sodium	1.6
Chlorine	21.1
Magnesium	5.4
Potassium	33.3
Sulfur	6.8
Other metals	0.2

5.5 Conclusion

The cylindrical waveguide applicator is useful for many laboratory investigations. The applications for larger-than-normal analytical laboratory sample sizes are advantageous for investigations at atmospheric pressures. Similar advantages might be achieved for organic and organometallic synthesis reactions that have been successful at atmospheric pressure on a small scale in microwave ovens. Many fine chemicals in industry are synthesized on a small scale and this type of applicator can be designed to house suitable reactors. The major advantages of using microwaves over the other traditional laboratory heating methods are the speed and the excellent temperature control. A large (20 l) reactor for mineral processing is presently being designed.

The major limitations of the present unit were that the power was low for the large volumes concerned and the applicator had to be tuned using a Network Analyser which could only be done at room temperature. Although a microwave oven could also be modified for temperature control (see section 8.1), the oven is a bulky implement and offers no tuning facilities. The cylindrical cavity is easy and relatively cheap to manufacture from available tubing. For many of the industrial investigations, it is necessary to calculate the power absorbed so that suitable calculations on the power consumption can be made. This requires that the system be tuned so that the maximum efficiency is achieved. Thus on-line tuning is desirable. A different design using a 1.2 kW generator (Appendix 1) is presented in Chapter 8.

CHAPTER 6

NEW MICROWAVE APPLICATOR FOR PROCESSING MULTIPLE LABORATORY SAMPLES

6.1 Introduction

The application of microwave heating for carrying out digestions at atmospheric pressure using acids and acid mixtures has been adequately demonstrated (Chapter 4). A major problem, however, is to deal efficiently with the large volumes of acid vapours emitted during the reactions. When one sample only is to be processed, for example, in waveguide applications, it is not difficult to extract the acid fumes using a simple pump and an on-line scrubber. Where there are many samples the situation is different and the presently available commercial microwave ovens for laboratory applications are not designed to deal with large volumes of acid fumes and thus cannot be used for routine processing of several samples at the same time. The problem is particularly serious with sulfuric acid, which is commonly used in the digestion of biological materials and for nitrogen determination (the Kjeldahl digestion). The low vapour-pressure fumes condense readily and have to be particularly well-treated by adequate extraction and scrubbing procedures. Until now no instrument has been available for the open digestion of many laboratory samples simultaneously.

The objective of this work was to develop a microwave applicator suitable for processing several samples at atmospheric pressure with a means of dealing with the large amounts of gaseous products efficiently.

6.2 Development of the applicator

In order to deal with the acid fumes it was found necessary to introduce the reaction vessels through cylindrical metal ports into a multimode cavity. The metal ports were of such dimensions (150 mm x 42 mm internal diameter) that microwave leakages were much below permisible levels. The tube diameter was below the cutoff frequency for propagation of circular waveguide modes. Similar metal ports were used previously in modified microwave ovens (Chapter 3). The reaction vessels most commonly used are tubes made of glass, quartz, or PTFE when it is necessary to use hydrofluoric acid with certain samples. Since the openings of the vessels are outside the cavity, it is easy to extract the acid fumes in the traditional way (Figure 6.1). A "bench-top" chemical scrubber system that was built for such purposes is shown in Figure 6.2. The system was built from clear PVC and includes a high-velocity extraction fan, a pump, storage tank and nozzles for spraying a caustic solution in the scrubber column (for neutralization of the acid fumes). The caustic solution contains a pH indicator reagent which is useful to monitor the efficiency of the scrubbing solution, which is

recirculated until discarded. The resulting effluent gas is safe enough to be pumped outside the laboratory.

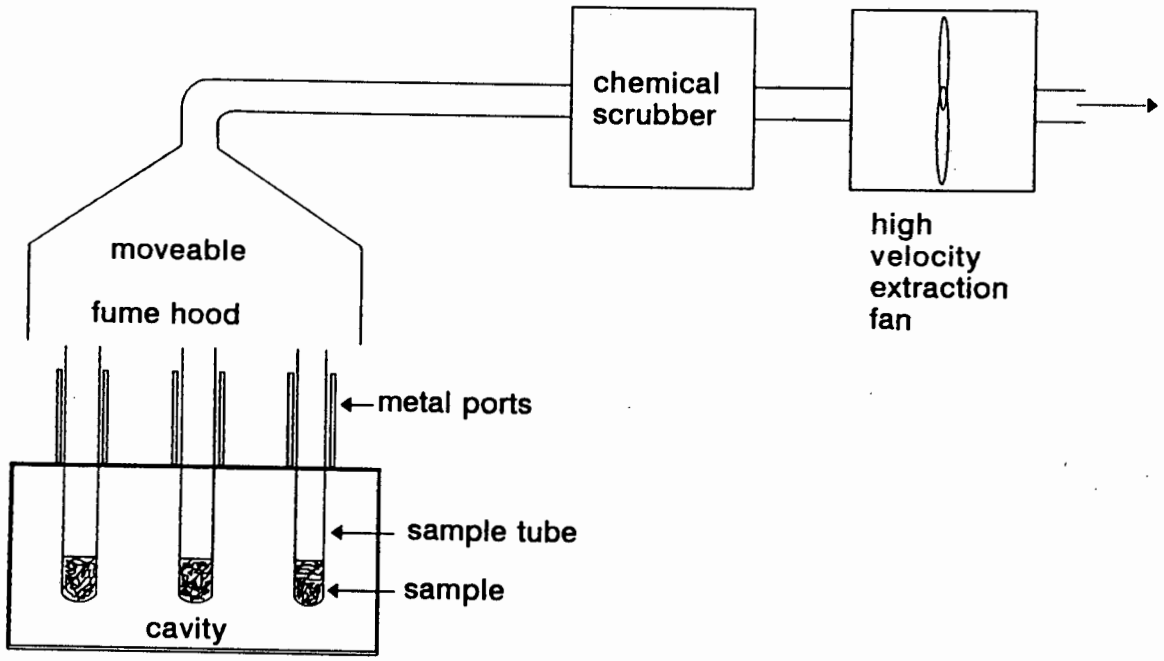


Figure 6.1 Microwave cavity with introduction ports and fume extraction system.

While the above idea provided an easy means to deal with the acid fumes, the uneven heating of several samples in a multimode cavity was the other important problem to solve. In routine sample preparation, all the samples and chemicals are normally of the same composition and of equal volume and it is critical that all the samples achieve the same reaction rates (*i.e.*, by receiving the same energy exposure).

Several structures were investigated in attempts to obtain uniform heating of several tubes containing exactly the same volume of liquids. These are briefly described below with some illustrations of the test equipment that was used.

Figure 6.2 Scrubber system.

6.2.1 Temperature measurement system

In order to investigate the power absorption by the loads, an exact amount of liquid was placed in each of the sample tubes. The temperature was measured before and after irradiation. The increase in temperature was calculated and compared for all the loads.

Initially, the above measurements were made using a single thermocouple probe. However, with many loads it was not possible to measure accurately the temperatures after irradiation since the cooling rates were too great, especially at the higher temperatures, and large errors were introduced. The best tool for this kind of investigation would be a multichannel fibre-optic system which could be left inside the tubes during irradiation. This would allow

continuous monitoring of the temperature increase. This equipment was, however, not available and in order to facilitate the measurements, the following device was constructed.

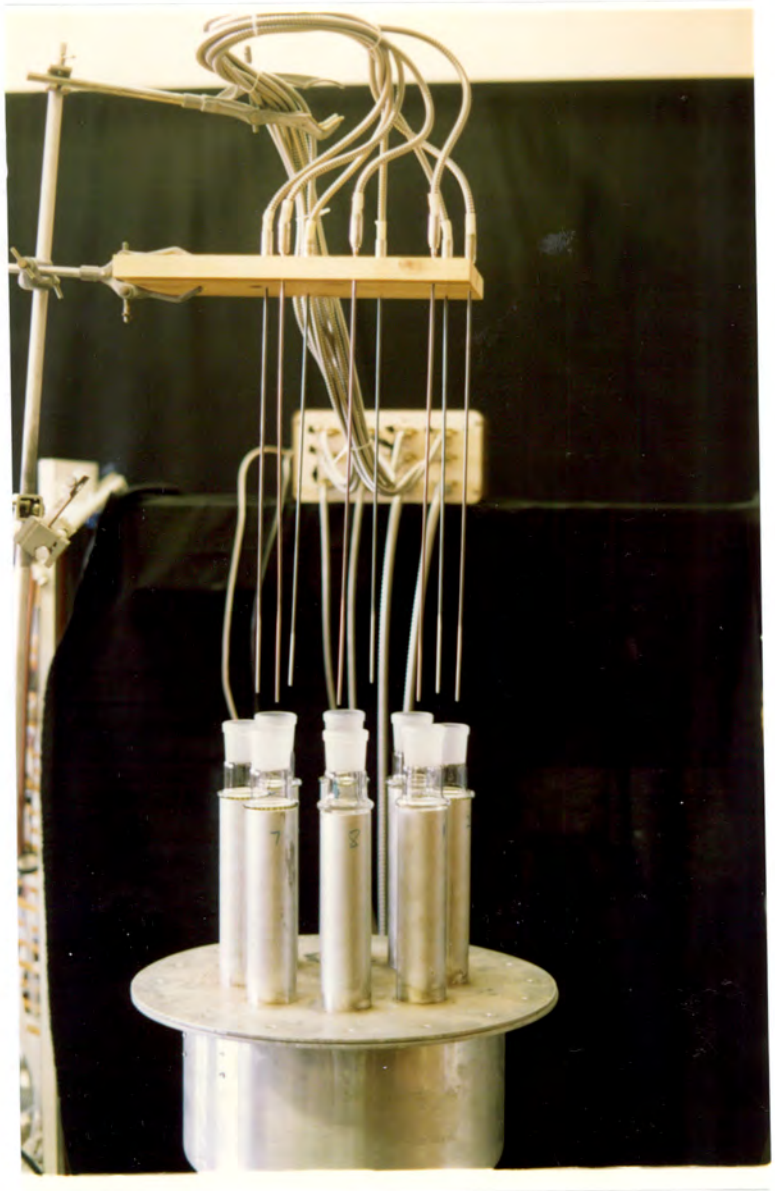


Figure 6.3 Thermocouple arrangement to measure temperature.

A multiplexing measurement system capable of monitoring the signals from twelve K-type thermocouple probes, as well as appropriate software for control by a personal computer, was developed. The circuit diagram can be found in Appendix 2. The thermocouple probes were fixed on a wooden base with the position of the thermocouples corresponding exactly to the centre of each tube in the applicator (Figure 6.3). This was mounted on top of the applicator.

Before and after irradiation the base and the thermocouples were lowered so as to introduce each thermocouple into the respective loads. The computer program was started and the temperature recorded for a predetermined time (*e.g.*, 20 seconds). The temperature in each tube was displayed on a monitor and written to file. After the measurement period, the mean temperature for each load was calculated and displayed. The temperature increase was calculated for each load. This system of measurement was found to be reproducible and adequate for this investigation.

6.2.2 Mode stirrers

The efficiency of mode stirrers to provide even heating of several loads in a multimode cavity was investigated. A cavity was built for this purpose and is shown in Figure 6.4. The energy from an 800 W magnetron was launched through a waveguide at the bottom of the cavity. The top of the cavity was interchangeable for positioning different numbers and sizes of metal ports. Several mode stirrers were fabricated from aluminium sheets and these were mounted at the bottom of the cavity and rotated by electric motors.

No satisfactory results were obtained with mode stirring only (see results below), even if two mode stirrers were used. The unevenness of heating depended on the geometrical arrangements, the sizes of the loads, and their positions inside the cavity.

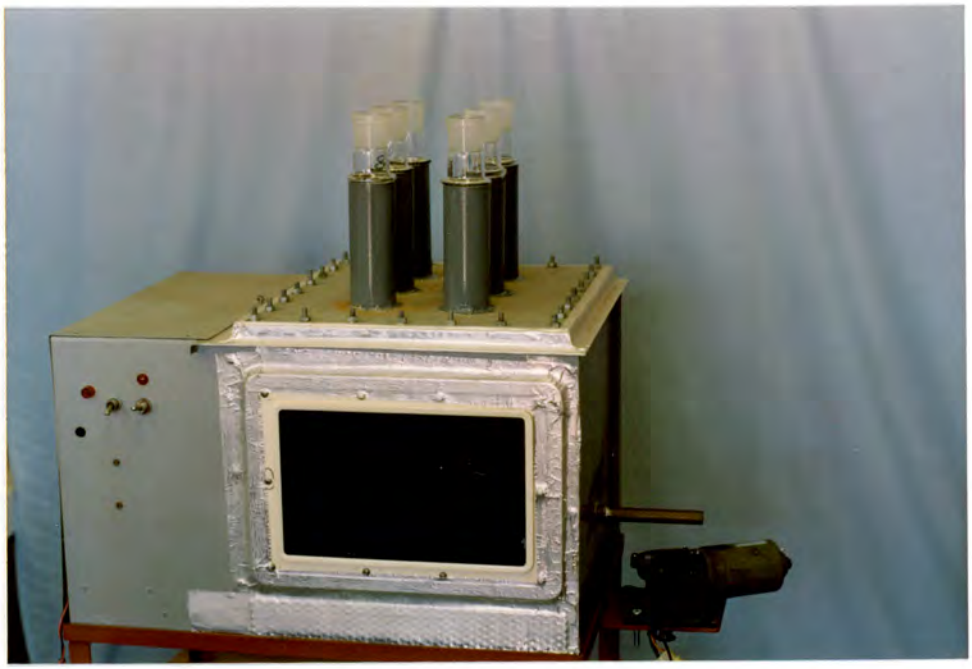


Figure 6.4 Multimode cavity for investigating the use of mode stirrers.

6.2.3 Coaxial launching

Since the microwave field in a coaxial line is symmetrical (see Chapter 1), it was assumed that if the power was radiated from the centre of a symmetrical cavity with the loads also symmetrically arranged around the centre conductor which protruded into the cavity, a uniform field would be achieved and even heating of the loads would occur. The experimental system used for this investigation is shown in Figure 6.5.

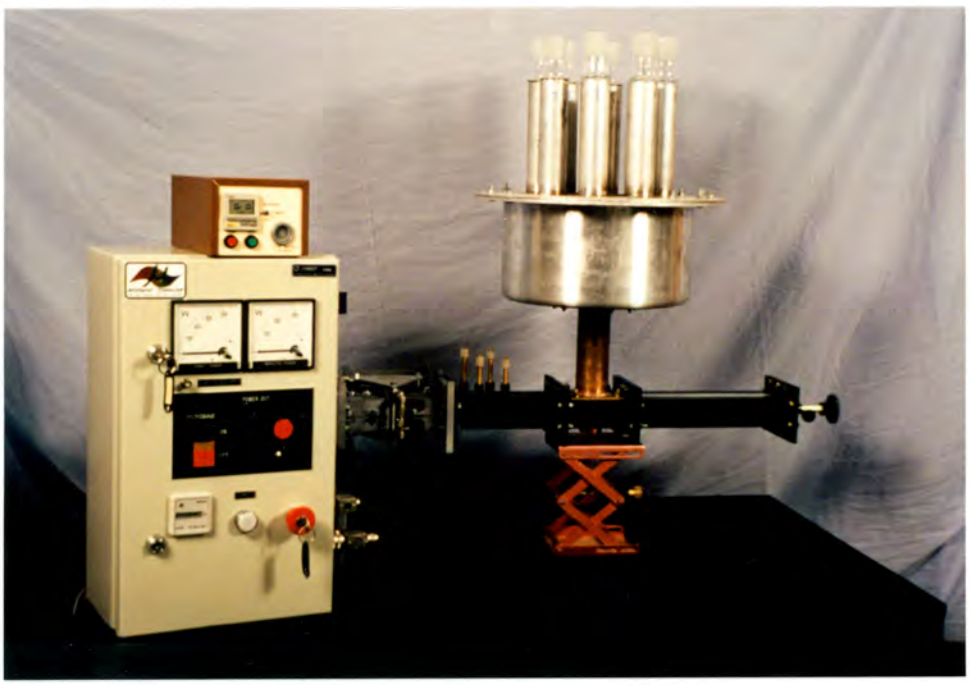


Figure 6.5 Experimental setup for coaxial launch of microwaves into a cylindrical cavity.

An aluminium cavity of 300 mm diameter and 170 mm depth containing eight ports arranged symmetrically was used. Microwaves from the R26 waveguide (TE_{10}) were transferred into a coaxial line (Chapter 1, Figure 1.7) manufactured from copper tubing. The inner and outer conductors had diameters of 15 mm and 49.5 mm, respectively. The inner conductor was made to protrude into the cavity by a length of 30.5 mm (one quarter-wavelength). A plunger tuner terminated the waveguide and was used to obtain the best coupling of the power to the cavity. With careful tuning, efficiencies of better than 90% could be achieved with a reasonable load (*e.g.*, 160 ml of water). However, the power absorbed by the loads was found to be critically dependent on the tuning, the position of the loads (height in the cavity),

the volume of the loads and most critically the position of the centre conductor. It was noticed that every time the equipment was dismantled and put back together a different pattern of heating was obtained. The centre conductor could be rotated and tightened before applying power. The effect of rotating the centre conductor is clearly seen in Figure 6.6. Although care was taken in the machining of the waveguide, cavity and coaxial line, it appears that the symmetry is absolutely critical. This was not investigated any further.

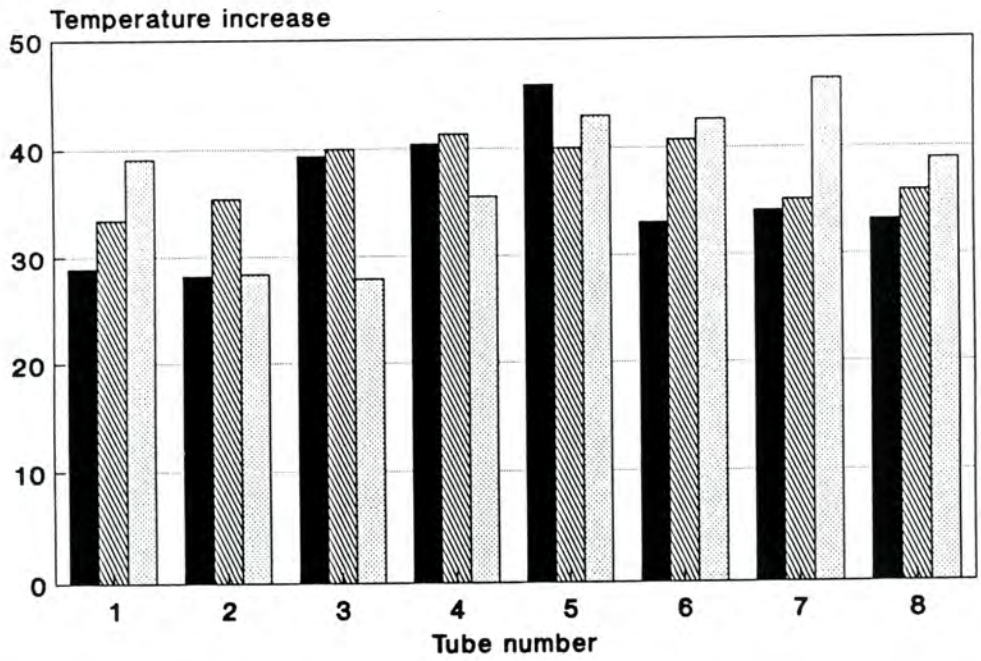


Figure 6.6 Effect of centre conductor position on heating of the loads in the cylindrical cavity with coaxial launch. The results for three experiments (20 ml water loads, 400 W, 3 min) are shown.

6.2.4 Rotation of the cavity

It was decided to investigate the uniformity of heating of the loads in a cavity that was rotated relative to the power feed section. For this application a rotating radial choke was developed.

The design of the quarter-wave choke is shown in Figures 6.7 and 6.8. It operated in the same way as the oven door choke (section 1.1.3). The choke was manufactured by machining thick aluminium alloy plates. From the inside of the cavity, there was a section of 30.5 mm with a very small clearance (0.5 mm) which was followed by an indented section 30.5 mm

long and 12 mm deep in the lower part of the choke, and grooves in both halves of the choke were machined to accommodate 6 mm diameter ball bearings. The bearings were used to maintain the clearance between the two parts of the choke and allowed rotation.

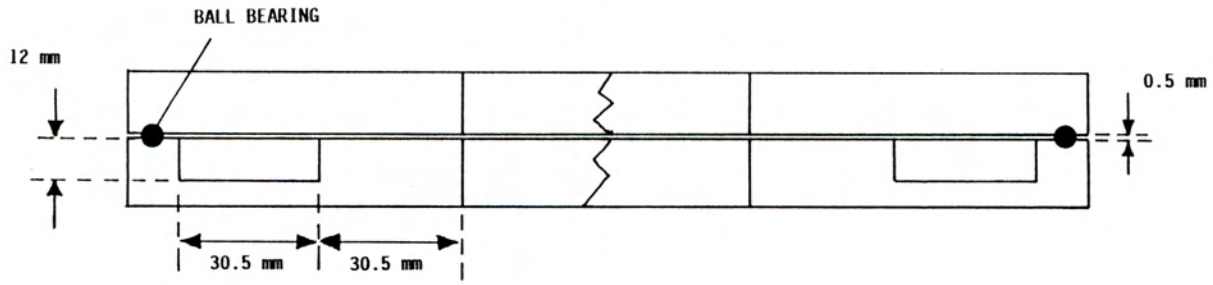


Figure 6.7 Schematic diagram of the quarter-wavelength radial choke (cross section).

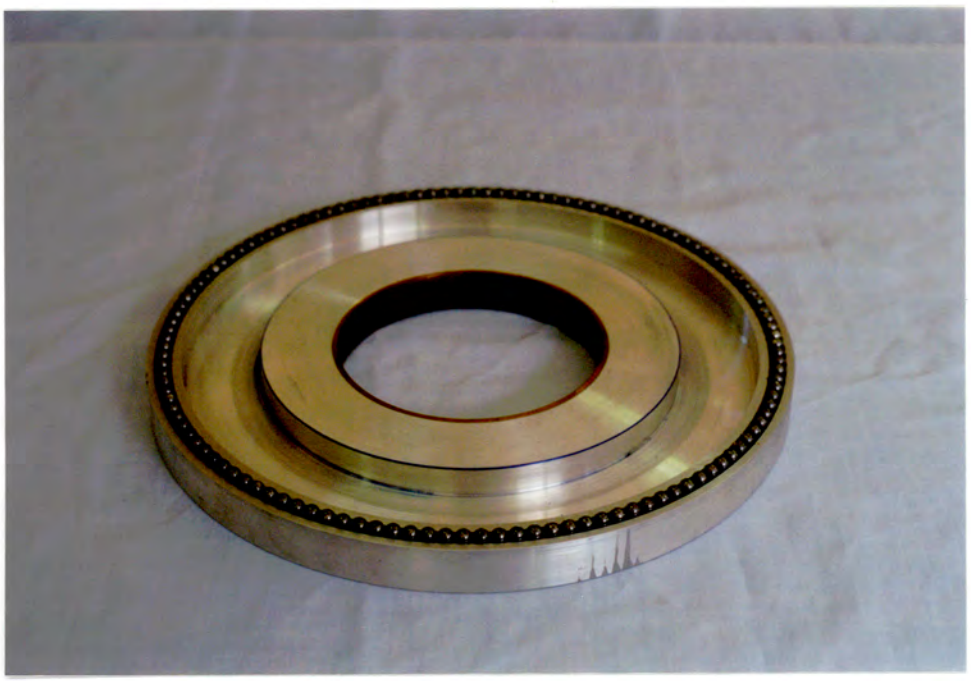


Figure 6.8 Top view of the quarter-wavelength radial choke.

The choke was first tested for microwave leakages using the applicator shown in Figure 6.9. The choke was mounted between two lengths of circular waveguides (101 mm internal diameter) and power was fed to the cavity from the circular waveguide. The tuning screws on the rectangular part of the waveguide were used for matching. With a load of 10 ml water in each tube and 1200 W of microwave power, no significant radiation leakage was measured during operation.

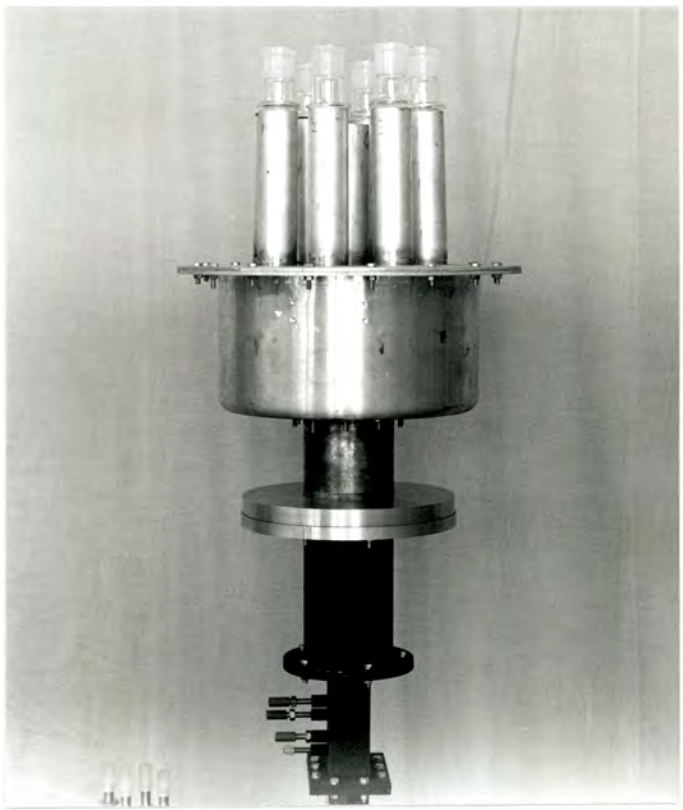


Figure 6.9 The radial choke mounted in a circular waveguide for power transfer into a cylindrical cavity.

The above applicator (Figure 6.9) was rebuilt so that a motor could be used to rotate the cavity (Figure 6.10). As can be seen from the Figure, a different transition from rectangular to circular waveguide was used. The bottom part of the circular waveguide was made from perforated stainless steel sheets so that air from a fan could be passed into the cavity for cooling of the load; this structure was also used in other applications, see Chapter 8. The teeth machined in the top part of the choke were used for rotation by the cog on the variable

speed motor. Three bearings were also mounted vertically on brackets underneath the rotating top part and these ran on the underneath of the bottom part to prevent accidental separation of the two parts of the choke during operation. The cavity could be rotated at a speed of about 7 rpm. The three tuning screws on the rectangular waveguide were used to optimize the power transfer. Good power transfers were achieved with this applicator and microwave leakages were below the permissible levels. The heating characteristics of a variety of loads heated at different forward powers and for various periods of time, as well as the effect of varying the vertical positions of the loads in the cavity were investigated. As can be seen from Figure 6.11, relatively even heating of the loads was obtained (8% relative standard deviation in the illustrated case) but the uniformity of heating was still affected by the load size and position. The temperature profiles in Figure 6.11 suggest the establishment of a standing wave in the applicator. This was also observed with another larger cylindrical cavity and the heating pattern was similarly affected by the size and position of the load.

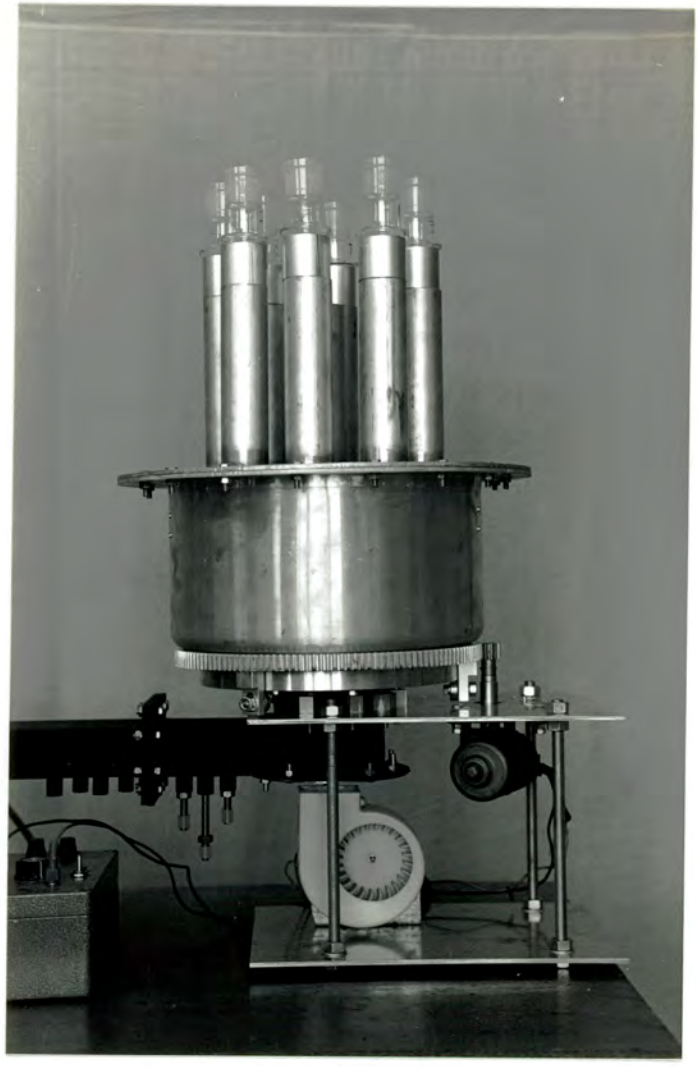


Figure 6.10 The rotating cavity.

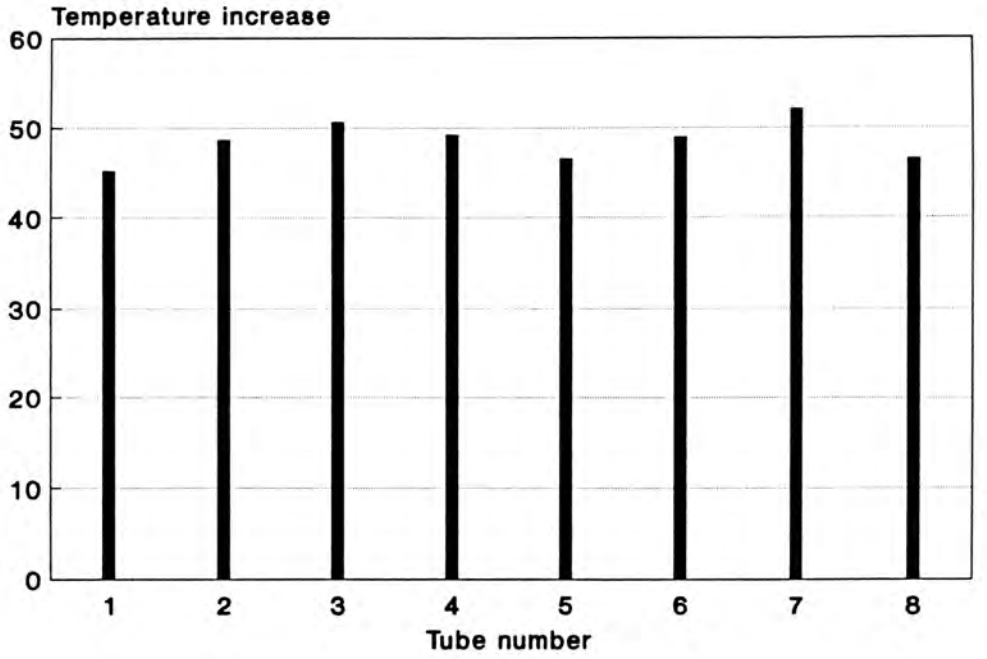


Figure 6.11 Temperature increase of eight 10 ml water loads in the rotating cavity (4 minutes, 200 W).

6.2.5 Multimode cavity with rotating choke

While the above system performed much better than when the mode stirrers and coaxial feed were used, the major drawback was the need to rotate mechanically such large and heavy structures if more tubes were to be accommodated. It was decided to extend this principle to a system where the bottom half of the choke was part of a multimode cavity and the half including the ports was made to rotate.

The prototype for the applicator is shown in Figure 6.12. A schematic diagram can be seen in Figure 6.13. This rectangular cavity had dimensions of 440 × 415 × 285 mm. Microwave power from the 1.2 kW generator was fed to the cavity through the R26 waveguide. A thin PTFE window was placed at the feed to the cavity to prevent accidental spillages into the waveguide. The top part of the choke contained eight ports arranged symmetrically and was rotated by a geared motor turning at 7 rpm around a brass axle through the cavity. Although the presence of the 15 mm brass axle has a large effect on the E field distribution in the cavity, it did not seem to create any problems. No microwave leakages were monitored at the bearings during operation. A close-up picture of the choke is shown in Figure 6.14. There were three perforated sections in the walls of the cavity which were used for illumination by a

lamp from the outside, for viewing, and for passing air at high velocity through the cavity to cool the materials after irradiation.

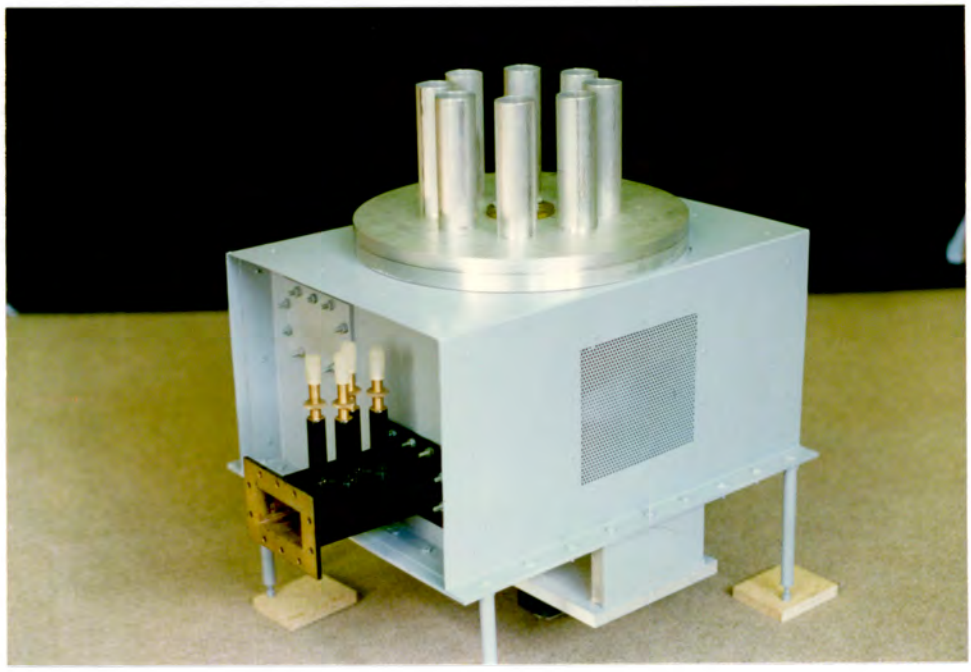


Figure 6.12 The applicator showing the rotating choke and the ports.

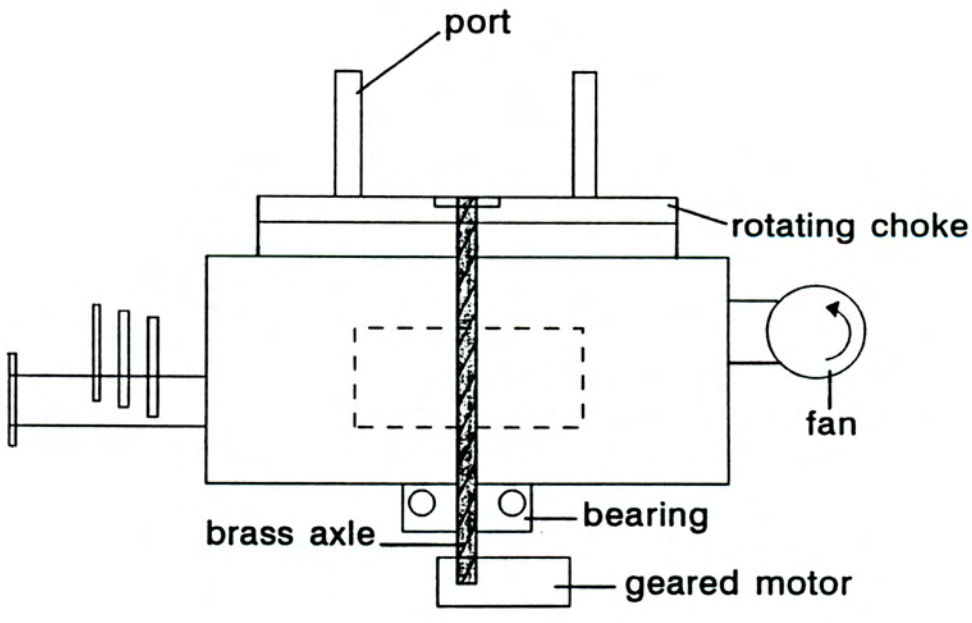


Figure 6.13 Schematic diagram of the applicator.

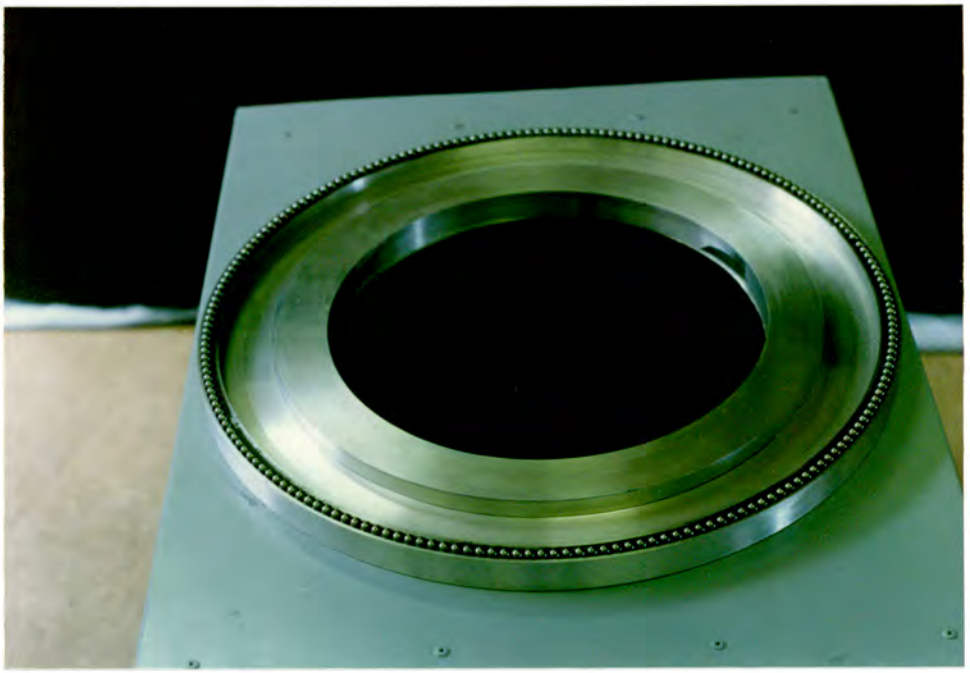


Figure 6.14 The base of the rotating choke.

Some results for temperature increases of various loads and for different irradiation conditions are shown in Figures 6.15 to 6.18.

It is clear from Figure 6.15 that if the loads are kept stationary in a multimode cavity, then extremely uneven heating occurs. In addition, the use of a mode stirrer does not yield satisfactory results, as mentioned above.

The results for 20 ml water loads irradiated at different powers and for different times, shown in Figure 6.16, indicate that uniform heating of all the loads was achieved using the rotating choke. Variation of temperature between loads was at worst about 3 percent relative standard deviation at the measured temperatures. Similar results were obtained for loads of 10 and 30 ml irradiated for the same time but at different power levels (Figure 6.17). Uniform heating was also achieved when only four loads were used, whilst keeping the symmetry of the loads within the cavity (Figure 6.18).

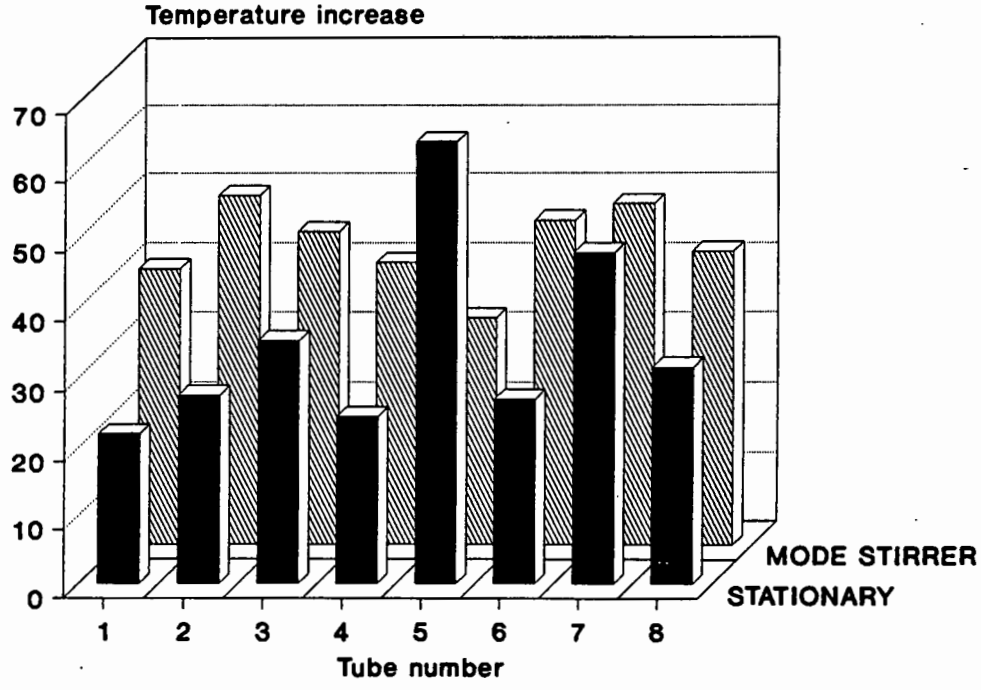


Figure 6.15 Temperature increases with the vessels kept stationary with and without the use of a mode stirrer. The loads were 20 ml of water and were irradiated for 3 minutes at 300 W forward power.

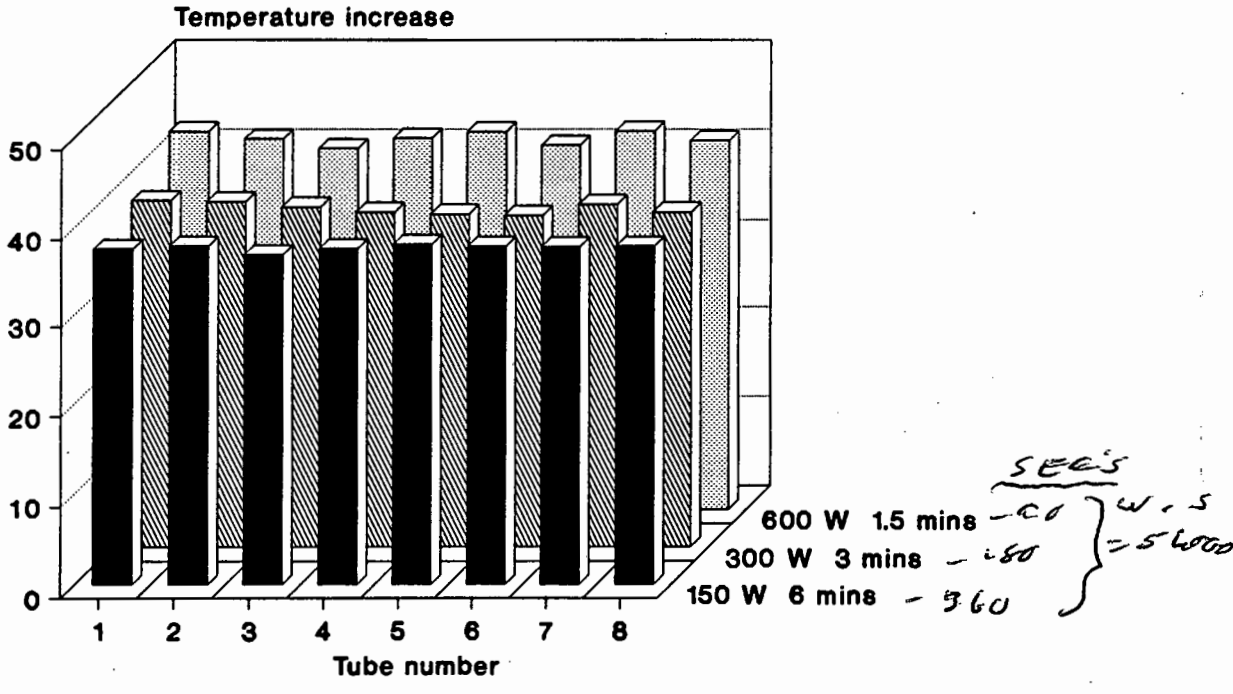


Figure 6.16 Temperature increases with rotation of the loads in the applicator for 20 ml water loads at different powers and irradiation times.

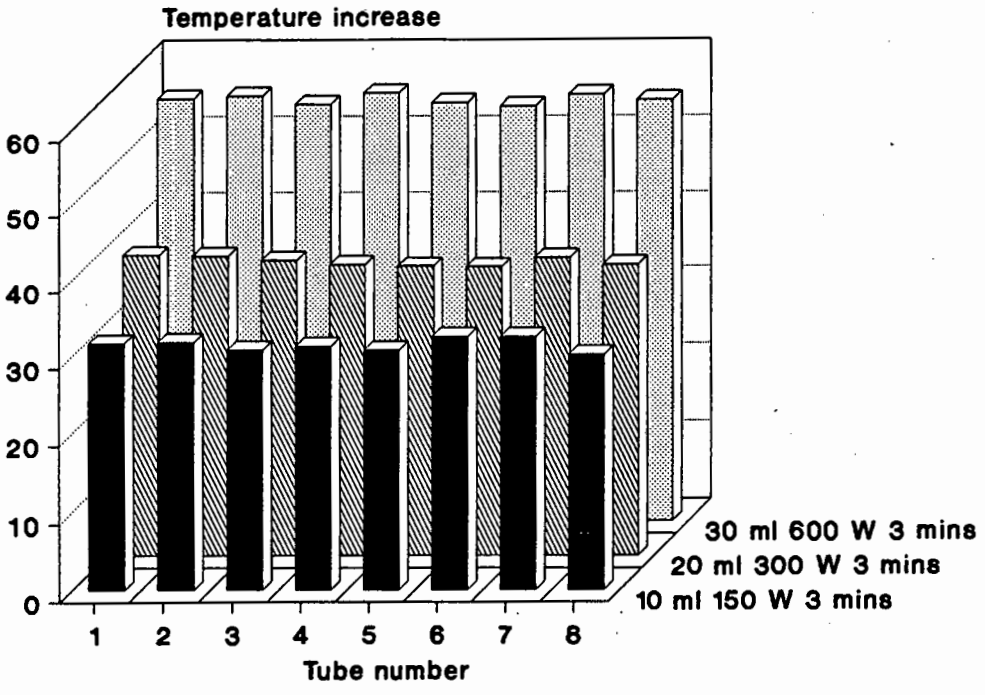


Figure 6.17 Temperature increases with rotation of the loads for 10, 20 and 30 ml water at different powers for 3 minutes irradiation.

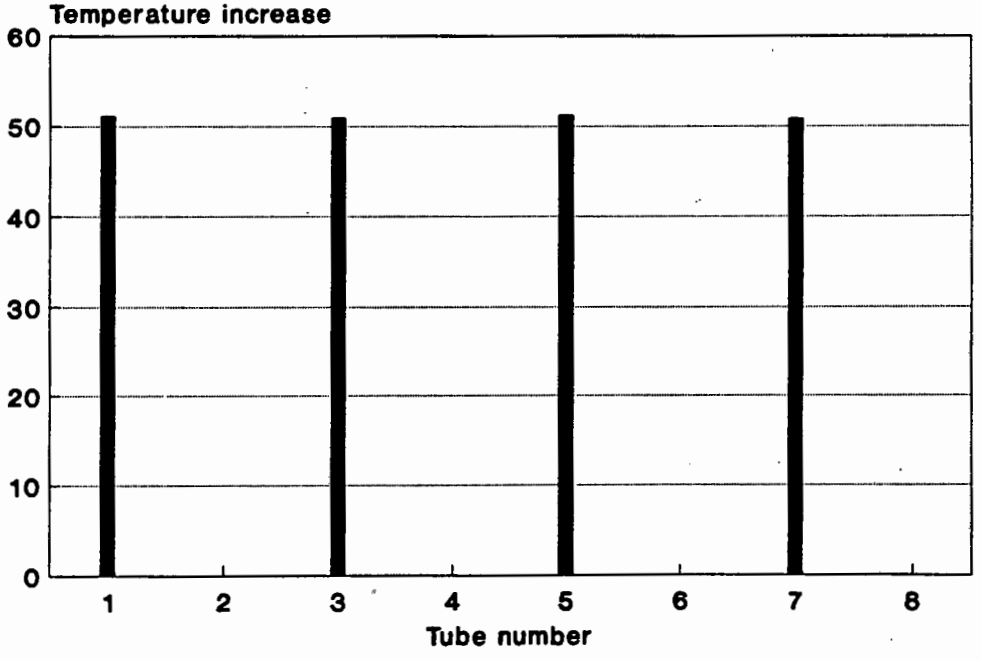


Figure 6.18 Temperature increases for four 30 ml water loads irradiated at 300 W for 3 minutes

6.3 Conclusion

In real applications acids (or mixtures) would be used, but similar results are anticipated for the real samples provided that the compositions, volumes and initial temperatures for all the loads are kept constant. It was not possible to investigate the uniformity of heating of acids because of corrosion of the thermocouple probes and the difficulties of extracting the acid fumes during the measurements.

The use of multiple ports for the introduction of samples into a microwave cavity is a definite advantage over equipment based on traditional microwave oven designs. No special care in protecting the cavity from corrosion is necessary (*e.g.*, PTFE coating or polypropylene liner) since fumes are easily extracted out of the vessels by normal means (fume hood). The ease of introduction of samples in such an applicator means that automation (loading and unloading) would be relatively easy to implement. Such systems for loading and unloading are commercially available for use with resistance block heaters. The diameter of the rotating choke is not limited to that used in the present applicator: larger ones that could accommodate many more samples could be manufactured. Furthermore, the port layout could be configured for different requirements *e.g.*, smaller diameters or longer tubes, *etc.* A manifold could also be positioned above the tubes for addition of reagent(s) if necessary (*e.g.*, use of hydrogen peroxide, Chapter 4). No special safety interlock system is required but a trap can easily be implemented for cleaning in the event of spillage inside the cavity.

This applicator is well-suited for batch processing of several samples. One major application would be for digestion of biological materials and for nitrogen determination (the Kjeldahl digestion or chemical modifications of this method). Microwave irradiation has been shown to be advantageous in these applications, cutting down the time of digestion significantly. The application of the Prolabo automatic system (Chapter 1) is useful in that respect. However, it is slow because one sample is processed at a time; furthermore, it is expensive, presumably due to the use of the robotic system. Until now no microwave instrument capable of processing a large number of samples in a short time has been designed. Many other applications in analytical laboratories might be found for this applicator, including the leaching of ores and minerals and many extraction procedures. In general, the use of microwave irradiation is far superior to the use of block heaters as far as control of the process is concerned, especially with profusely foaming reactions, as mentioned in Chapter 4. In terms of electricity consumption, the microwave applicator would be more efficient compared with block heaters which generally have large losses of heat to the laboratory and require extraction and are slow to reach the required temperatures.

CHAPTER 7

MICROWAVE IRRADIATION SYSTEMS FOR LABORATORY PRESSURE VESSELS

7.1 Introduction

Until now, the microwave oven has been the most widely used applicator for laboratory applications of pressurised reactions in the specially designed pressure vessels made of polymeric materials. While for many of the applications, *e.g.*, routine sample digestion, the present technology is adequate, several limitations can be found in specific applications. Temperature and pressure measurements can cause problems. For example, the fibre-optic probes that are used nowdays are fragile and it is difficult to seal the vessels with these probes if high pressures are required. Similarly, the plastic pressure lines have limitations and are also difficult to seal at high pressures. When several vessels are used, the monitoring of these parameters is also made difficult since the reaction vessels and thus the monitoring lines have to be moved in the cavity. This is to ensure that uniform and reproducible heating of the reagents occurs. Furthermore, monitoring of the microwave power during the processes is not readily achieved, especially in ovens where average power is obtained with pulsing (on/off cycle) of the magnetron. When using a single vessel, with a small load of typically 10 ml of reagent, only a small fraction of the transmitted power is absorbed by the sample. Thus high reflected power levels occur, which can damage or reduce the lifetime of the magnetron. This is a fundamental problem caused by the sample or load being small compared to the microwave wavelength and thus having a small radar cross section. The problem could be solved by using a much higher microwave frequency, but high-enough power sources are not available for this purpose.

A further disadvantage of using an oven is the difficulty of making the system automatic. Although, as reported in Chapter 1, automatic systems have been developed, perhaps the complexity and high cost of the robotic systems have not permitted commercialisation of this equipment.

Vessels made entirely of polymeric materials are well suited for small samples but it would be impractical to expand the designs to larger vessels since the thickness of the material required would be such that very long cooling times would be necessary.

It thus appeared that there were opportunities for further research into the development of new equipment for solving the above problems.

The first objective of this work was to investigate simple ways for irradiating presently available pressure vessels so that it would be easy to load an unload them from the microwave device automatically.

The second objective was to investigate ways to heat efficiently the contents of traditional pressure vessels made of steel and lined with PTFE that could be used for larger than normal samples and for operation at high temperatures and pressures with the possibility of measuring and controlling these parameters.

7.2 Irradiation of pressure vessels in rectangular waveguides

7.2.1 PTFE vessels with metal closure

The design of the vessel has already been described in Chapter 4, where a non-standard waveguide was used. The limitation of the former applicator was the difficulty of on-line tuning and analysis of the system for varying loads. Since the R26 waveguide was large enough to accommodate the bottom of the vessel containing the load, an applicator was built to accommodate the vessel without any modification (Figure 7.1). Matching could then be achieved using tuning screws and a plunger tuner. With loads of more than 5 ml of liquid, the tuning was important (see discussion about tuning below) but good rates of heating were achieved. The main problem with this particular vessel was that the bottom PTFE section tended to deform during use, making it difficult to dismantle the vessel. Increasing the thickness of the PTFE wall would obviously help in preventing the structural deformation but would necessitate longer times of cooling. This vessel was therefore limited to relatively low temperatures and pressures ($< 150\ ^{\circ}C$ and 8 bar).

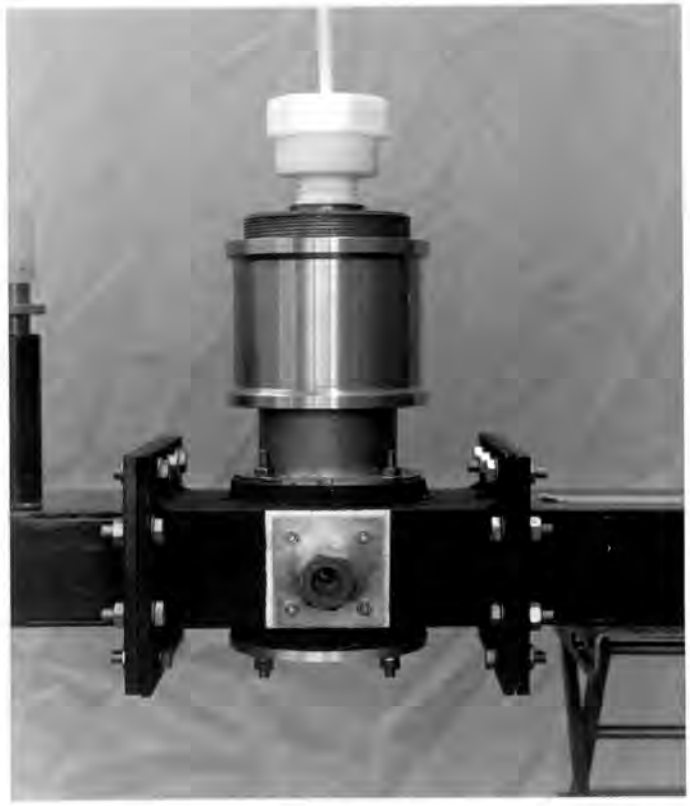


Figure 7.1 Irradiation of PTFE vessel with metal closure in R26 waveguide.

7.2.2 Small PTFE-polypropylene vessels

The 10 ml capacity vessels described in Chapter 2 were suitably irradiated in the standard R26 waveguide as illustrated in Figure 7.2. The portion of the vessel containing the load was placed in the centre of the waveguide through a port. Because of the small loads, efficient power transfer was achieved using a coupling iris between the sample and the circulator and a plunger tuner at the end of the waveguide. This generally creats a high Q-factor cavity which ensured improved power absorption in the small sample. A variable coupling iris similar to that described by Metaxas [MET90] was built for this investigation (see Appendix 1). The facility for quickly changing the iris (aperture) size greatly simplified such investigations.

The effect of the coupling iris size was investigated by heating a 1 ml water load for 20 s at a forward power of 100 W and measuring the temperature increase in each case. The plunger tuner was used to optimize the power transfer by adjusting its position to obtain the lowest

reflected power. These adjustments were carried out at low powers and as quickly as possible to prevent high increases of temperature during the tuning process. Tuning was normally achieved below a temperature of 40 °C. The results obtained are shown in Figure 7.3. It can be seen that the iris size is very critical for adequate power transfer. The desired rate of heating was adjusted by the forward power. For example, with a forward power of 300 W, 1 ml of water could be made to boil in 30 s. The measured reflected power during the heating cycle averaged to 225 W. This reflected power was absorbed by the water load on the circulator. A forward power of 300 W was necessary to carry out the digestions of biological material in this vessel. Satisfactory digestions were completed in a few minutes.

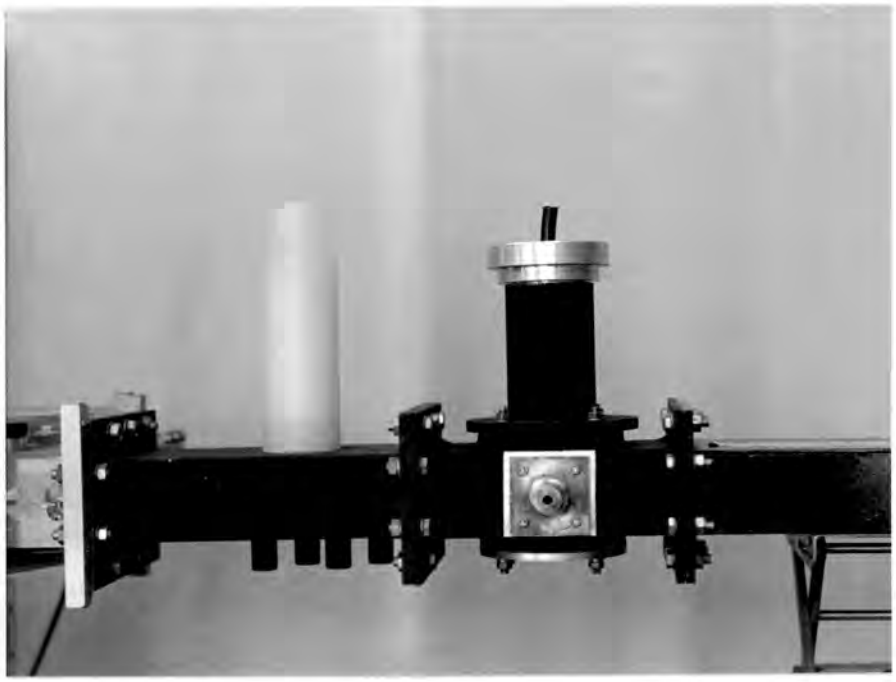


Figure 7.2 Irradiation of 10 ml vessels in R26 waveguide.

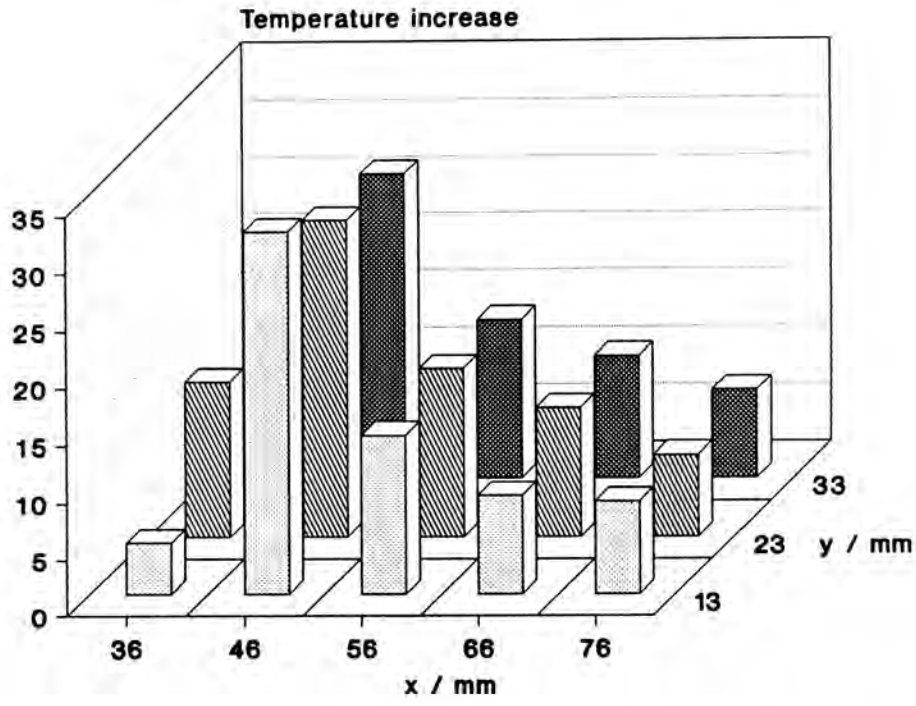


Figure 7.3 Effect of iris size on the heating rates of 1 ml water loads. Variables *x* and *y* are the iris sizes corresponding to the wide and narrow dimensions of the rectangular waveguide, respectively.

7.3 Irradiation of standard pressure vessels normally used in microwave ovens

The design of a general purpose vessel used for sample preparation in microwave ovens was discussed in Chapter 2. Vessels with such dimensions (100 mm diameter) could not be irradiated in the standard R26 waveguide. Two cavities were tested for this application. The first cavity is shown in Figure 7.4. The microwaves were guided from the R26 waveguide into a cylindrical cavity of 102 mm diameter in which the vessel was placed, resting on the interfacing circular flange between the rectangular and circular waveguides. The cylindrical waveguide acted as a cover and could be opened easily with two spring-loaded fittings. Microwave leakage was kept within safe limits by using compressible metallic seals between the cylindrical waveguide flange and the flange on the rectangular waveguide. A port in the top of the cavity allowed for evacuation of the acid fumes in the event of any leakages. Tuning was achieved with tuning screws. In such a cavity 15 ml of water was irradiated for

30 s with a forward power of 200 W, resulting in an increase in temperature of 35 °C. The usual mineral acids also achieved similar rates of heating under optimum conditions, and these were adequate for pressurization of the vessels and initiation of the chemical reactions.

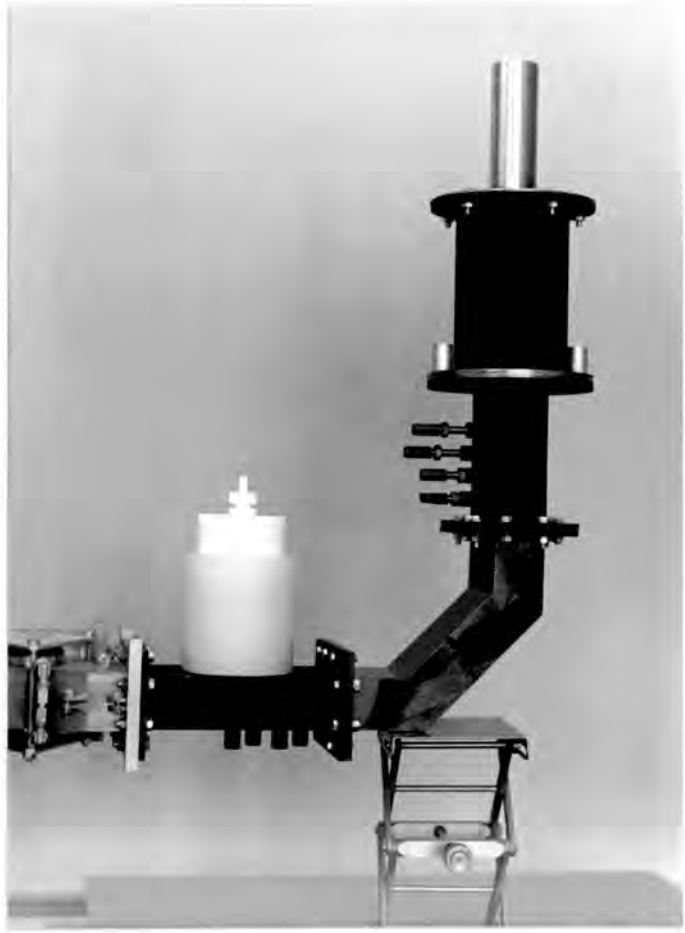


Figure 7.4 Irradiation of 85 ml capacity PTFE vessel in cylindrical waveguide. A vessel is shown standing on the waveguide.

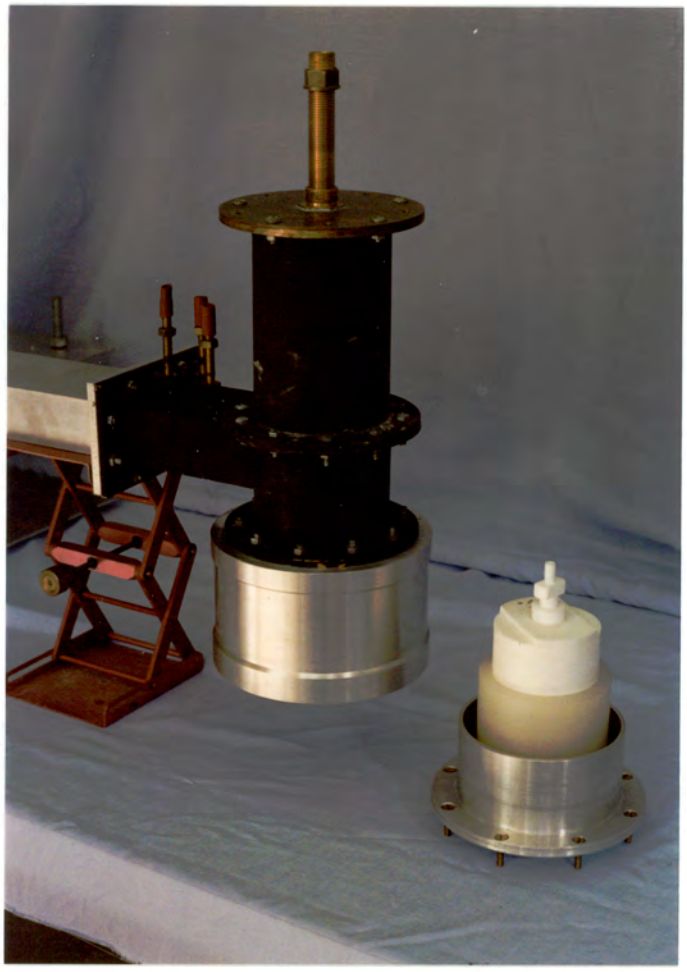
The above system did not permit easy automatic loading of the vessel in the cavity and required manual locking of the metallic seal to prevent microwave leakages. A different applicator was designed to simplify the loading and unloading while keeping microwave leakages to a permissible limit. The applicator is shown in Figure 7.5 and a schematic diagram is shown in Figure 7.6. As above, a cylindrical cavity was choosen for the applicator and microwaves were transferred from rectangular waveguide (TE_{10} mode) to the circular waveguide cavity (TM_{010} mode). The cavity was made of aluminium and

incorporated a quarter-wave choke with dimensions shown in the Figure 7.6. The bottom section, which contained the pressure vessel (located by a polypropylene block), was introduced in the cavity and was maintained into position during irradiation. Due to the efficient choke there was no need for a tight fit or good electrical contact to prevent microwave leakages.

In order to optimize the power transfer and heating efficiencies, two modes of tuning were investigated. It was possible to achieve reasonable tuning using the three tuning screws only, as was found for the previously described applicator. However, when frequent tuning is required (*i.e.*, when varying the load or position in the cavity due to different requirements and vessel capacity and design) the adjustment of the three tuning screws is a laborious task. For most of the work optimization was achieved using the plunger tuner.

For this cavity it was not possible to monitor the temperature of the small loads during irradiation using a thermocouple probe, because the probe coupled with the field and resulted in self-heating, which introduced measurement errors. The temperatures of the loads were measured before and after heating and the power absorbed was calculated. These values were used to compare the effect of the tuner on the efficiency of microwave absorption in the various loads. While these tests were not entirely satisfactory due to the non-linear rate of heating which is associated with the change of reflected power (and therefore power absorbed by the loads) with temperature (see below), they provided nonetheless useful information on the sensitivity of the tuning process.

(A)



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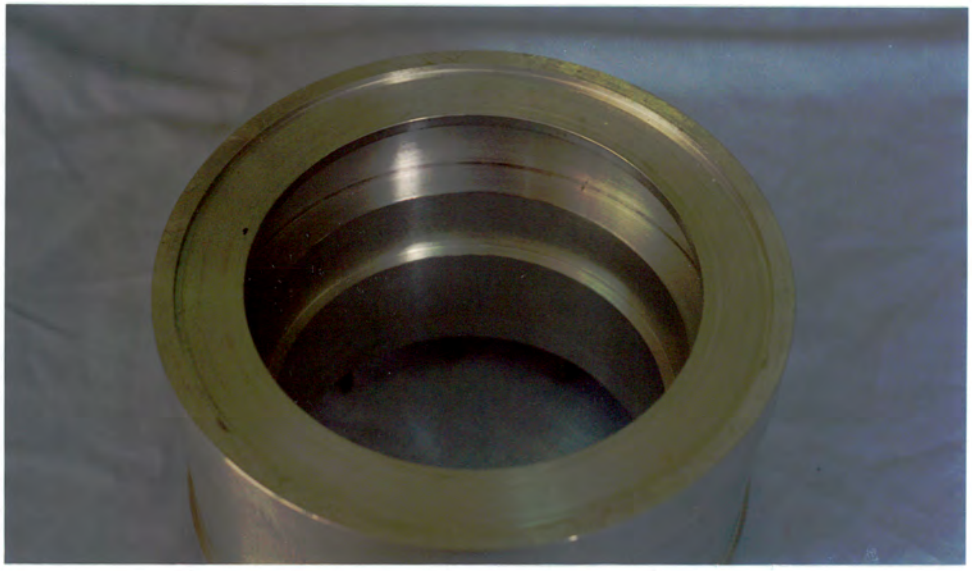


Figure 7.5 Applicator with choke system for irradiation of pressure vessels: (A) cavity and vessel holder shown separately on the RHS; (B) view of the choke section of the cavity.

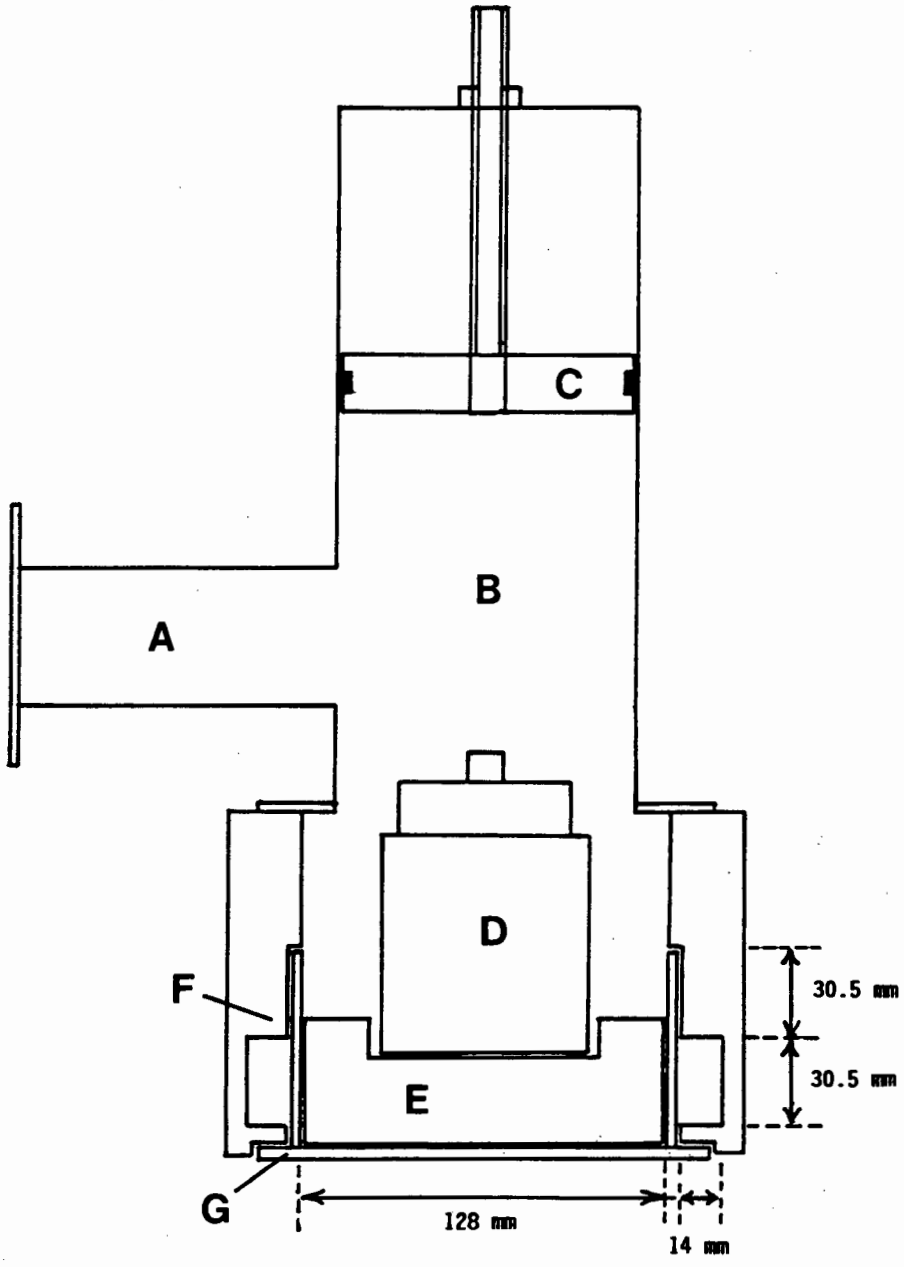


Figure 7.6 Schematic diagram of the applicator with choke system: (A) rectangular waveguide, (B) circular waveguide, (C) plunger, (D) pressure vessel, (E) polypropylene spacer, (F) choke section, (G) vessel holder.

Various loads of water (7.5, 15, 30, and 45 ml) were placed in an open digestion vessel in the cavity. The loads were approximately 80 mm from the bottom of the cavity and the position of the plunger was varied (from 0 to 80 mm from the top of the cavity) and the power

absorbed by the loads was calculated. The forward power was kept at 350 W and the loads were heated for 20 s. The results are shown in Figure 7.7. It is clear that the plunger position is crusial and determines which size of load is heated more efficiently. This mode of tuning was, however, very easy compared to using the tuning screws.

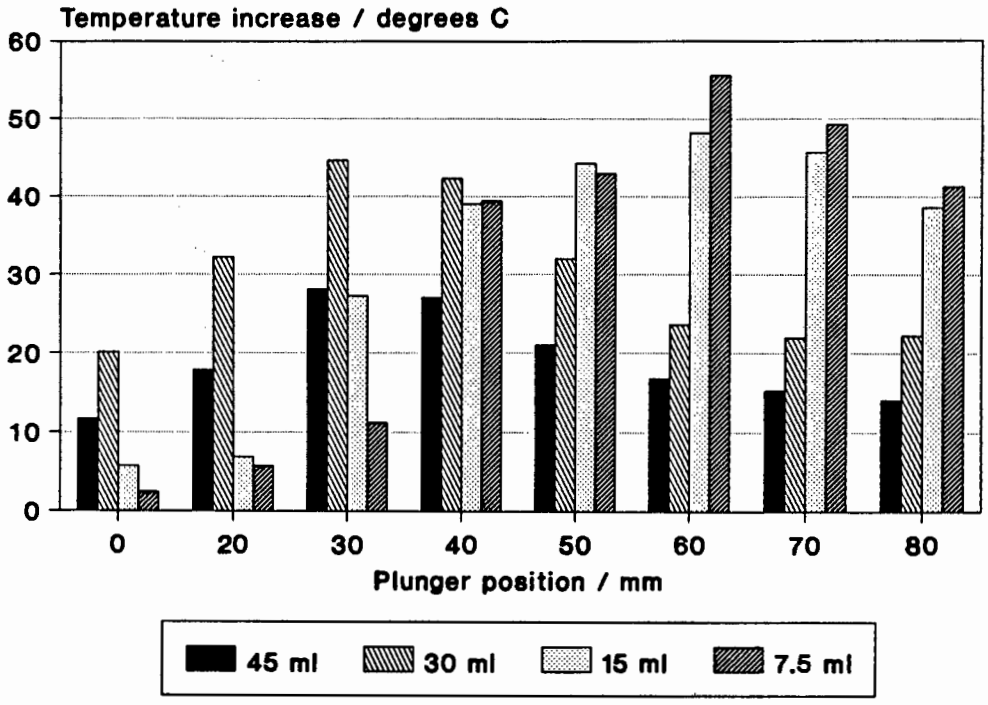


Figure 7.7 Effect of the plunger tuner position on the heating efficiency of water loads. The forward power was 350 W and the irradiation time 20 s.

In another set of experiments the cavity was tuned with the plunger tuner for a load of 20 ml of water (at about 30 °C) placed at a distance of 55 mm from the bottom of the cavity. Various loads of water were placed at the same position and the temperature increases were measured after irradiation with 350 W of forward power for 20 s. The results are shown in Figure 7.8. The reflected power during heating of these loads was also measured and is shown in Figure 7.9. The power was shut off after the loads started to boil. A wide variation of the reflected power measurements always occurred during boiling (at the end of the reflected power curves), presumably due to the vigorous boiling and associated changes in impedance. The 20 ml load reached its boiling point after about 30 s and the reflected power is seen to vary considerably during the heating cycle (see also next section). Generally good power absorption was obtained for all the loads, although the reflected power remained high

for the smaller loads. If a circulator is available for absorbing the reflected power, it seems that a compromise tuning (*e.g.*, for 20 ml) can be adequate for a relatively wide range of loads. It is also seen from Figure 7.9 that the reflected power changes considerably with temperature and it is therefore not possible to prevent this behaviour by tuning at any specific temperature. To maintain the lowest reflected power and greatest efficiency throughout the heating cycle, the cavity would have to be tuned continuously with a feed-back automatic tuning system (*i.e.*, using a motorized plunger and a suitable software).

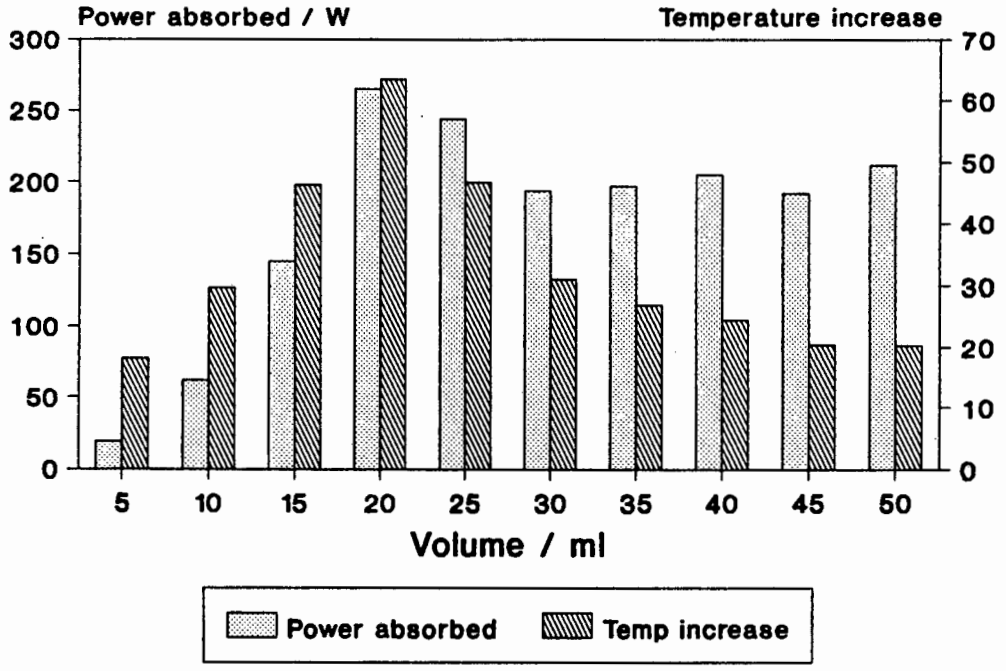


Figure 7.8 Temperature increases and power absorbed in water loads in the cavity tuned for a 20 ml load. The forward power was 350 W.

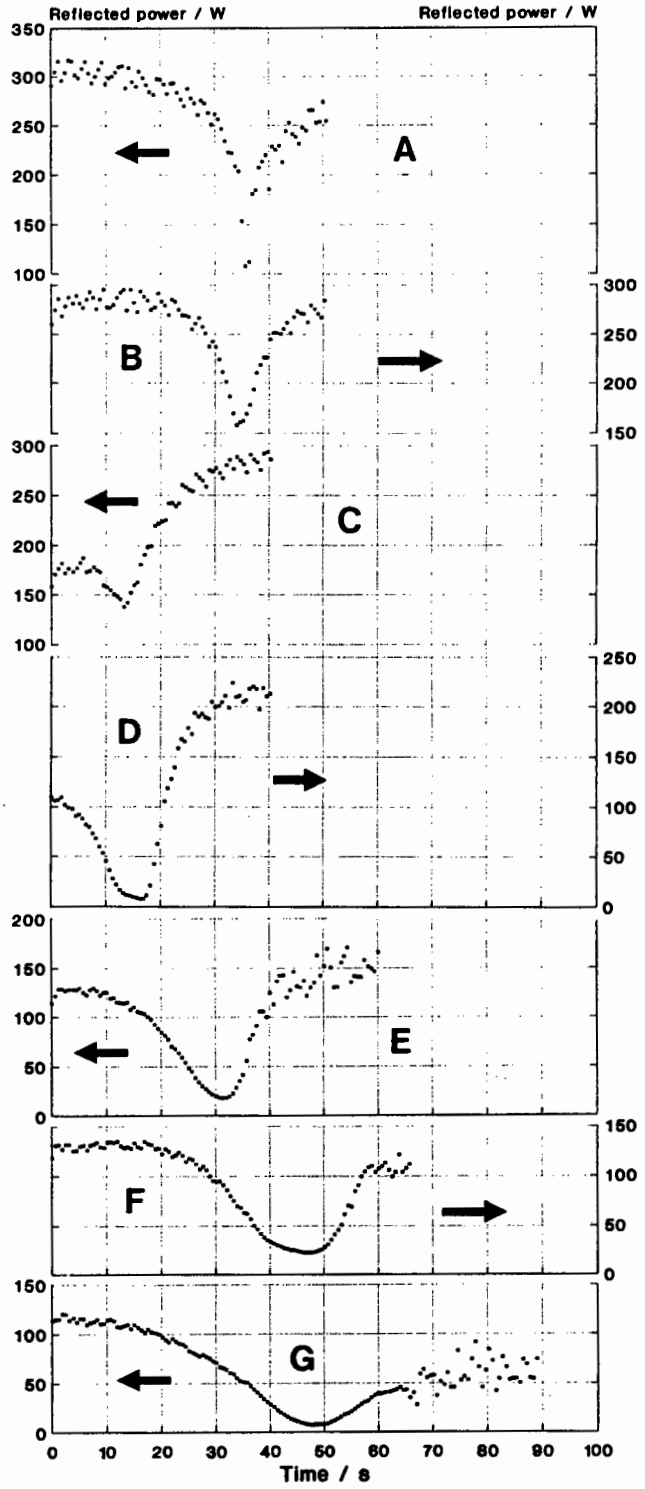


Figure 7.9 Reflected power measurements during heating of water loads. The forward power was 350 W.
(A) 5 ml, (B) 10 ml, (C) 15 ml, (D) 20 ml, (E) 30 ml, (F) 40 ml, (G) 50 ml.

7.4 PTFE-lined steel pressure vessel

Because of the mechanical limitations of vessels constructed entirely of polymeric materials, designs to implement the microwave heating of solutions in PTFE-lined steel structures were investigated. The designs of similar vessels for heating in traditional ovens or with heating mantles are well established and they have been widely used in analytical laboratories for the dissolution of difficult materials and for other chemical reactions. Processing times are relatively long (several hours) and often not acceptable in modern laboratories.

Two approaches were investigated: coaxial launching and aperture slot coupling of the microwave energy inside the cylindrical steel structures.

7.4.1 Coaxial launching

The design of the vessel using a coaxial probe to couple the power from a rectangular waveguide to the pressure vessel is shown in Figure 7.10. A rigid coaxial guide (*ca.* 50 ohms) was made from copper tubing with a gold-plated copper centre-conductor supported by PTFE rings. The steel vessel (60 mm internal diameter) was positioned into the vessel holder, which allowed the centre conductor to protrude inside the vessel. A thin thermocouple probe was used to monitor the temperature of the PTFE cup temperature at a position corresponding to that of the sample level where the highest temperatures were expected.

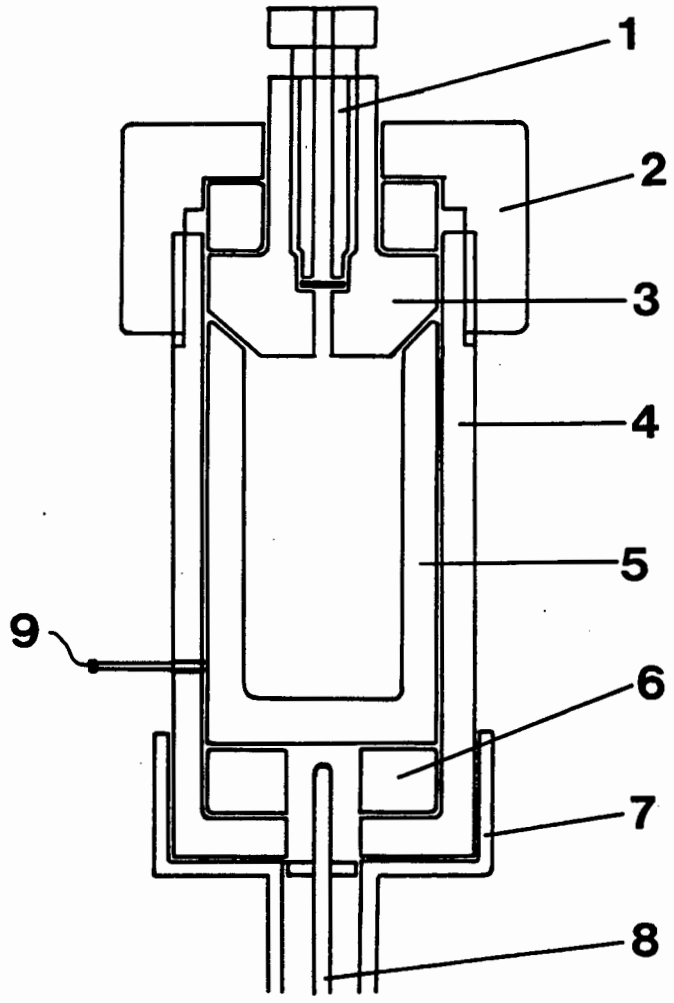


Figure 7.10 Design of the PTFE-lined steel vessel with coaxial coupling: (1) bursting disc holder, (2) brass screw cap, (3) PTFE sealing plug, (4) stainless steel vessel, (5) PTFE cup, (6) PTFE spacer, (7) vessel holder and coaxial outer conductor, (8) coaxial center conductor, (9) thermocouple probe.

In initial experiments using this design, power from a 500 W magnetron was matched to a circulating tapered water load in a waveguide (Figure 7.11). The position of the vessel holder and thus the coaxial probe in the waveguide was varied to obtain the best power transfer into the load in the vessel. Results showing the temperature increases of various water loads in the vessel (for a fixed irradiation time of 20 s) are shown in Figure 7.12. As can be seen, adequate power transfer was achieved for the smaller loads (20-30 ml).

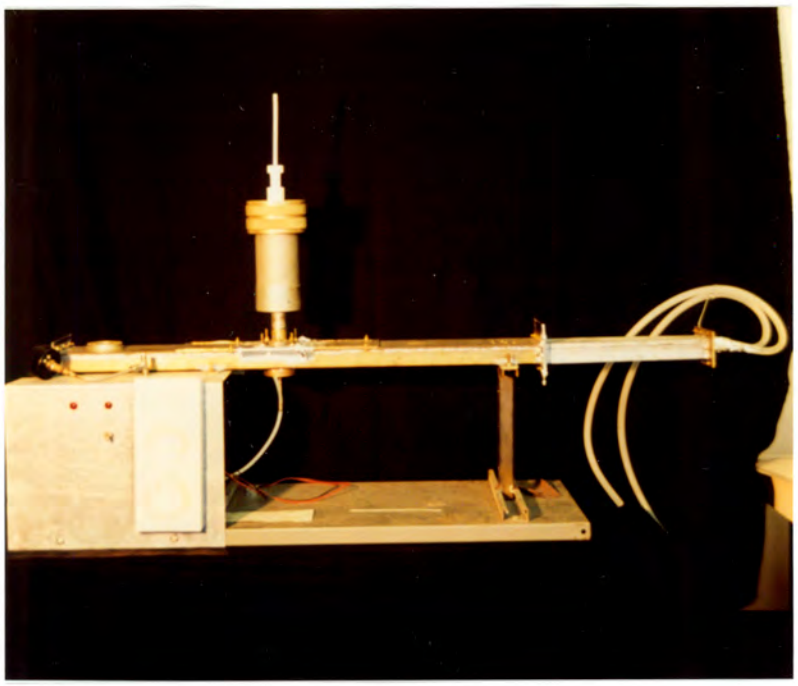


Figure 7.11 Waveguide terminated by a water load (on RHS) for coupling of power in the PTFE-lined steel pressure vessel.

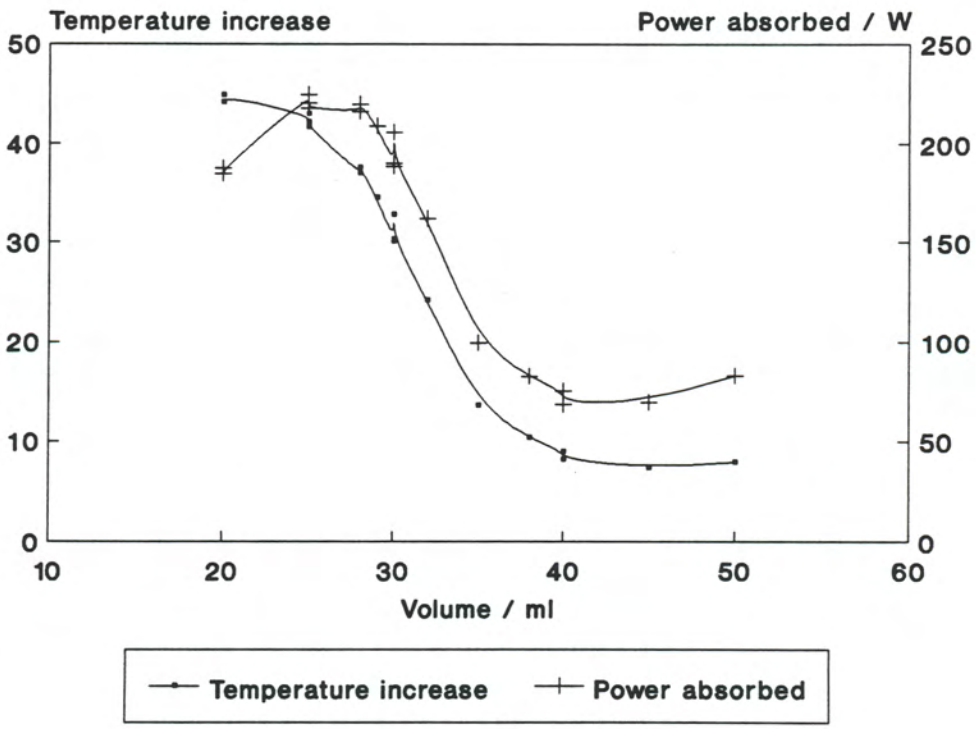


Figure 7.12 Temperature increases and power absorbed by water loads heated in the vessel for irradiation times of 20 s.

Digestion of biological materials was carried out in the pressure vessel. With 0.4 g of dried leaf sample and a mixture of 6 ml of concentrated nitric acid and 0.5 ml of hydrogen peroxide, the digestions were found to be satisfactory for analysis by inductively coupled plasma atomic emission spectroscopy [POU86] after 50 seconds of irradiation at full power. When longer irradiation times were attempted (for larger volumes), the centre conductor became hot and frequent sparking occurred inside the vessel. A jet of air was used to keep the probe cool but this was not found to be entirely satisfactory. This vessel was also used with the 1.2 kW microwave generator and a plunger tuner was used to optimize the power transfer (Figure 7.13). While this was superior to the above system, the sparking problem was found to remain a limiting factor for power handling. The power handling capacity of coaxial structures is limited by the high field intensity and high current density around the centre conductor. This can be improved by using a larger diameter centre conductor and water cooling through a hollow centre conductor but that was not a practical solution for this application.

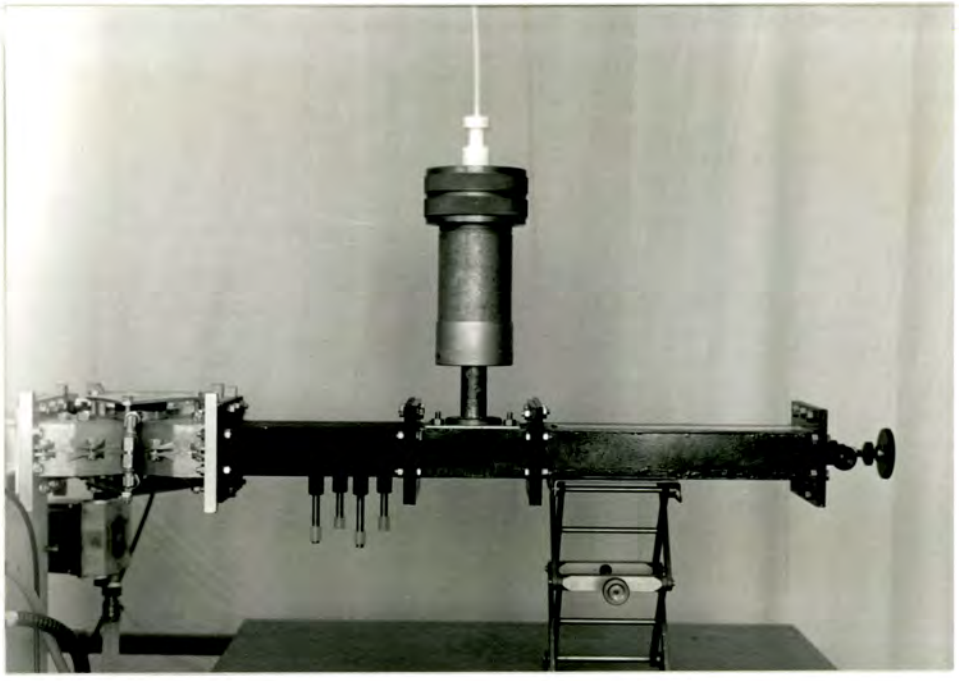


Figure 7.13 R26 waveguide and plunger tuner (on RHS) for coupling of power in the PTFE-lined steel pressure vessel.

7.4.2 Aperture coupling

An aperture (slot) was cut in the bottom of a vessel of similar construction to the one described above (Figure 7.10). Two configurations for coupling the power into the vessel were investigated. Firstly, coupling from the broad side of a rectangular waveguide and secondly coupling at the end of the waveguide.

The thickness of the bottom of the steel vessel and the width of the aperture had to be restricted to dimensions that were constrained by the strength requirements of the vessel in the desired temperature and pressure ranges. Because of the same limitations, the PTFE spacer had to be kept a certain thickness (12 mm, see below). However, the results presented in Table 7.1 show the effect of aperture and spacer dimensions on the power transfer for a vessel positioned in the broad side (x) of a waveguide. In this experiment the waveguide was terminated by a matched water load and the magnetron of 500 W was operated at full power.

Table 7.1 Rate of heating of 20 ml water loads with varying aperture and spacer dimensions.

Aperture dimensions		Spacer thickness	Irradiation times	Temperature increase
Thickness (mm)	Width	(mm)	(s)	($^{\circ}$C)
8	4	10	30	9.5
		20		14.7
		30		36.6
		40		39.5
10	8	10	15	6.7
		20		17.6
		25		30.8
		30		27.9
		35		14.6
		40		7.5

In other experiments, tuning was achieved with tuning screws and a plunger tuner. For small loads, high reflected power was experienced with an increase in temperature, and matching conditions were found to be extremely critical. The experiments were performed with a steel vessel of 60 mm internal diameter having a bottom thickness of 12 mm and a slot width of 10 mm. The length of the slot was the same as that of the diameter of the vessel. The PTFE spacer was 20 mm. With a load of 20 ml water and forward power of 300 W, temperature increases of typically 55 $^{\circ}$C were achieved in 20 seconds if the system was initially matched at a temperature of 17 $^{\circ}$C. However, it was possible to match at different temperatures thus achieving satisfactory heating rates over the required temperature range (see below).

The second approach was to have the vessel at the end of the R26 waveguide and to use the tuning screws to match the system under various conditions. In order to investigate fully the efficiency of heating of various loads under high temperature and pressure conditions, a vessel was fitted with a manifold made of stainless steel (see below) to accommodate a thermocouple probe that was sealed by a compression fitting and a connection for a pressure transducer (Figure 7.14). Other construction features were unchanged from the previously described design. The aperture in the bottom of the vessel is shown in Figure 7.15. A PC was used to monitor temperature, pressure, as well as the reflected power during the heating cycles.

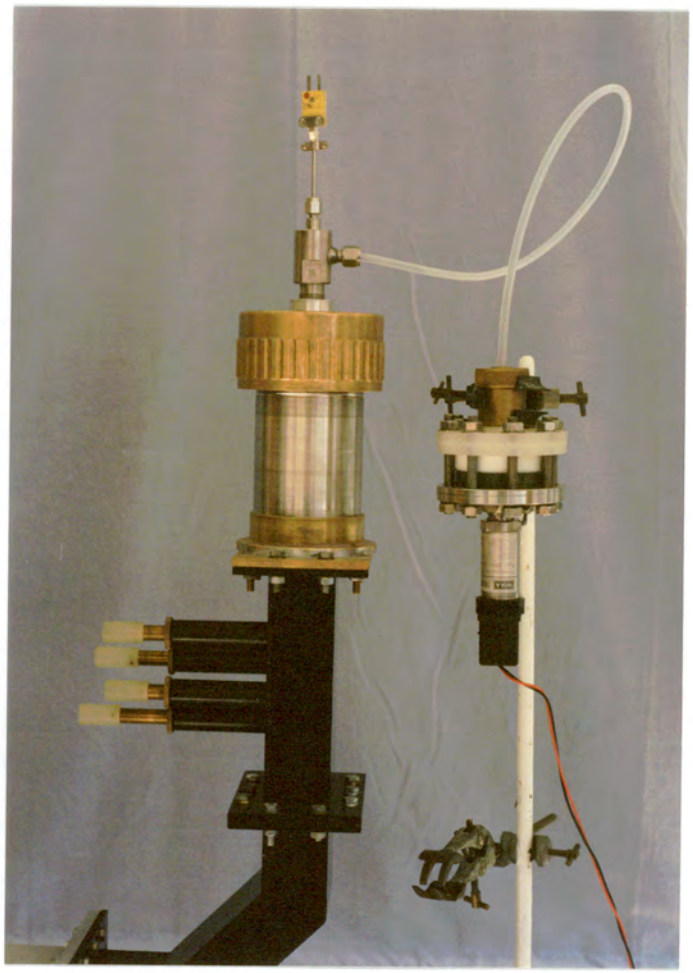


Figure 7.14 Experimental setup for irradiation of the PTFE-lined steel vessel with aperture coupling.

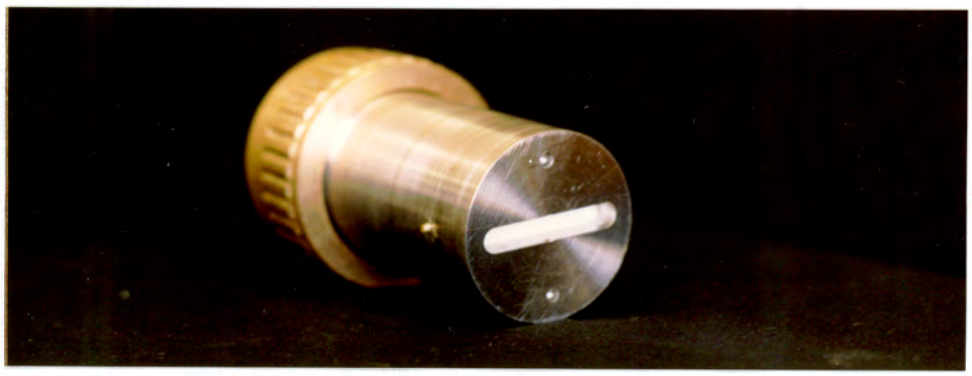


Figure 7.15 Aperture in the bottom of the pressure vessel (length 62 mm, width 10 mm, thickness 12 mm).

The heating rates of several loads of water were measured at constant power (450 W) with the system unmatched (the tuning screws withdrawn). The reflected power was measured simultaneously but in these experiments the transducer was not connected. The results obtained for loads of 5 to 40 ml heated to boiling point are shown in Figures 7.16 to 7.23. The scales on all the graphs were made similar for ease of comparison. A temperature of 100 °C was achieved for all the loads in less than 55 s showing that for the wide range of loads, satisfactory rates of heating were achieved without any tuning. It can be seen from the Figures that the reflected power differed widely for the different loads during the heating cycles. It is interesting to note the drop in reflected power at the higher temperatures (occurring just before boiling temperature). This is particularly well defined for the 5, 15, and 20 ml loads but is also apparent in the other cases, except in the case of 10 ml. This drop of reflected power was also noted in the case of the cylindrical cavity designed for irradiation of PTFE pressure vessels (Figure 7.9). The drastic change of reflected power over this temperature range, about 250 W in the case of the 15 ml load, indicates that the system is extremely sensitive to the conditions inside the vessel (see discussion below).

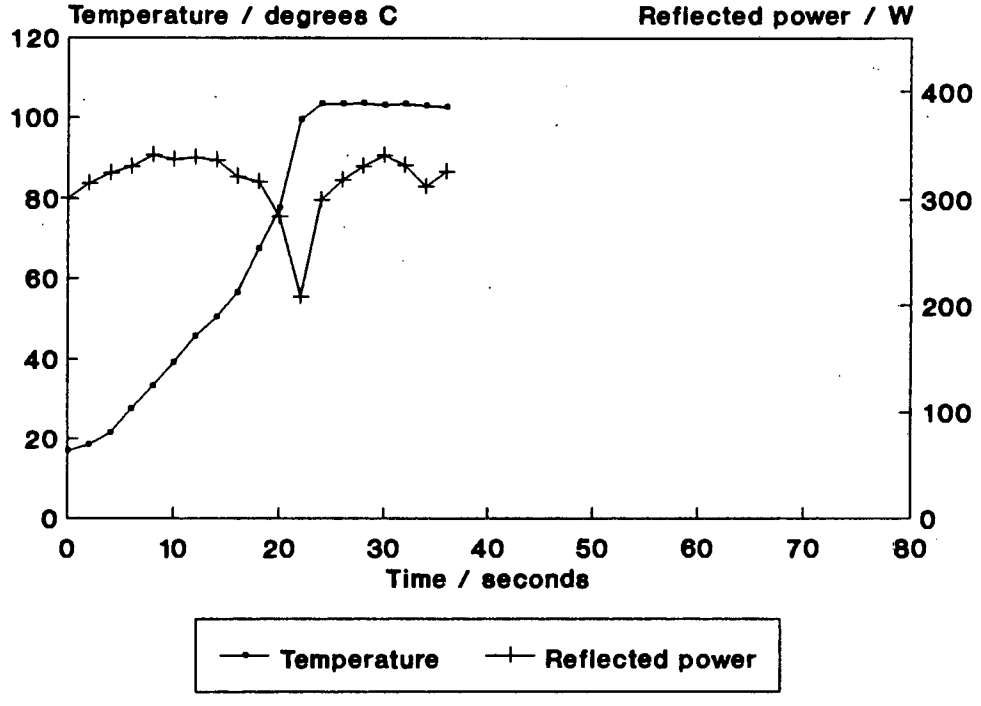


Figure 7.16 Temperature and reflected power curves for 5 ml of water.

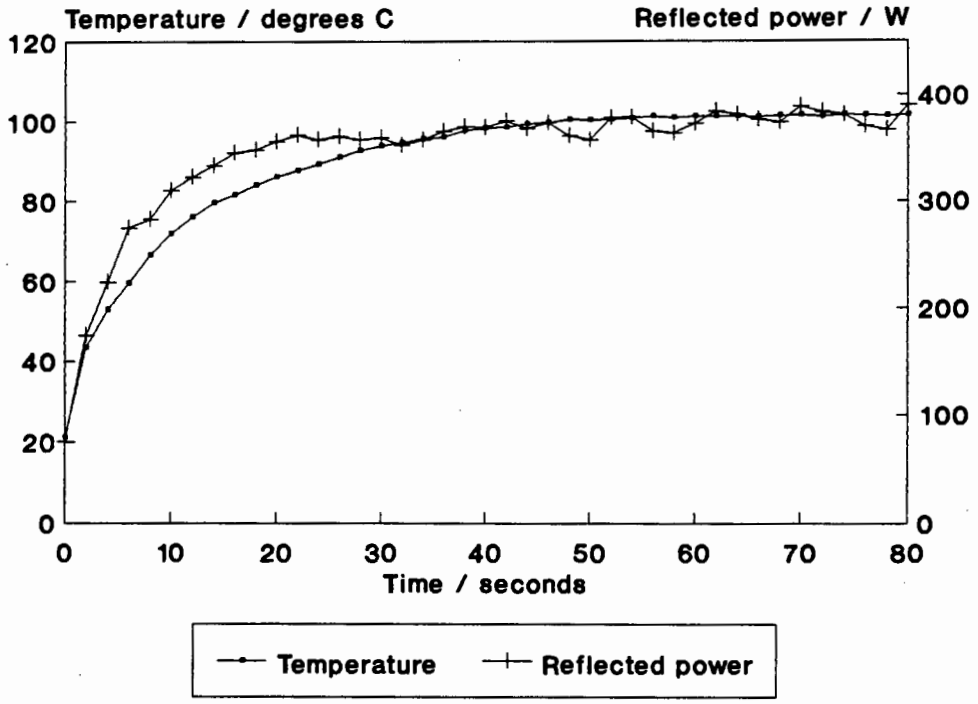


Figure 7.17 Temperature and reflected power curves for 10 ml of water.

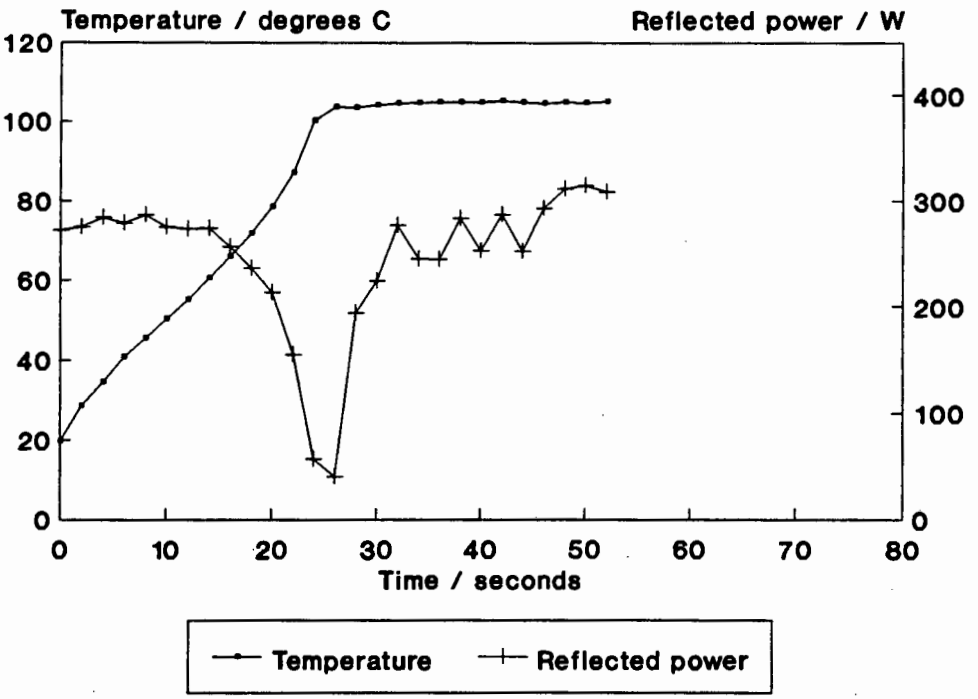


Figure 7.18 Temperature and reflected power curves for 15 ml of water.

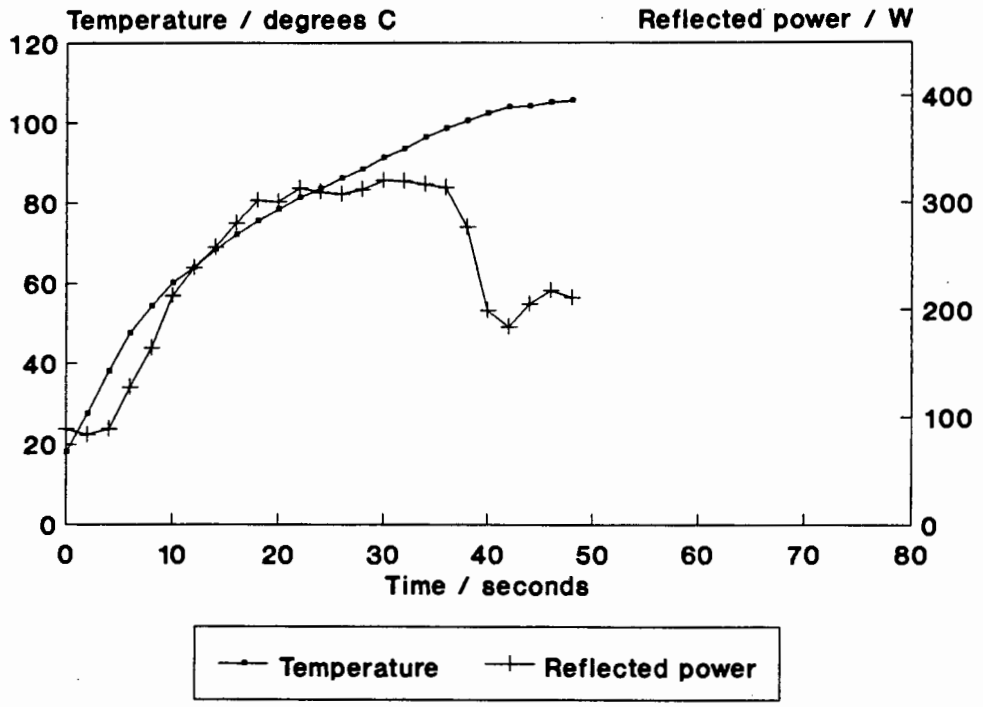


Figure 7.19 Temperature and reflected power curves for 20 ml of water.

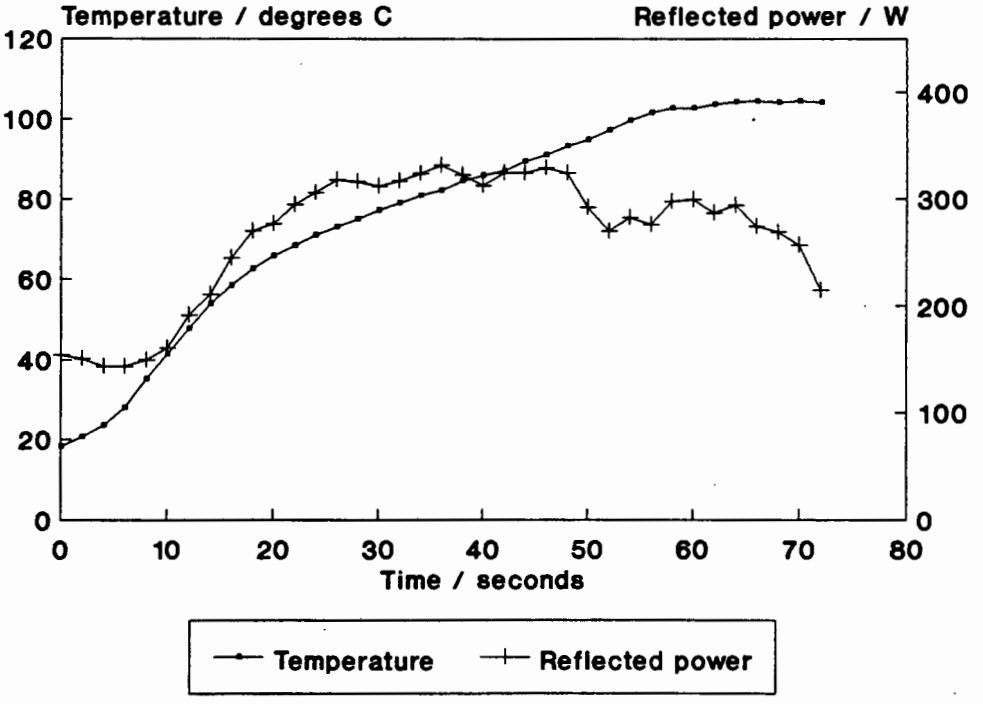


Figure 7.20 Temperature and reflected power curves for 25 ml of water.

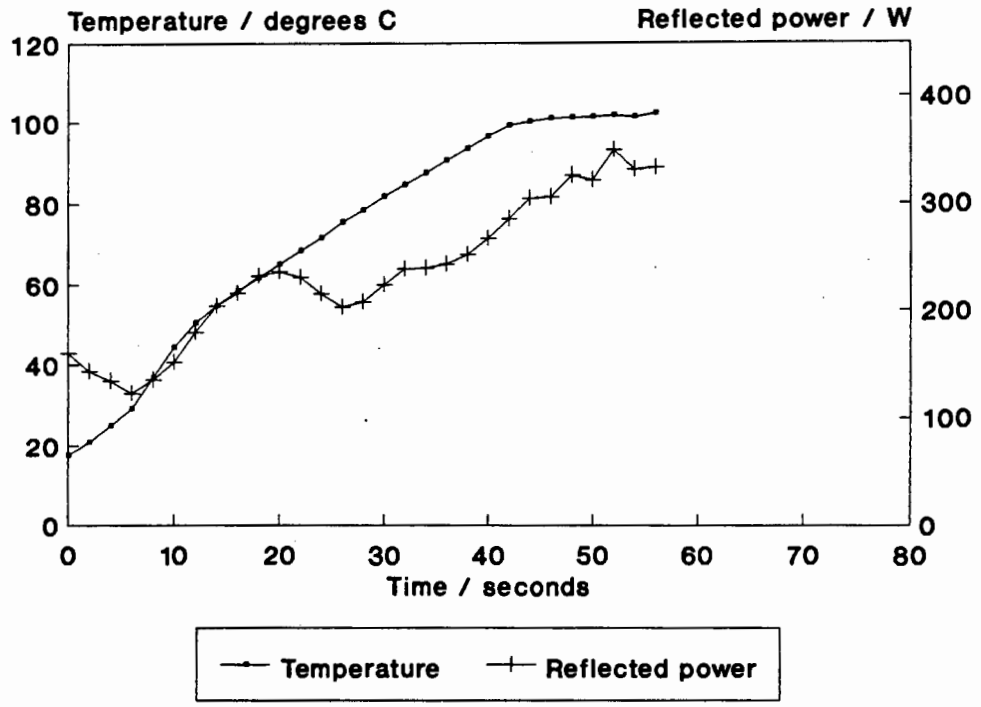


Figure 7.21 Temperature and reflected power curves for 30 ml of water.

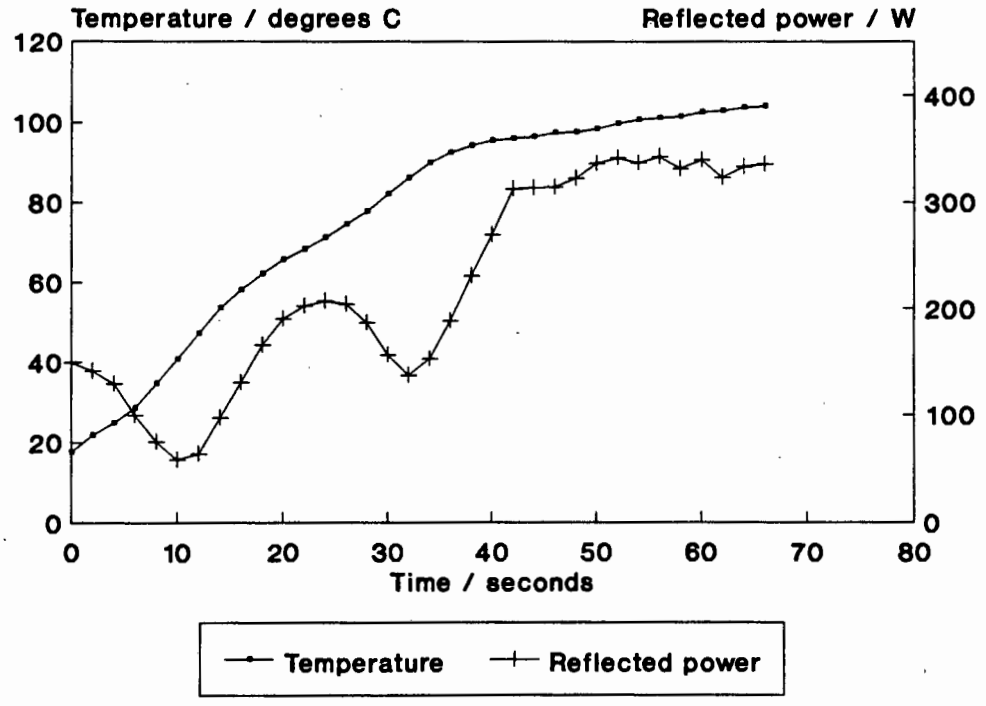


Figure 7.22 Temperature and reflected power curves for 35 ml of water.

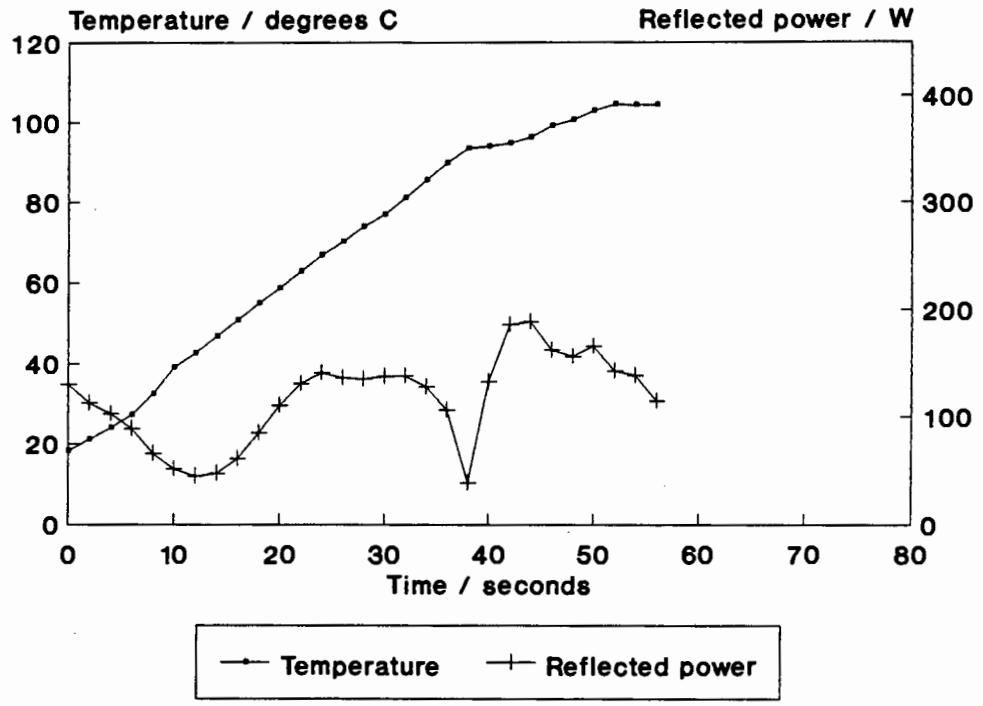
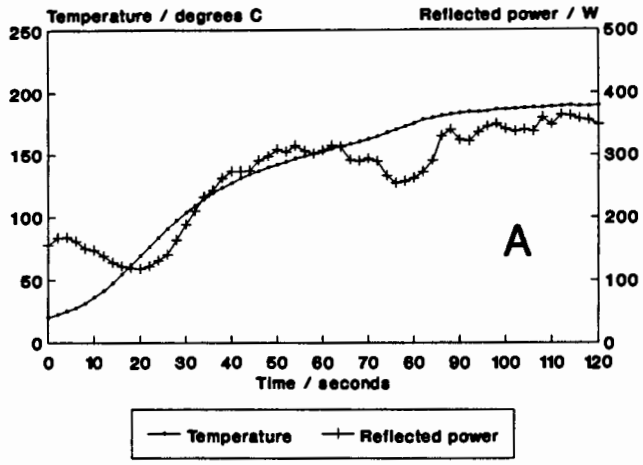
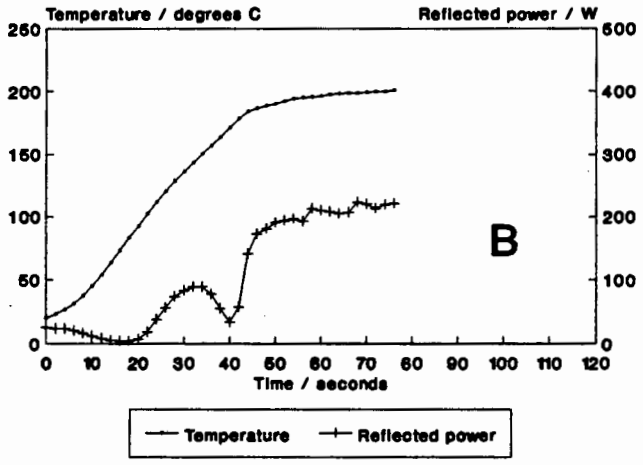


Figure 7.23 Temperature and reflected power curves for 40 ml of water.

The effect of tuning on the heating rates is illustrated for the high boiling temperature ethylene glycol (boiling point 198 °C) in Figure 7.24. The ethylene glycol was heated and the system was tuned at a specific temperature (approximately 100 or 190 °C), the liquid was cooled to room temperature and the heating cycle was then monitored. The best rate of heating was obtained when tuned at 100 °C, and the reflected power minimum was found to correspond closely to that of the tuning temperature. In these cases, a drop of reflected power was also observed just before boiling started.





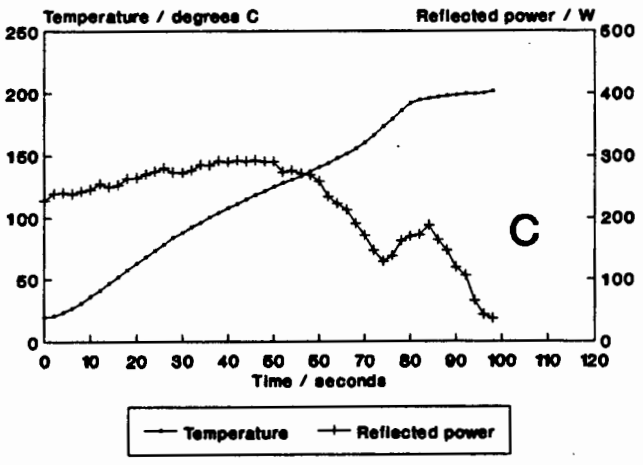


Figure 7.24 Temperature and reflected power curves for 30 ml ethylene glycol with a forward power of 450 W: (A) not tuned, (B) tuned at 100 °C, (C) tuned at 190 °C.

The temperature and pressure increases and reflected powers were recorded for various loads of water with a forward power of 450 W and the system untuned. Duplicate runs for a load of 20 ml water are shown in Figure 7.25. It can be seen that the conditions were very reproducible, as could be expected for this type of system. Results for 15 and 25 ml water loads are shown in Figure 7.26 and 7.27, respectively. As previously observed, a drop in reflected power was observed around 100 °C which caused more power to be absorbed by the load and an accompanying increase of pressure. More interesting was the further drop in reflected power at higher temperatures which resulted in a high rate of power absorption, an increase in temperature and a high rate of pressure increase.

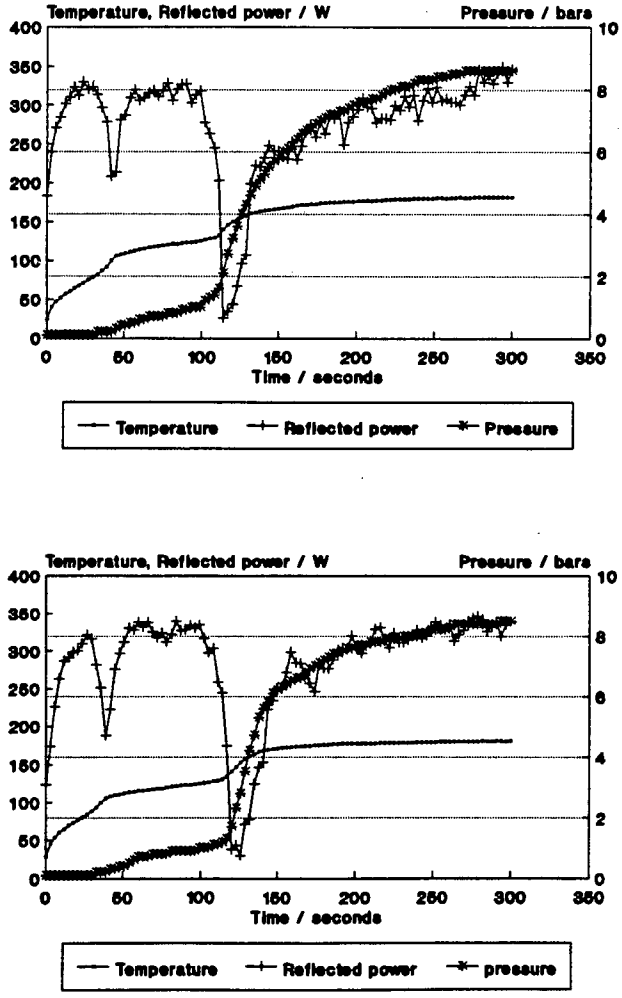


Figure 7.25 Temperature, pressure and reflected power curves for 20 ml of water (duplicate runs).

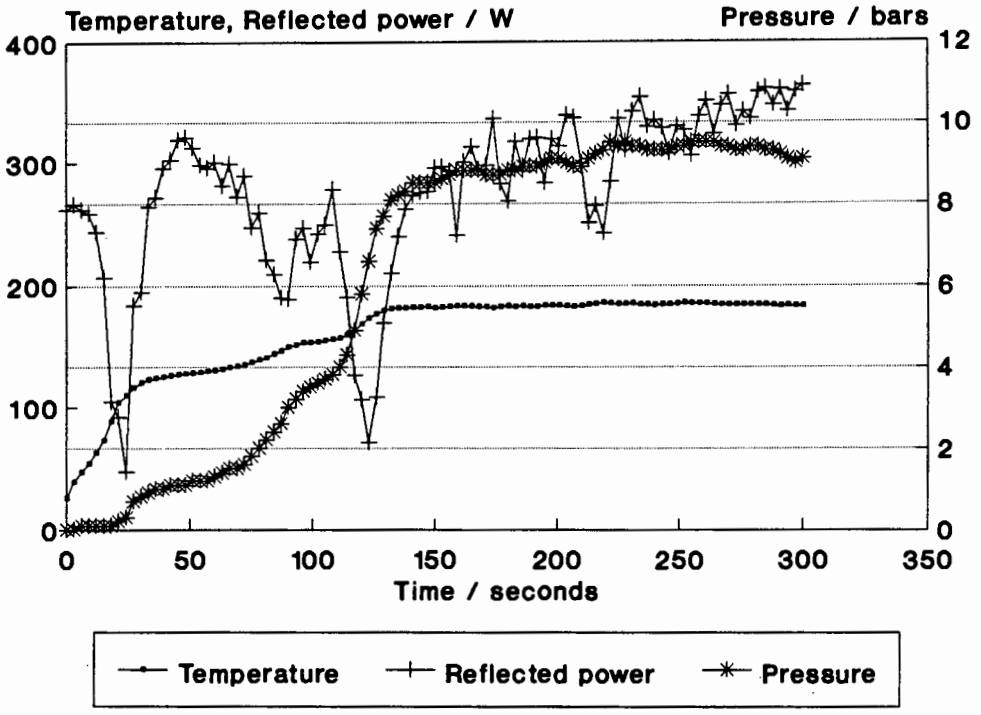


Figure 7.26 Temperature, pressure and reflected power curves for 15 ml of water.

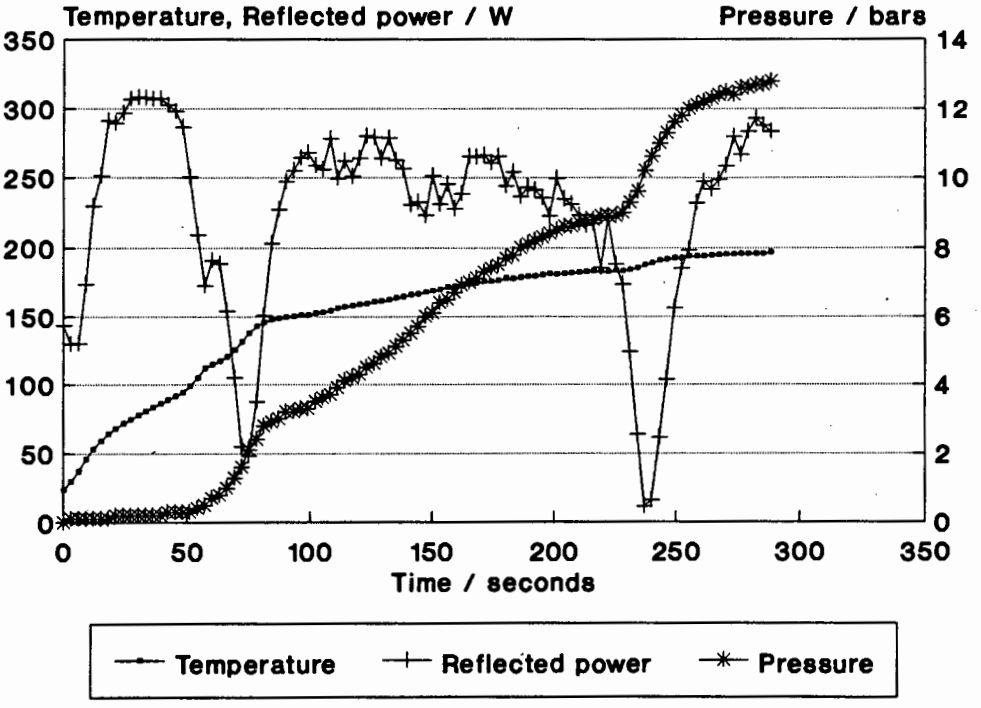


Figure 7.27 Temperature, pressure and reflected power curves for 25 ml of water.

The results obtained for a 10 ml water load under exactly the same conditions as above (450 W forward power) are shown in Figure 7.28. In this case, it can be seen that the reflected power remained high after the water reached its boiling point and the temperature increase over a time of more than 100 s was very small, thus causing a very small pressure increase. It was possible, however, to use the tuning screws to increase the coupling which resulted in a significant rise in temperature and a rapid increase of pressure.

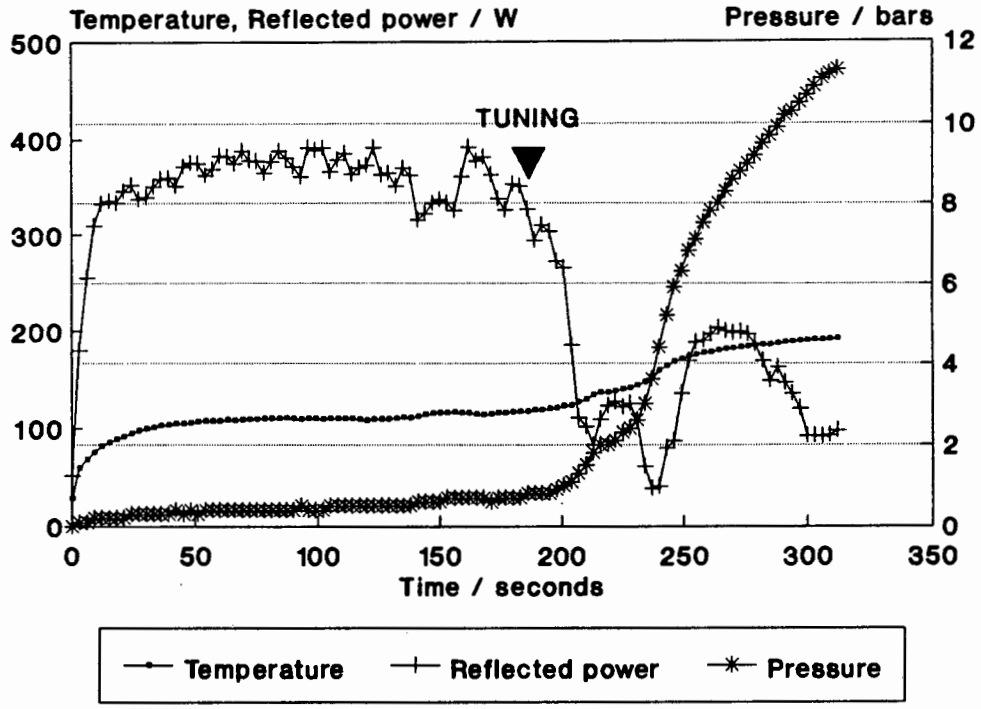


Figure 7.28 Temperature, pressure and reflected power curves for 10 ml of water. Tuning was started at 180 s.

From the results presented above, it is obvious that this system is extremely sensitive to the load conditions. An examination of the design shows that the diameter of the steel vessel is below the cutoff frequency for propagation of waveguide modes when the cavity contains air only and is thus too small to allow efficient transmission of the energy. This could be shown by placing a water load at a higher position in the vessel (without the PTFE spacer and cup), held by a piece of glass tubing, and monitoring the temperature during irradiation. The rise of temperature was very small even with a forward power of 600 W. Thus, during use, the microwave leakages through the hole in the cover (locating the PTFE sealing plug) were negligible. However, in the presence of the PTFE spacer and the PTFE of the cup, the

dielectric-loaded cylinder presents a more favourable situation for propagation of the microwaves since the cutoff frequency is reduced. Thus when the load is placed in the PTFE cup, relatively efficient transfer of the energy occurs but this is affected by the size of the load. When the thermocouple probe was placed inside the vessel through a hole in the PTFE sealing plug, the microwave leakages were very large, indicating that a fair amount of energy was propagated inside the vessel. An in-depth analysis of the mode of propagation and the exact coupling mechanism inside the cavity is required to explain the sudden reduction of reflected power and resulting increase in temperature and pressure shown in Figures 7.26 and 7.27. When the thermocouple was in place, it formed a coaxial cavity with the wall of the vessel and microwave energy in a TEM mode (which can propagate through a small aperture) could propagate and leak past the hole in the cover of the vessel. It was therefore necessary to use the stainless steel manifold to prevent leakages when the temperature was monitored. In order to check the effect of the thermocouple on the energy transfer characteristics, the thermocouple probe was removed and only the reflected power and pressure increase were monitored for a 15 ml water load (Figure 7.29) under exactly the same condition as above (Figure 7.26). Comparison of these two Figures indicates that the general behaviour was similar but that a shift of the second large reflected power peak occurred with an attendant shift in the pressure curve. Thus it appears that the thermocouple did affect the coupling slightly. This experiment was not repeated for all the loads.

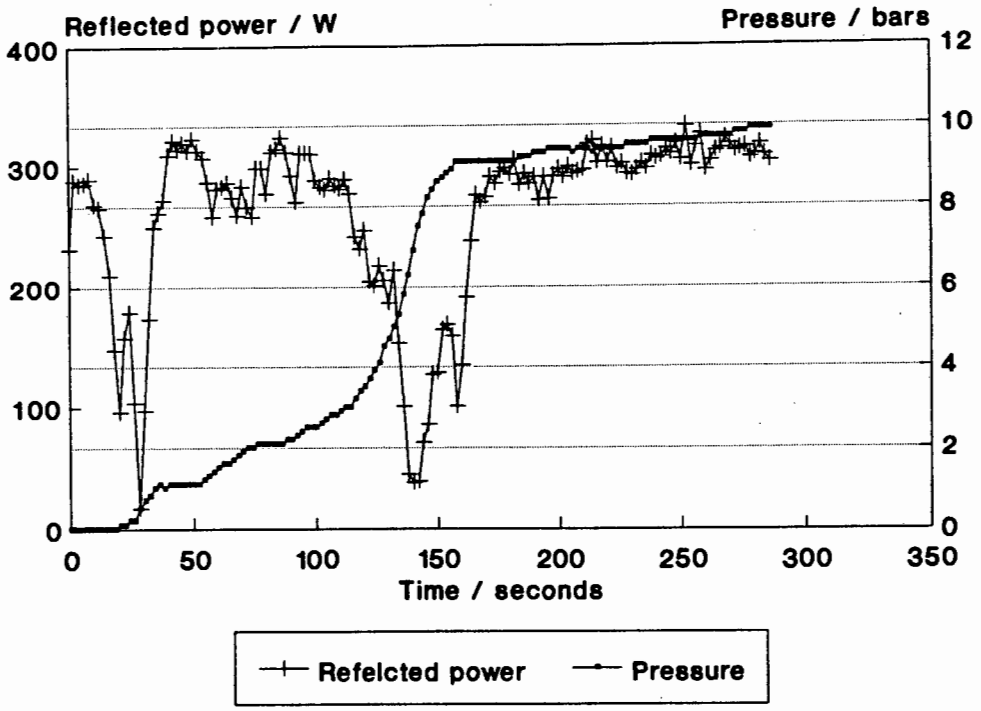


Figure 7.29 Reflected power and pressure curves for 15 ml of water without the thermocouple probe.

To test the efficiency of the present design, oxidation reactions of biological materials (acid digestion) were chosen as model reactions since experience with other systems was available and this allowed a comparison to be made. Different biological materials were used and the ratio of acid to the mass of material, as well as the forward power and irradiation times, were varied. The reflected power and pressure were monitored during the heating of 15 ml of concentrated nitric acid with the system untuned. The results are shown in Figure 7.30. As can be seen the reflected power remained high and constant during the heating cycle and a pressure of 3.5 bar was achieved after 300 s. Nitric acid was thus seen to behave differently from water. The pressure and reflected power were monitored during a digestion using 0.5 g of dry cereal and 15 ml of concentrated nitric acid, using an untuned system and with a forward power of 450 W. The results are shown in Figure 7.31. As in the case of pure nitric acid, the reflected power was seen to remain constant throughout the heating cycle, and during this time the pressure increased to 14 bar. The biological material was completely digested. Nitric acid has a boiling point of 120 °C and in a closed container can reach 176 °C at about 4 bar, these conditions being achieved in a PFA digestion vessel that was heated in a microwave oven [KIN88]. According to these results, a high temperature was reached in the vessel under these conditions and extremely efficient oxidation was achieved.

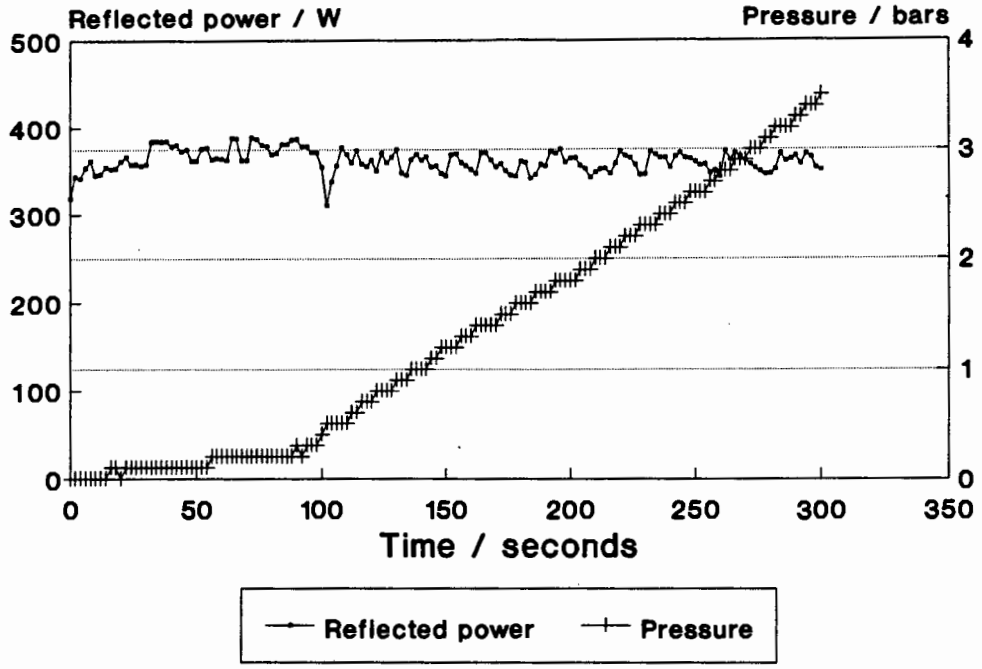


Figure 7.30 Reflected power and pressure curves for 15 ml concentrated nitric acid.

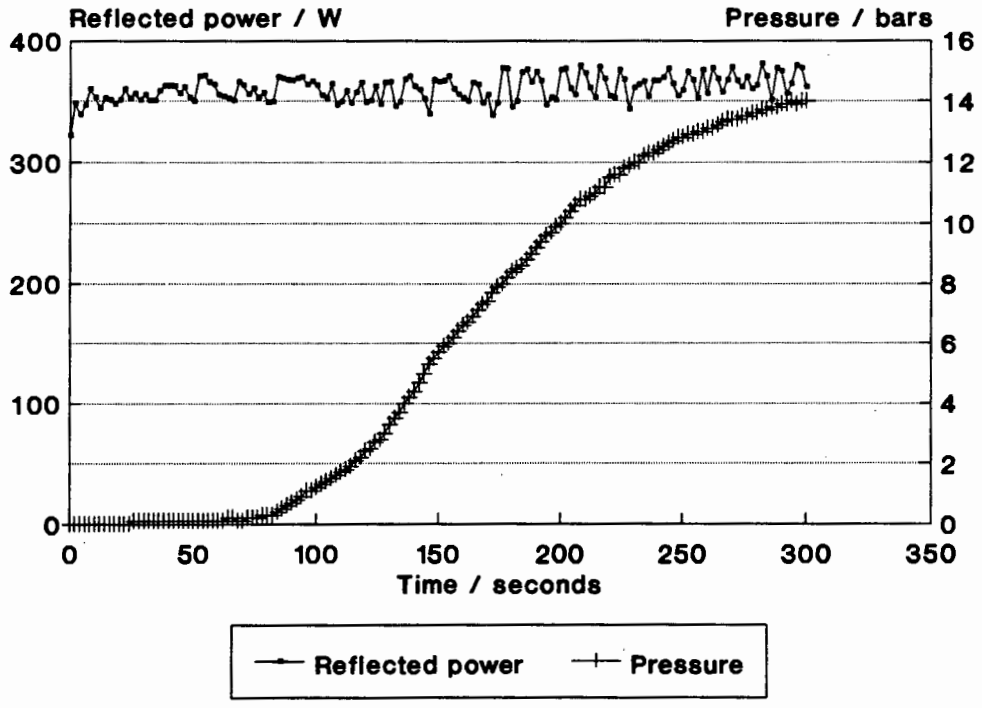


Figure 7.31 Reflected power and pressure curves during the digestion of biological material with untuned system.

The difference between the digestions and the heating and pressurization of water (or other liquids) is that in the case of water the pressure is achieved by the formation of steam, while in the case of an oxidation reaction the pressure is developed by the formation of steam as well as the gaseous products that are formed. The latter cannot recondense and thus are beneficial for achieving fast pressurization and fast rates of heating at lower temperatures. In the case of water, the only possible explanation for the drastic change in reflected power is the change of dielectric properties with temperature (the dielectric constant for water at 20, 100 and 200 °C is approximately 80, 55 and 36, respectively [CRC76]), which must cause the observed temperature dependence of the tuning. At the higher temperatures and pressures (*e.g.*, 180 °C and 10 bar) it can be shown that the actual amount of water in the vapour phase is a very small fraction of the total load, thus the size of the water load is not expected to be a determining factor in the change of reflected power. In the case of nitric acid and the digestion which is expected to be more complex due to the rapid changes in the load (*i.e.*, breakdown of the acid, increase of the ionic strength due to the sample dissolving, and gas formation), no simple answer can be given for the very constant power absorption measured. No data on the dielectric properties of nitric acid or their variation with temperature could be found.

An example of the reflected power observed during a digestion carried out with the system tuned with pressurized water at a temperature of about 150 °C is shown in Figure 7.32. In this case, 0.5 g cereal was digested with 7 ml nitric acid and the forward power was 200 W. The total time of digestion was 120 s. The reflected power remained relatively constant during the first 70 s and then a decrease of reflected power became apparent, as previously observed for water. Although the reflected power was high during that time, an almost perfect digestion was achieved under these conditions.

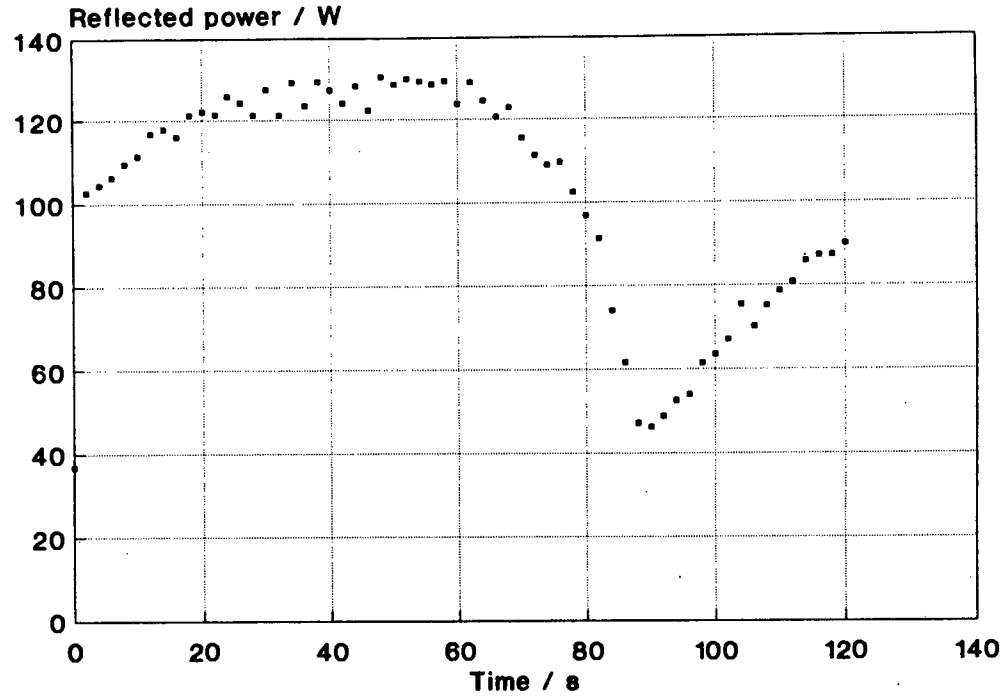


Figure 7.32 Reflected power curve for digestion of biological material with the system tuned at high temperature.

It is clear from the above results that although the system is very sensitive to the loads and the tuning, power can be transferred efficiently into the loads through an aperture into a pressure vessel. This configuration is simpler than the coaxial system and has much less limitation for power handling. However, because of the mismatch that occurs with the varying load characteristic during the heating cycle, a circulator has to be used unless on-line matching is performed automatically. The system is complex and transmission line modelling of the cavity partly filled with PTFE and acid is beyond the scope of this work. Finite element analysis of such microwave waveguide problems and the use of computer programs to do this is a very specialized field of research. This field has been reviewed by Watkins [WAT86].

7.5 Conclusion

It has been shown that through simple designs of microwave applicators the contents of pressure vessels can be efficiently heated and that the heating rates are reproducible. When non-routine or infrequent processing is required, waveguide applicators seem advantageous compared to the use of specially designed microwave ovens, since the system is simpler and easier to manufacture. In automating pressure digestion this approach should also be advantageous due to the simplicity in introducing the vessels into the microwave cavity and the good reproducibilities in the heating rate. With microcomputer control it is possible to program conditions (power, irradiation times and tuning) for each sample and process different materials automatically.

The use of microwave heating and PTFE-lined steel vessels might not be competitive compared to using vessels constructed entirely from polymeric materials such as PTFE and PEEK (polyetheretherketone), since high enough temperatures and pressures are achieved for most routine sample digestions. However, the steel vessels could offer other advantages that might be useful for specific applications, such as for reactors in chemical syntheses where the monitoring of parameters is of importance in the study and control of the chemical processes. The following features can easily be implemented using these vessels: high strength (therefore high pressures), accurate measurement of forward and reflected power (with possibilities to implement on-line tuning), temperature and pressure measurement and feedback control, introduction of gas and external pressurization, and stirring. Compared to vessels constructed from polymeric materials with relatively thick walls, the steel vessels cool faster and can be force-cooled by using a refrigeration coil around the steel structure or by using a Peltier cell. A combination of external heating (isothermal heating through the use of resistance coils) and microwave heating is also possible. Finally, since such structures can be designed with high strengths, reactors of larger capacities than are presently used in laboratories could be made. Such reactors could find applications in fine chemical manufacturing, where the volumes of the materials to be processed are relatively small.

It is also suggested that the monitoring of the reflected power in such systems could provide additional information on the changes that occur during a chemical reaction, though further work needs to be done on this interesting aspect.

CHAPTER 8

EQUIPMENT FOR MISCELLANEOUS MICROWAVE APPLICATIONS

In this chapter, equipment is described in each of the sections 8.1 to 8.6 for a range of microwave applications.

8.1 A microwave oven with temperature control for laboratory application

The aim of this work was to construct a general purpose microwave oven for laboratory applications including chemical reactions in pressure vessels (for organic and inorganic reactions), drying of materials, and the possibilities of performing reactions under reflux and with temperature monitoring and control.

For this particular requirement, it was simpler and more cost-effective to modify an existing commercial oven than to build the cavity. The chosen oven was rated at 800 W, was fitted with a turntable and was microprocessor-controlled. The original magnetron and its high-power supply as well as the safety interlock system and the turntable mechanism were used.

The modified oven is shown in Figures 8.1 and 8.2.

Four metal ports were fitted to the cavity, as described in Chapter 3, for extraction of the vapours from the cavity One port was specifically designed for temperature measurement using an ungrounded K-type stainless steel shielded thermocouple probe of 3 mm diameter (Figure 8.1). The thermocouple was grounded to the cavity using a pressure fitting on the thermocouple probe and a threaded cover on the cavity port. This ensured that there was no arcing and that no microwave leakages occurred.

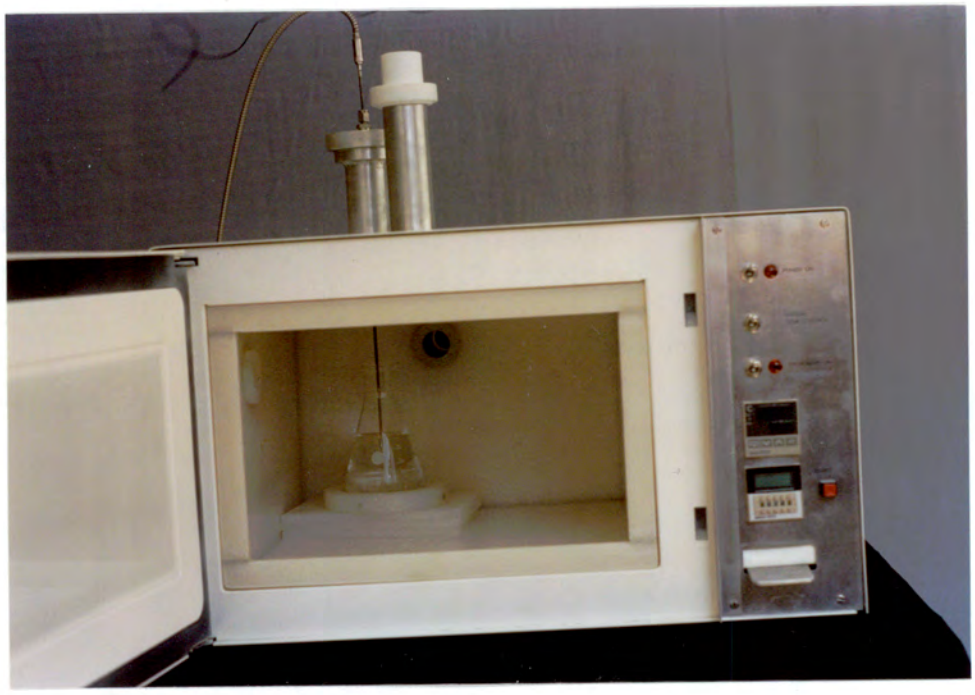


Figure 8.1 The modified microwave oven showing the polypropylene liner, two ports on the top and the thermocouple probe.

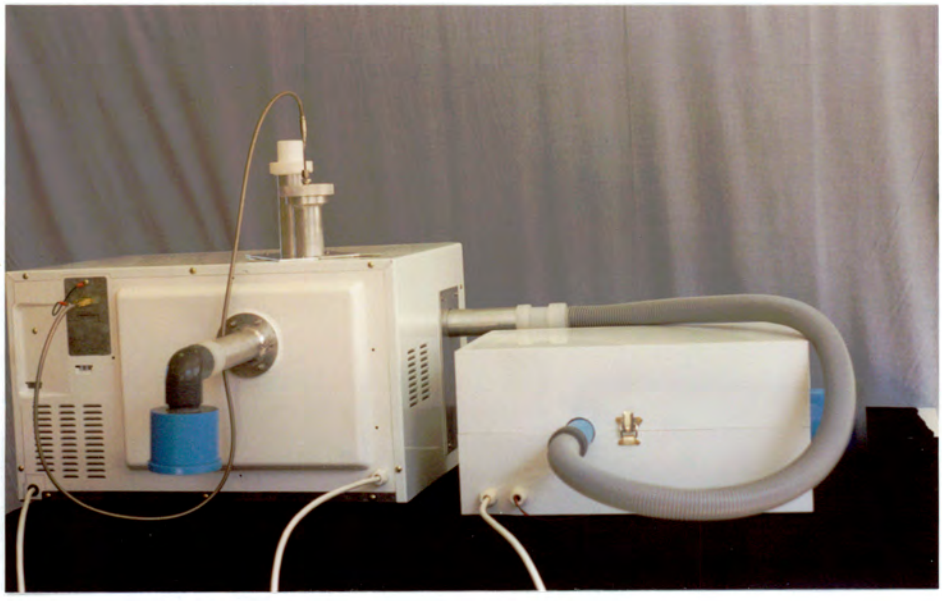


Figure 8.2 Back view of the modified oven showing all the ports, connection to the extraction system and the thermocouple connnection.

The cavity was lined with polypropylene as described in Chapter 3 and the same extraction system was also used. The ports were lined with polypropylene and one additional port liner was made of PTFE for use in experiments where the reactor inside the cavity was connected to an external device (*e.g.*, a reflux condenser) and where the temperatures were relatively high. The glass turntable was replaced by a polypropylene turntable. A separate filament transformer was built for the particular magnetron and fitted. A mode stirrer was fitted in the top of the cavity, between the cavity wall and the polypropylene liner. The mode stirrer was rotated using a small electric motor of the same type used for the turntable. The microprocessor was removed and replaced by a commercially available timer (Omron model H3CA-A) and temperature controller (Omron model E5CW) which were built in the control panel. A heavy duty contactor was used to switch power on and off to the high voltage circuit, with a solid state relay for controlling the high voltage transformer when using feed-back control of temperature (*i.e.*, by pulsing the magnetron). The circuit diagram is shown in Figure 8.3.

In this oven, control could be manual (*i.e.*, no temperature control, and manual operation through the timer) or through the programmed temperature control (*i.e.*, at set maximum temperature). The temperature was monitored on the temperature controller display and on a chart recorder if necessary.

When required for laboratory sample drying, the polypropylene liner could be removed, the turntable fitted and the extraction system connected normally through one of the ports.

Many reactions in glass tubes could be carried out at atmospheric pressure by introduction of the tube through the port in the top of the cavity. This enabled condensers and scrubbers to be fitted externally, which allowed continuous addition of reagents to the vessel.

The oven could also be used for pressure reactions in PTFE vessels and a Pyrex-glass reactor similar to the one shown in Chapter 5.

The use of the thermocouple arrangement was found to perform well provided that the temperature port cover and the probe were well grounded. No self-heating or arcing were experienced.

This simple modification of an existing oven using available hardware offered the necessary safety features and was found adequate and useful for many laboratory experiments.

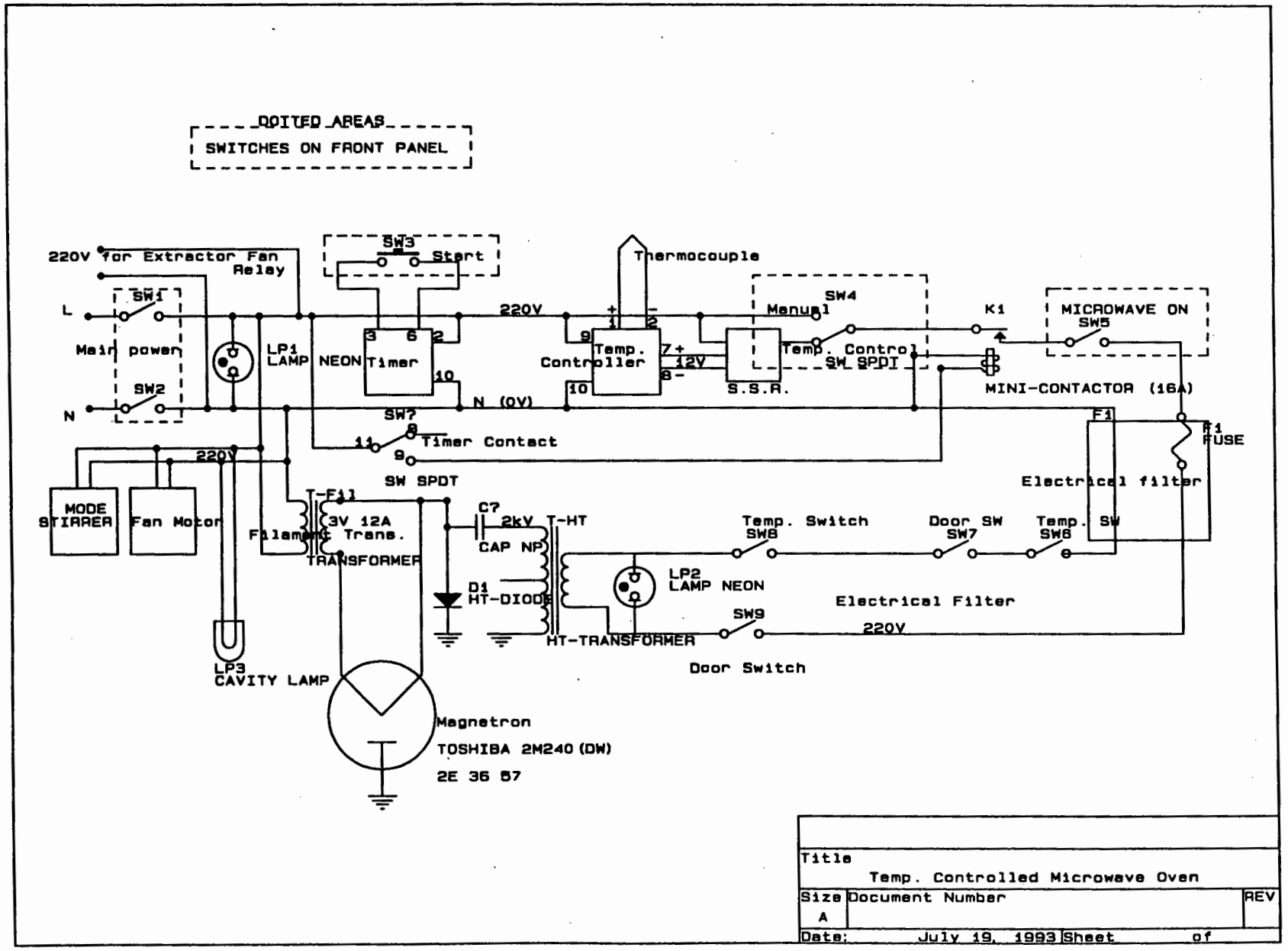


Figure 8.3 Circuit diagram.

8.2 Design of a cylindrical reactor

The design of the cylindrical applicator (Chapter 5) was well suited for heating relatively large loads. The limitations of the cylindrical applicator were the low power and the problems associated with tuning. In this new design, a 1.2 kW source was used to provide faster rates of heating and on-line tuning was also incorporated.

The applicator is shown in Figure 8.4. A transition from rectangular waveguide to circular waveguide (102 mm internal diameter) was fabricated using brass and copper tubing (see Chapter 7). A flange and a cover containing the ports were available at the top of the cavity for introducing the reactor and connecting the thermocouple and other devices. The bottom of the cylindrical cavity was perforated and a fan was used to pass air into the cavity to cool the load. Three tuning screws on the rectangular waveguide section were used for matching of the various loads. The Pyrex-glass container (Chapter 5) was used for the experiments described below.

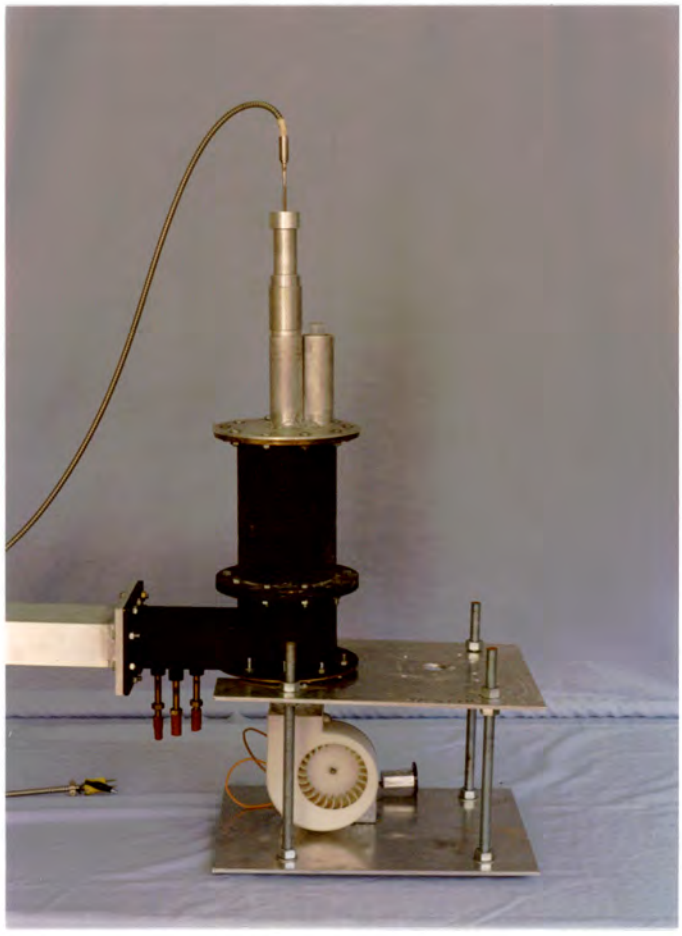


Figure 8.4 Cylindrical reactor with thermocouple probe.

A heating curve as well as the measured reflected power for a load of 200 ml of water are shown in Figure 8.5. In this case, the cavity was tuned at a temperature of about 70 °C prior to the measurement. The forward power was set at 1000 W. As can be seen a good match was maintained up to the boiling point and a sharp increase in reflected power occurred during boiling as a result of the change in impedance of the load. However, this power remained low (average 65 W) during the boiling cycle. A calculation of the power absorbed by the load during the heating cycle (using the temperature rise from room temperature to 70 °C in Figure 8.5) gave a value close to 1000 W as was expected from the low reflected power.

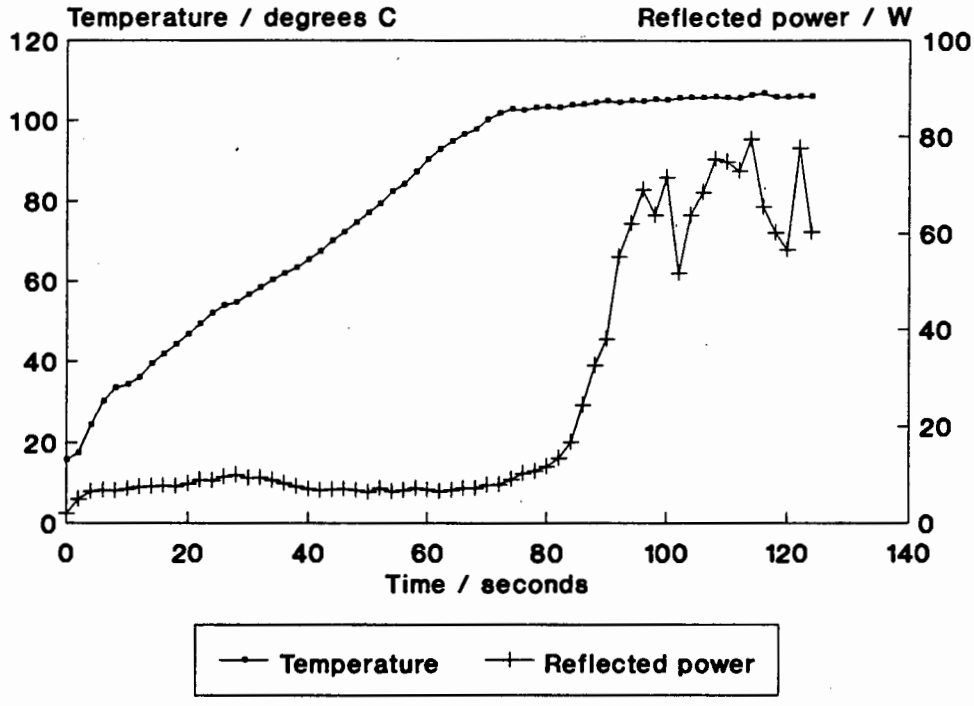


Figure 8.5 Heating and reflected power curves for 200 ml water with a forward power of 1000 W and tuning done at 70 °C.

The experiment was repeated with 200 ml of ethylene glycol with the tuning unchanged from that used for the water above. The heating curve is shown in Figure 8.6. The reflected power stayed low until a temperature of about 110 °C, after which a relatively sharp increase occurred and rose to about 280 W during boiling. This change of reflected power was again a result of changes in the load impedance as the liquid load bubbled during boiling. The ability to provide on-line tuning in this applicator is illustrated in Figure 8.7, where for a load of 200 ml of ethylene glycol tuning was manually done during the heating cycle. The reflected power could be kept at less than 20 W even during boiling.

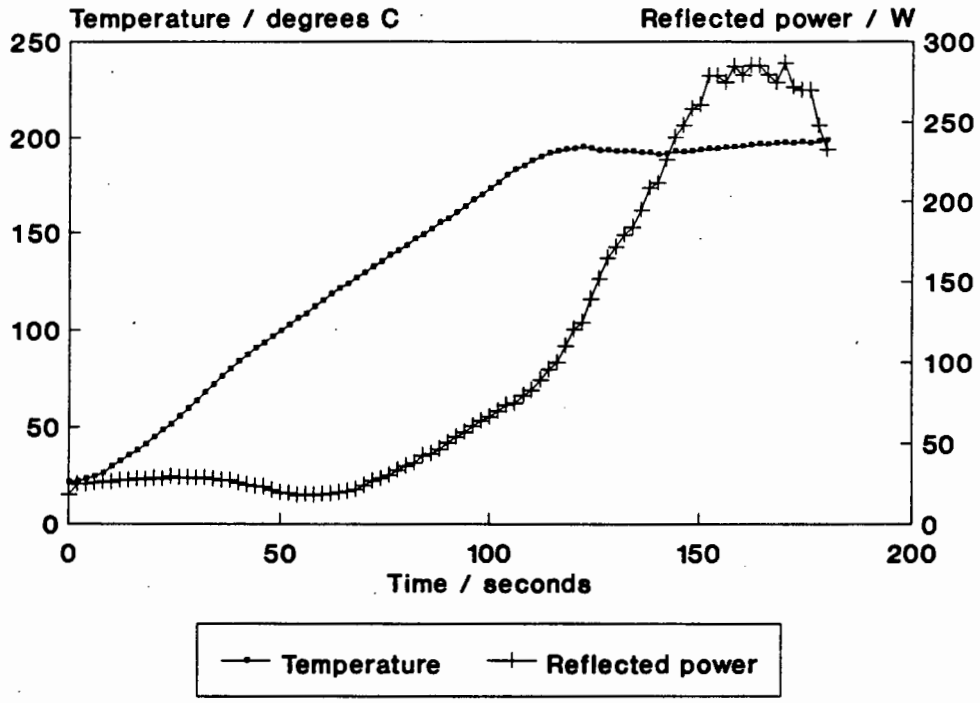


Figure 8.6 Heating and reflected power curves for 200 ml of ethylene glycol with a forward power of 1000 W and tuning done at 70 °C with water.

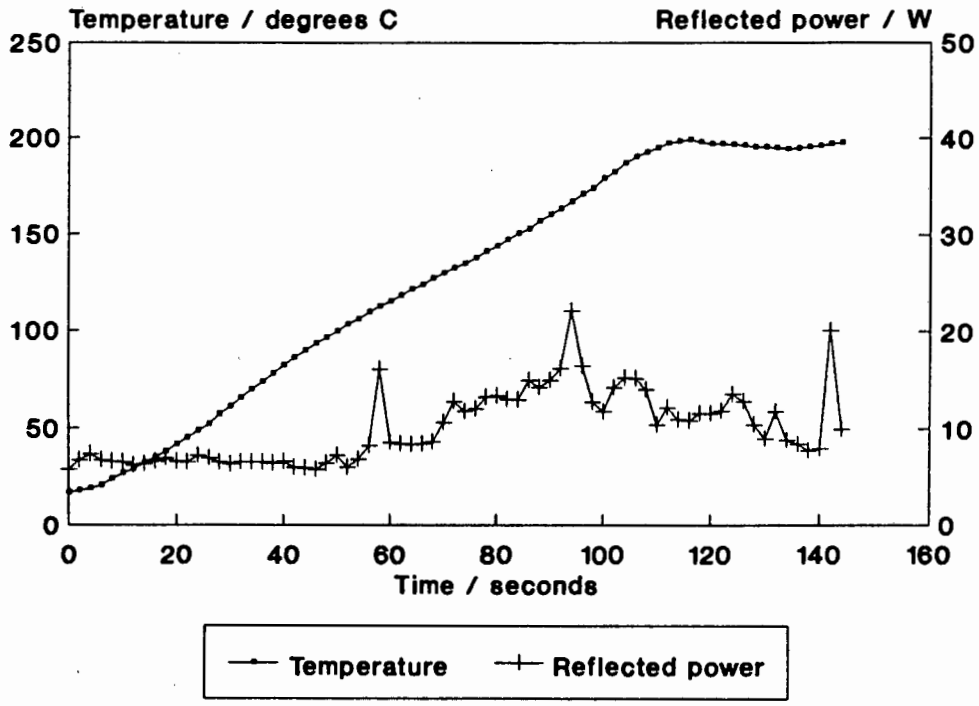


Figure 8.7 Heating and reflected power curves for 200 ml of ethylene glycol with a forward power of 1000 W and on-line tuning.

For these relatively large loads, this type of cavity is very efficient and the initial tuning for different processes is easily achieved with the tuning screws. The applicator is also easily constructed, compact and can be easily placed in a fume hood while the generator can be kept at a distance to avoid exposure to corrosive or other chemical fumes.

8.3 Waveguide system for on-line heating of liquids

Microwave on-line heating of fluids has been used in the laboratory for sample digestion and organic synthesis (Chapter 1). Most of the work reported by other authors has been done in microwave ovens. The microwave oven, although efficient in heating the flowing liquid, suffers from two disadvantages. Firstly, in most ovens control of the power to the load is achieved by pulsing. Thus uneven heating of the flowing liquid occurs as the magnetron is operated at full power and the average power is controlled by varying the on to off time. The control of temperature can be achieved by using a dummy load (to reduce the power absorbed by the liquid in the coil) and by adjusting the flow rate. However, a flowing dummy load has to be used to prevent the change of impedance with temperature which results in a change of heating rate of the flowing liquid in the coil. The other disadvantage of using a microwave oven is that it is very bulky and therefore difficult to integrate into an existing experimental setup.

Two applicators that were investigated for laboratory applications are briefly discussed below.

A small applicator is shown in Figure 8.8. The cylindrical section which terminated the waveguide section contained a thick-wall PFA coil of 2 mm internal diameter tubing supported on a PTFE cylinder. Three tuning screws were used to obtain a perfectly matched system with high efficiency and good temperature control. A variable speed peristaltic pump was used to pump the liquids through the coil. For example, phosphoric acid flowing at a rate of 9 ml min^{-1} could be maintained at 130 $^{\circ}C$ with about 90 W forward power.

The second applicator was designed for longer residence times using much longer tubing lengths that were coiled and supported on a glass tube inside a cylindrical waveguide. The applicator was positioned vertically so that the liquids could also be fed by gravity (Figure 8.9). Tuning was achieved using a circular plunger at the bottom of the cavity. With a coil length of approximately 6 m and a flow rate of 65 ml min^{-1}, water could be heated at a temperature of 50 $^{\circ}C$ with 200 W forward power. This applicator was used for a project that investigated the leaching of metals from power-station ash. The ash was mixed with the acid and the slurry was kept homogeneous in an ultrasonic bath. It was then pumped through the coil for heating. It was thus possible to investigate easily the effect of temperature on the leaching efficiency of certain metals.

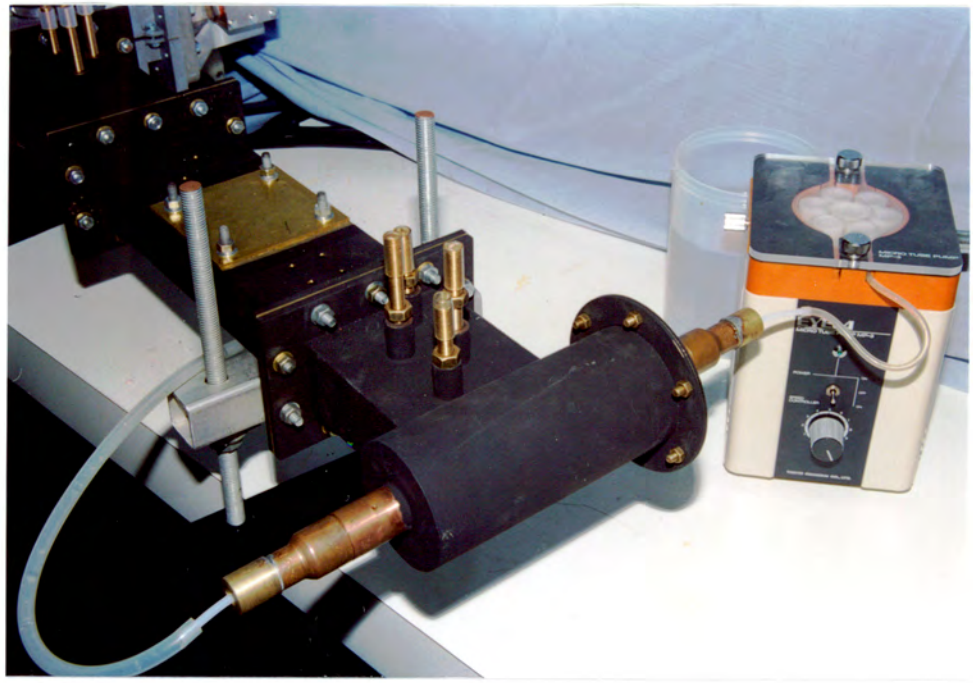


Figure 8.8 Applicator for on-line heating of liquids in 2 m PFA coil.

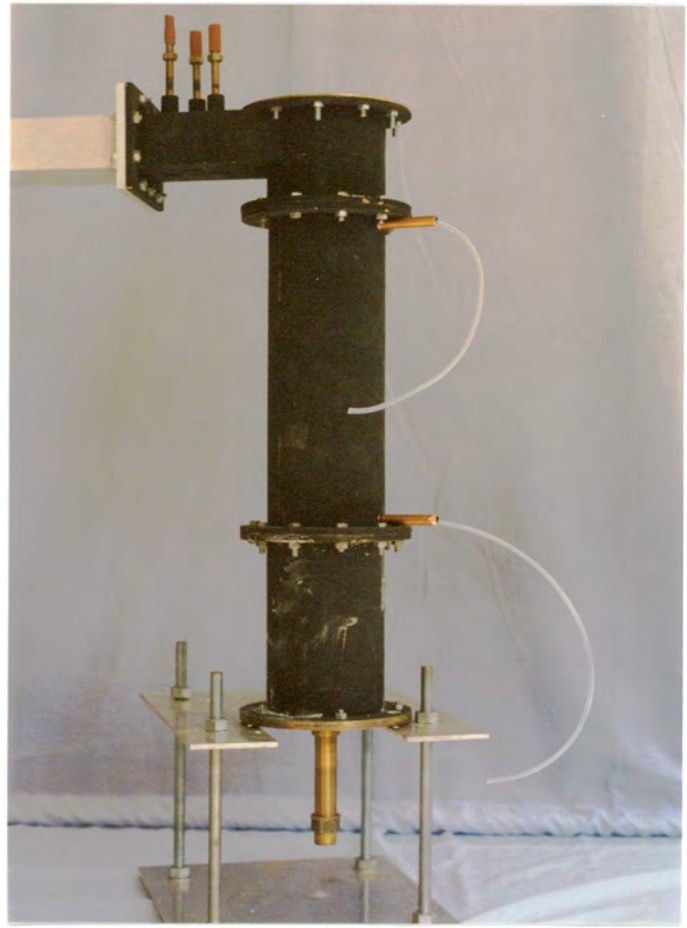


Figure 8.9 Cylindrical waveguide applicator for on-line heating.

These on-line microwave heaters are easy to tune and extremely efficient. They are also compact and easy to build. The important practical advantage of using such applicators is that the microwave source can be placed at any distance from the area where the heating is required. A case at hand where this approach will be useful is in the on-line heating of solutions being aspirated into the nebulizer of an ICP-AES spectrometer. Due to the limitation in space and the requirement that the interface between the heater and the nebulizer be as short as possible, a waveguide system as in the first example above would be used and the microwaves would be fed to the rectangular waveguide by a coaxial line so that the generator could be positioned away from the sample injection section. In this case the power required is about 50 W. Many such applications could be found for low-power on-line microwave heaters in the laboratory.

8.4 Cavity for gas discharge experiments

The aim of this study was to set up facilities to carry out experiments on gas discharges and in particular to investigate certain reactions with singlet oxygen species that are generated in the oxygen discharge (Chapter 1).

A simple cavity was fabricated for generating discharges in gases (Figure 8.10). A variable iris coupler and a plunger tuner were used to optimize the coupling of the microwaves into the gas. Four cylindrical ports of 42 mm internal diameter were positioned in each face of the aluminium waveguide section. The one at the top was used to measure the intensity of the gas discharge using a large (40 mm diameter) silicon diode detector, or the temperature of the discharge tube was measured using a infrared pyrometer which was directed at the centre of the gas discharge tube through the port. Ducting for a fan was connected to the bottom port, so that the discharge tube could be cooled during operation if necessary. The gas discharge tube made of Pyrex-glass or quartz (15 mm internal diameter) was centrally positioned between the two side ports in the waveguide. One side of the tube was connected to a needle valve, a gas flow meter and a cylinder of gas. The other end was connected to a Pyrex-glass reactor and a manifold with a vacuum gauge, three cold traps, and a vacuum pump.

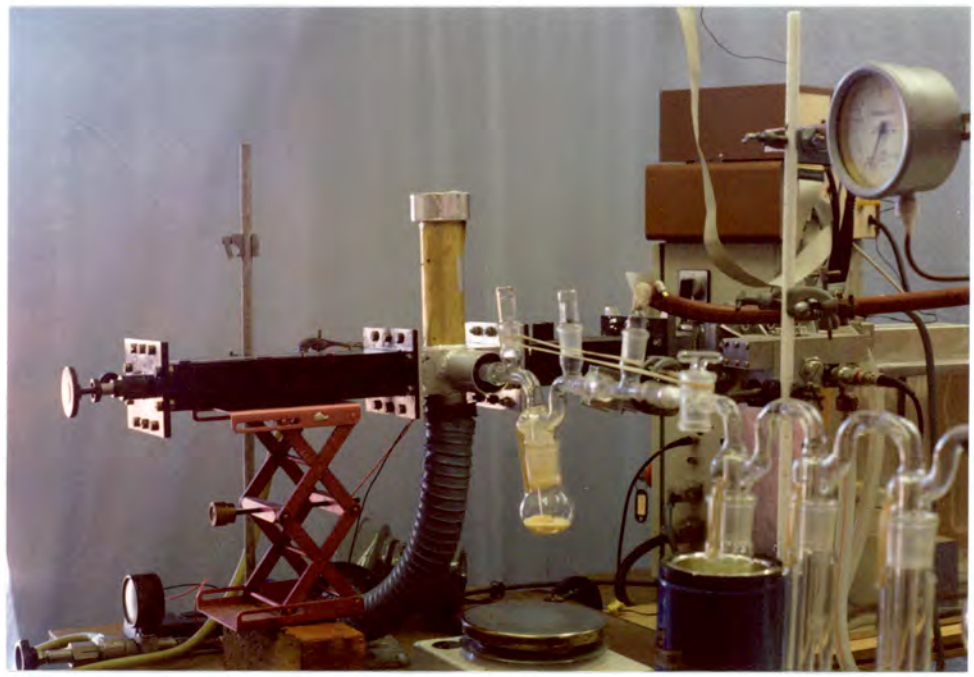


Figure 8.10 Microwave cavity for gas discharge, showing vessel for reaction with singlet oxygen (centre) and manifold traps leading to vacuum pump (right).

The cavity was used to generate discharges in nitrogen, argon and oxygen. The effects of pressure (1 to 20 mm Hg), coupling iris size, position of plunger tuner and magnitude of forward power (up to 1000 W) were studied for each gas discharge. The optimum conditions could then be found for each gas discharge. Depending on the operating conditions, a forward power as low as 50 W was sufficient to initiate and maintain the discharge. However, under some conditions much higher powers were necessary to initiate the discharge, after which the power could then be lowered. The nitrogen and argon discharges were found to behave similarly while the oxygen discharge required higher powers and was more sensitive to the operating conditions. Most of the work concentrated on the generation of singlet oxygen and the design of a suitable reactor and a manifold to carry out oxidation reactions. A vacuum pump filled with Fomblin oil (perfluoro polyether) was used for the oxygen discharge experiments to avoid a possible explosion that could occur when using normal hydrocarbon vacuum oil.

Biological samples that were placed in the glass vessel downstream from the discharge tube (visible in Figure 8.10) were used to indicate the formation of the singlet oxygen by turning brown as the oxidation occurred. The operating conditions (especially the gas flow rate) were found to be critical for the generation of the singlet species. At a pressure of 2 mm Hg and a forward power of 400 W (reflected power of 90 W), complete oxidation of filter paper and other fibres was achieved in about 5 minutes.

The present cavity and tuning facilities have been found to be versatile for investigating microwave gas discharges and the configuration of chemical reactors using excited oxygen species. The four ports allow discharge tubes of large dimensions (40 mm) to be used either in a vertical or horizontal position to suit various configurations of chemical reactors. On-line tuning is easily achieved for the different tubes and operating pressures. No such cavity is commercially available and those mostly used for spectroscopic studies or small scale gaseous reactions (*e.g.*, coaxial cavities as supplied by Opthos Instruments Inc., USA) are of small dimensions and of low power and do not offer the versatility for the general investigations of chemical reactions.

8.5 Development and evaluation of a gas thermometer for operation in the microwave field

Fiber-optic systems are undoubtedly the ideal tools for measurement of temperature in a microwave field since the probes are transparent to microwaves and therefore no problems with arcing or self-heating occur. The probes are also of small dimensions and are relatively flexible and are therefore easy to place in the load. However, these devices are very expensive and the probes are relatively fragile. Furthermore, many chemicals could destroy the probes and indirect ways have to be used to monitor the temperature in such chemicals.

The use of thermocouple probes has been adequately demonstrated in this work. Their advantages are that they are readily available at low costs and the associated electronics are available or easily constructed. . The probes can be designed in many configurations (*e.g.*, stainless steel shielded) and they are robust. They can be used at low and high temperatures. One disadvantage, however, is the problem of corrosion when operating in acidic or strongly alkaline solutions. While PTFE shielding is effective, it has temperature limitations of about 250 °C for prolonged exposure times and about 350 °C for short times. It has also been noticed that acids do diffuse through the thin sheath after long exposures at high temperatures and cause corrosion of the thermocouple probes.

Other useful devices for measuring temperatures in microwave applicators are the infrared pyrometers which are widely used for high-temperature measurements, for example in ceramic processing. These instruments are generally expensive and are limited to surface temperature measurements only.

A fourth type of temperature measurement system is the gas thermometer which is based on the pressure generated by a gas when heated in a fixed volume. Karmazsin *et al.* reported on the application of such systems for microwave heating [KAR84]. Recently, Bond *et al.* have shown further applications for gas thermometers [BON92].

It was felt that these devices could be of use in specific applications where the thermocouple probes were inadequate.

The gas thermometers were constructed from Pyrex-glass capillary tubes (internal diameter 2 mm, external diameter 8 mm) as shown in Figure 8.11. A Wika model 891.14.525 pressure transducer (maximum 2.5 bar) was attached to the glass capillary by means of a compression

fitting. The electronics for the transducer were designed so that the output from the transducer (mV) could be adjusted using a potentiometer.

Figure 8.11 A gas thermometer.

Probes with glass bulbs of different volumes (same cross-section but different lengths of the bulb) were constructed and their sensitivities were compared. In this experiment, the bulbs were immersed in a water-ice mixture and the transducer connected. The potentiometer was used to set the mV reading to zero. The response of four probes with different volumes (internal bulb diameter 10 mm; lengths: 20, 30, 40, and 50 mm) were compared by immersing the bulbs into an ethylene glycol bath that was temperature controlled. The mV readings of the gas thermometers were recorded during slow heating and cooling of the bath using a thermocouple probe to measure the temperature accurately. The results are shown in Figure 8.12. The larger bulb showed better sensitivity, but in all cases the calibration curves were not linear. The non-linearity can be attributed to the non-ideal behaviour of the gas (air) and a small expansion of the glass at the higher temperature. However, the responses were found to be very reproducible. In order to achieve a more linear response, the thermometer was closed at atmospheric pressure under a dry nitrogen atmosphere. The calibration curve is shown in Figure 8.13 and was almost linear.

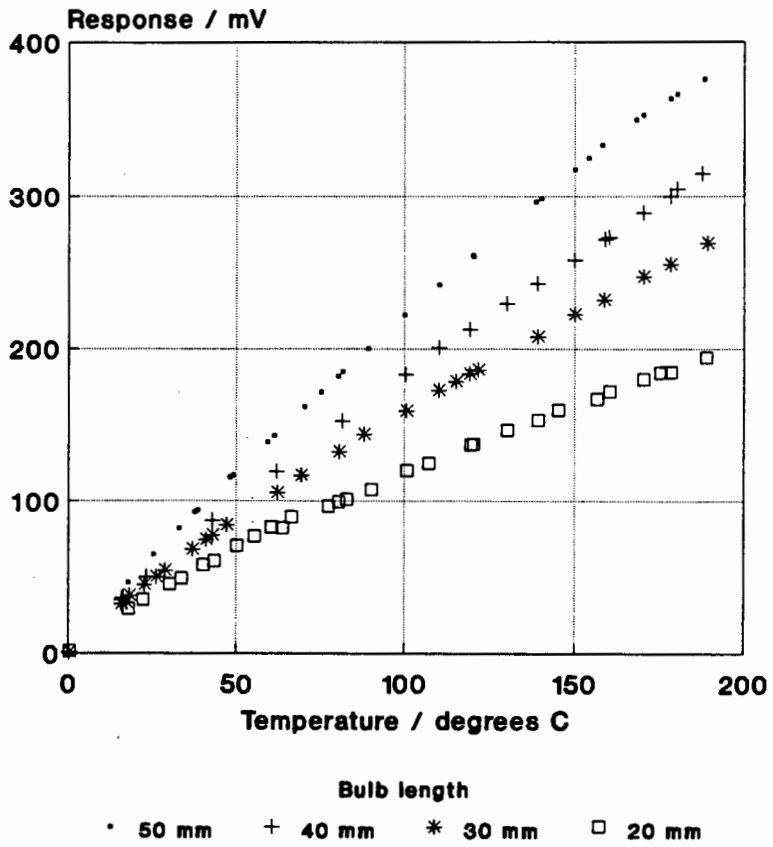


Figure 8.12 Calibration curves for four thermometers with varying bulb lengths.

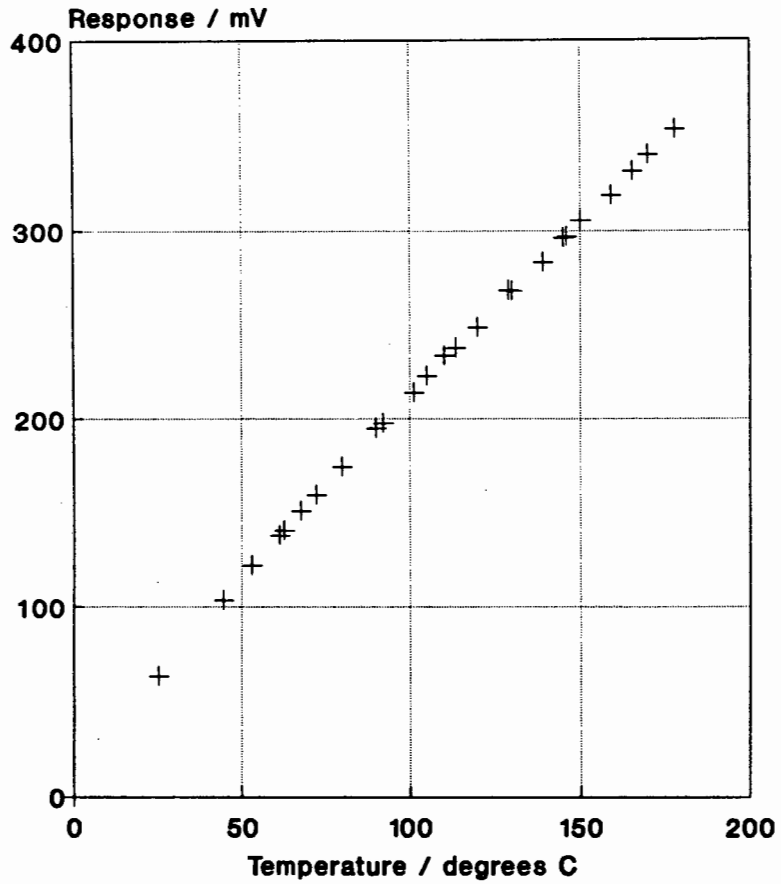


Figure 8.13 Calibration of 50 mm thermometer closed under nitrogen atmosphere.

Although the response of the gas thermometer was not as good as that of a thermocouple, these devices were found to perform well in liquids. The important condition for accuracy was that the whole bulb had to be completely immersed in the liquid. A linear response curve is desirable so that simple electronics can be used for monitoring the temperature, but this condition is not necessary if a PC is used as a monitor. The equation for the calibration curve (Figure 8.13) was determined and the parameters were used by a simple Turbo Pascal computer program to display the temperature in $^{\circ}$C. The program used for controlling the microwave equipment (Chapter 4) was adapted so that the gas thermometer could be used to monitor and control the temperature. The result for an experiment where a gas thermometer was used to control the temperature is shown in Figure 8.14. As can be seen at the beginning of the heating curve, the response is not as fast as a thermocouple but at the higher temperature, good control is obtained.

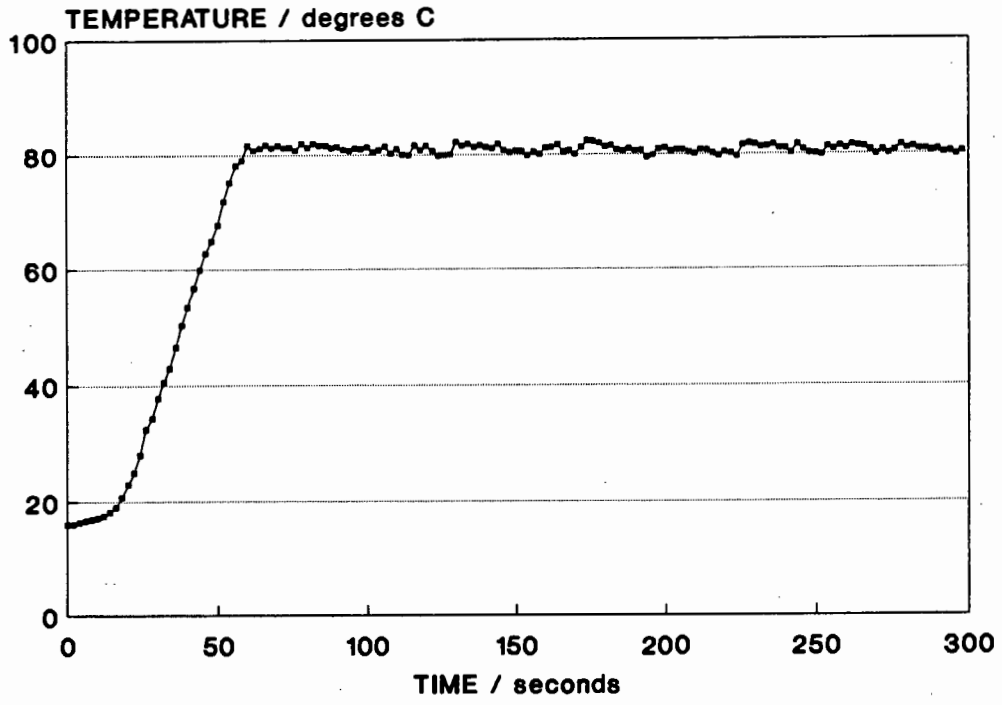


Figure 8.14 Control of temperature at 80 °C with a gas thermometer.

The gas thermometer has proved to be a useful tool, adding to the range of instruments necessary for investigations of microwave heating in the laboratory. The low-pressure transducers necessary for these thermometers are readily available and are inexpensive. As suggested by Bond *et al.* [BON92], the gas bulb of the thermometer can be integrated in the glassware (*e.g.*, reactor) that is used for the microwave heating of solutions.

8.6 Development and evaluation of a moisture meter for powders and granules

8.6.1 Introduction

Moisture content measurement is an important requirement in the chemical laboratory and the manufacturing industry. The traditional method of moisture content determination is to heat the material in an electric oven to drive off the water. The moisture is found by mass loss. Microwave ovens and infrared heaters have been used to speed up the drying process (where mass loss is also obtained by weighing before and after the drying process). The techniques based on mass loss measurements is precise, accurate and simple but their limitation is in the long time necessary for the drying process. Although infrared radiation and especially microwaves do speed up the drying process considerably, the total time taken for the measurements are often too long for many quality control procedures. Some commercial instruments using infrared radiation and microwaves have a built-in balance to monitor the mass loss during the drying cycle, and thus the instrument calculates directly the percent moisture content. These instruments are relatively delicate and they are normally used in laboratories. Their use could be problematic in some industrial environments and they are not normally portable instruments.

Other techniques that are used for moisture content measurements include the optical devices operating in the infrared region where the measurements are made by reflection of the electromagnetic waves from the surface of the sample. Such commercially available systems provide a reading instantaneously and do not perturb the sample. They have the added advantage that non-contact on-line measurements can be performed and therefore are suitable for monitoring the moisture content of flowing materials (*e.g.*, on a conveyor belt) in industrial processes. One disadvantage of these systems is that they are relatively complicated and are therefore expensive. The major disadvantage with infrared moisture measuring systems is that the reflection mechanism only measures moisture content at the surface.

Several designs of moisture meters operating at microwave frequencies have been reported previously [TIU80,SHI80,CHA80,CUT91,KHA92,NEL92]. Kraszewski has reviewed the principles of operation and the designs of the various types of measuring techniques [KRA73,KRA80]. Microwave energy is able to penetrate samples to a depth of several centimeters and in contrast to infrared techniques the measurements are not limited to the surface.

The aim of the present study was to design and evaluate a simple low cost instrument for off-line measurement of the moisture content of powdered and granular materials in the range of 1-15 % moisture. Three other desired requirements were applicability to a relatively small sample size (about 20 g), ruggedness and portability.

8.6.2 Construction of the moisture meter

Based on the above criteria, it was decided to use the method of microwave absorption and to use a length of standard waveguide (R100,WG16) as a suitable cell to hold the material. A suitable frequency for this application was 10 GHz (X-band), since the waveguide size was of a suitable geometry for the required sample size, and standard sources and detectors were easily available and resonably priced. The attenuation was about 30 dB at 15 % moisture in kaolin, which was a good-enough dynamic range to achieve reasonable accuracy.

A 100 mW Gunn diode (model MA-86569) operating at 10.525 GHz was used as the microwave source. This was modulated at 1.136 KHz to minimize mains interference. A microwave diode detector (model MA-86560) was used to measure the attenuated signal in the sample, which was amplified and filtered. Suitable power supplies for the devices and associated electronics were designed and built and the readings were displayed on a digital voltmeter [SMI92]. The output could also be fed *via* an Analogue to Digital Convertor and an interface to a PC. A layout of the system is shown in Figure 8.15.

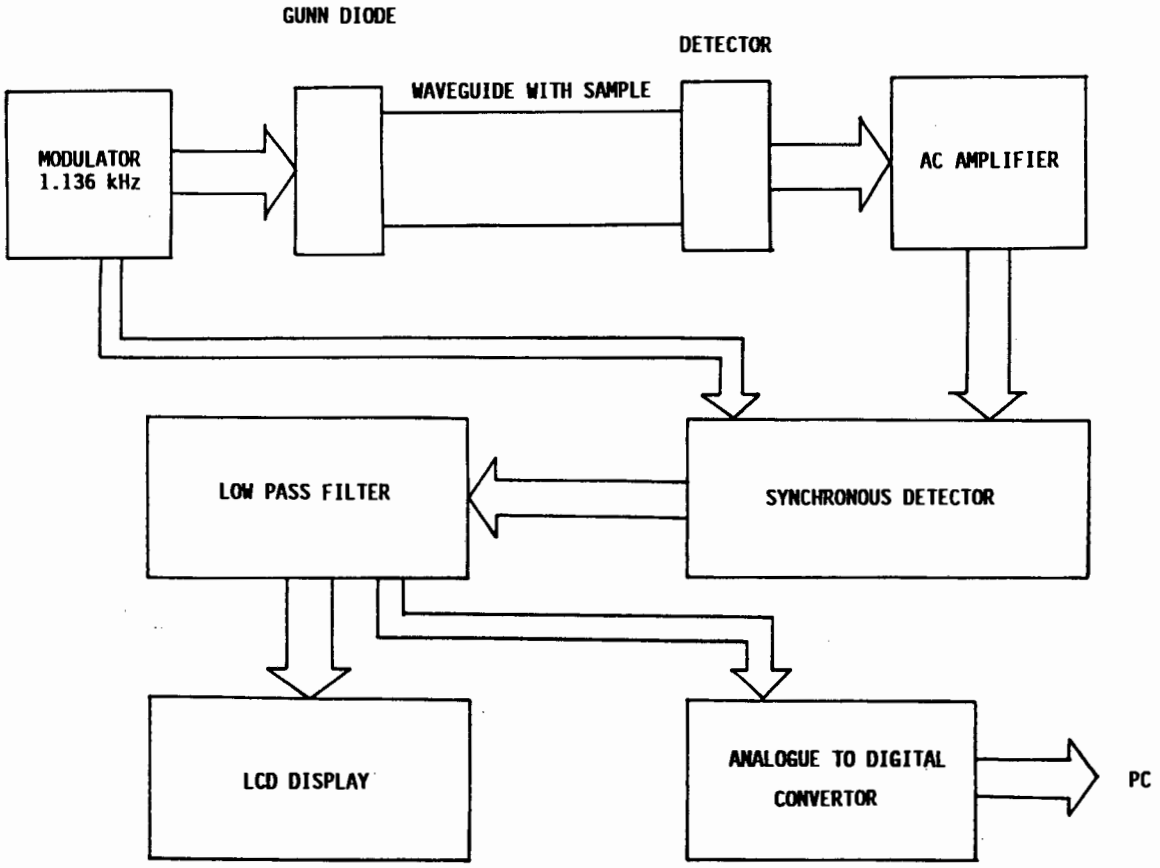


Figure 8.15 Schematic layout of the moisture meter.

A length of brass waveguide (120 mm long) with the bottom end plugged by a piece of PTFE (3 mm thick) was used as the sample cell. This cell could hold approximately 20 g of sample. After filling with the sample, the cell was inserted between the Gunn diode and the detector using spring-loaded waveguide sections connected to the two components (to ensure good electrical contact on the line). The instrument is shown in Figure 8.16.

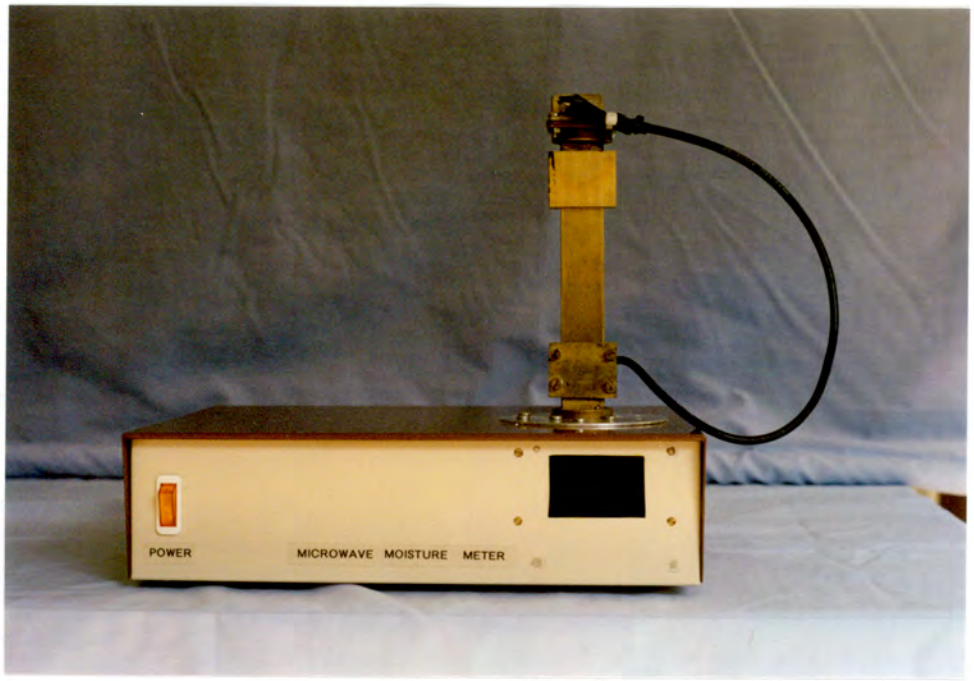


Figure 8.16 The moisture meter with the cell positioned for measurements. The vertical waveguide contains the sample, with the Gunn diode on top and the detector at the bottom.

In order to investigate the effect of the packing characteristics of materials when filling the cell on the precision of the measurements, a vibrating device was built to pack the samples in the cell reproducibly. It consisted of an electro-coil which caused the vibration of the centre core, and which was made to hammer the holder in which the cell was secured. The action (amplitude) of the device could be varied by changing the voltage to the coil. An electronic timer was used to ensure reproducible results. The device is shown in Figure 8.17.

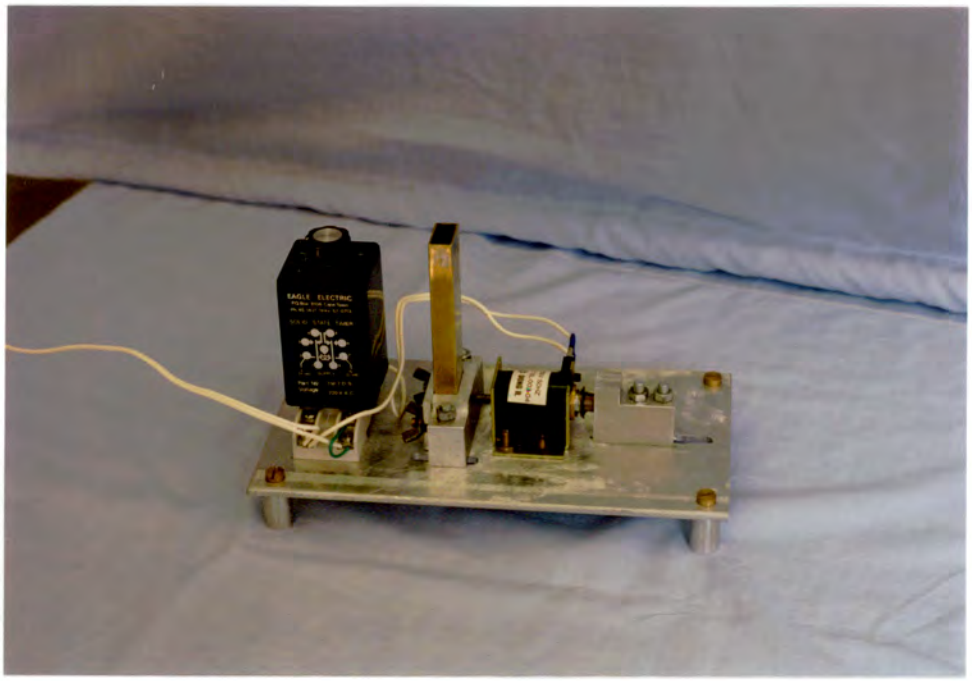


Figure 8.17 Vibrating device to pack the sample with the timer on the LHS, the waveguide in the centre and the electro-coil on the RHS.

8.6.3 Experiments and results

It was anticipated that materials of different constituents and particle sizes and shapes would have different packing characteristics that could affect the accuracy of the measurements. Two methods of filling the cell were compared. In the first method, 15 g of material was placed in the cell, which was then vibrated. It was found that the microwave attenuation through the sample at high moisture content was related to the vibration time. At low moisture contents, short times of typically 5 s were adequate for obtaining good precision. For materials with a high moisture content, the time had to be increased to typically 30 s to obtain a stable reading and the best precision. In this study a time of 30 s was therefore chosen.

In the second method, the cell was filled to the brim with the sample and the reading taken. These two tests were repeated at least 8 times using different sub-samples.

The results obtained for a few materials are shown in Table 8.1. It can be seen that better precision was obtained using the constant mass (with vibration) method although the precision worsend as the moisture content of the material increased. The effect was particularly noticeable for the finely powered Kaolin which yielded a 13% relative standard deviation when measured at constant volume. The magnitude of the readings are not directly comparable since different masses of materials were placed in the cell for the measurements used to compare the precision of analysis.

Table 8.1 Precision of measurements for the two cell-filling methods.

Sample	% moisture content	constant mass method			constant volume method		
		R[a]	σ[b]	%σ[c]	R[a]	σ[b]	%σ[c]
Molecular sieve	Dry	1414	2	0.1	1439	4	0.2
Molecular sieve	18.2	928	8	1	338	25	7
Kaolin	Dry	1442	8	0.5	1474	7	0.5
Kaolin	2	1367	5	0.4	1364	11	1
Kaolin	15	723	30	4	214	29	13
Corn-rice	3	1343	14	1.1	1301	13	1.0
Rice	12.5	1086	14	1.2	690	22	3.2
Couscous	7	1197	9	0.7	1084	12	1.1

[a] mean meter reading. [b] standard deviation. [c] % relative standard deviation.

In order to generate calibration curves for various materials, a number of samples of known moisture content were prepared. Two methods of preparing the samples were compared. In the first method, the material was saturated with water and progressively dried in an oven. Samples were taken periodically for the measurements. A sub-sample was dried completely in an oven to verify the moisture content (by mass loss). In the second method, dried material was allowed to absorb water and equilibrate slowly in a high humidity environment. Samples were periodically removed for the measurements.

The results obtained for molecular sieve by the two methods are shown in Figures 8.18 and 8.19. By comparing the two calibration curves, it is evident that the method of preparation is critical. Compared to the second method, the first method did not produce a linear relationship between the moisture content and transmission values measured in the working range. Furthermore, the first method gave poor precision. It appears that at higher moisture content, the first method does not produce a homogeneous distribution of moisture in the sample. This could be due to the relatively short time allowed for equilibration in the first method. All samples for calibration purposes were therefore prepared by the second method.

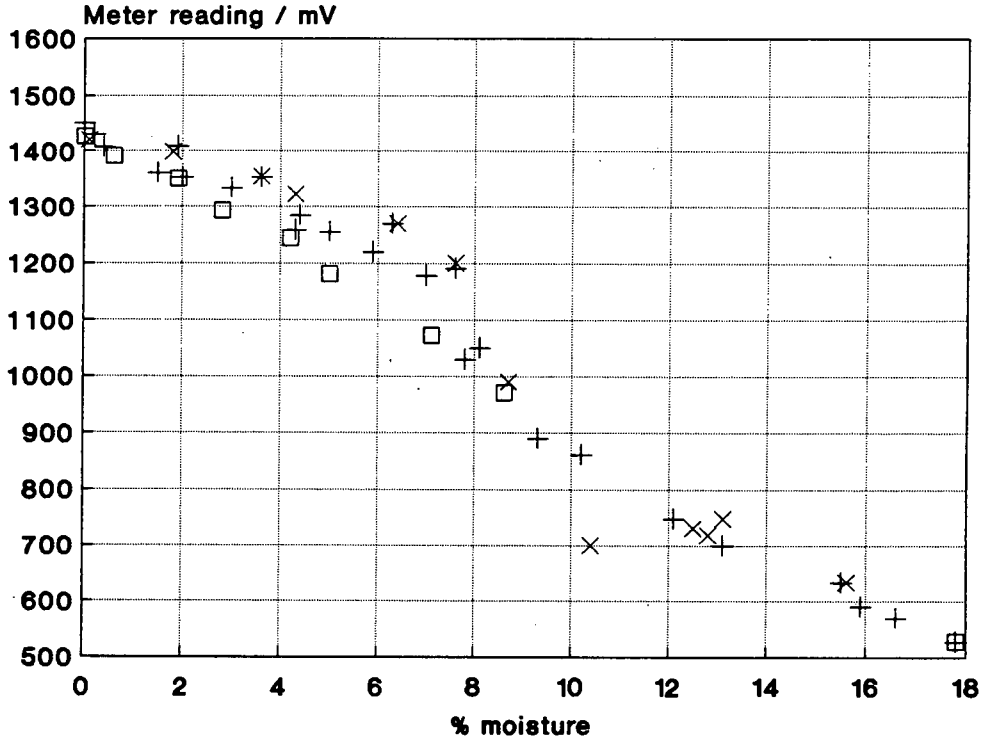


Figure 8.18 Calibration curve for molecular sieve prepared by the oven drying method.

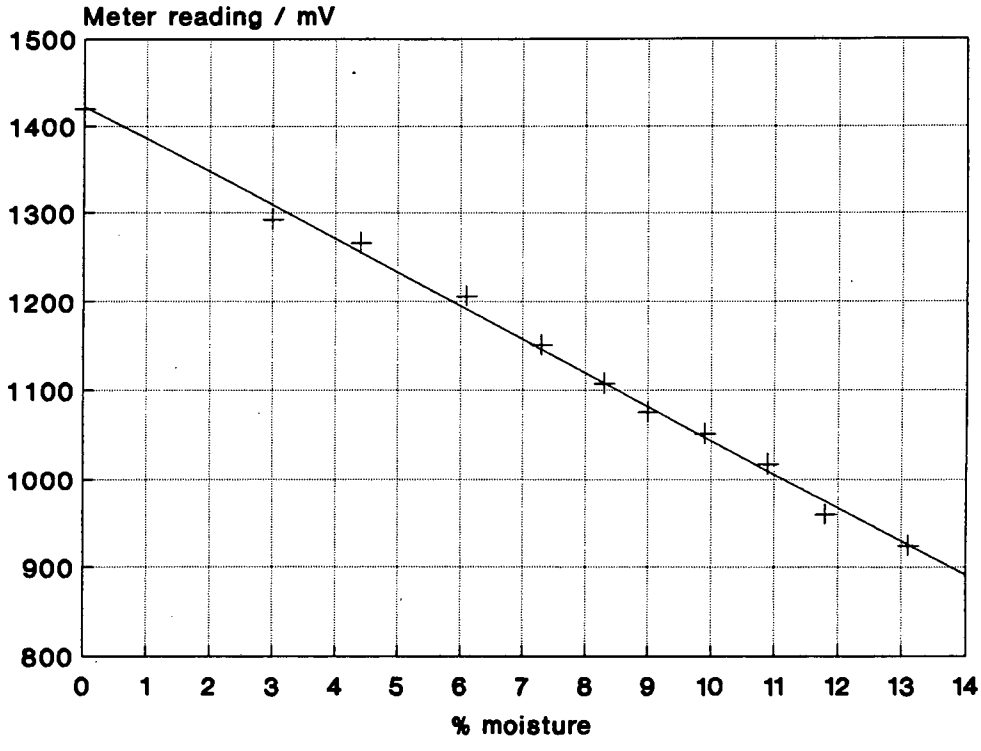


Figure 8.19 Calibration curve for molecular sieve prepared by the moisture absorption method.

A calibration curve for kaolin is shown in Figure 8.20. The samples were prepared by the constant volume and by the constant mass method. The transmission values measured over the working range did not vary by more than 3% between the two methods.

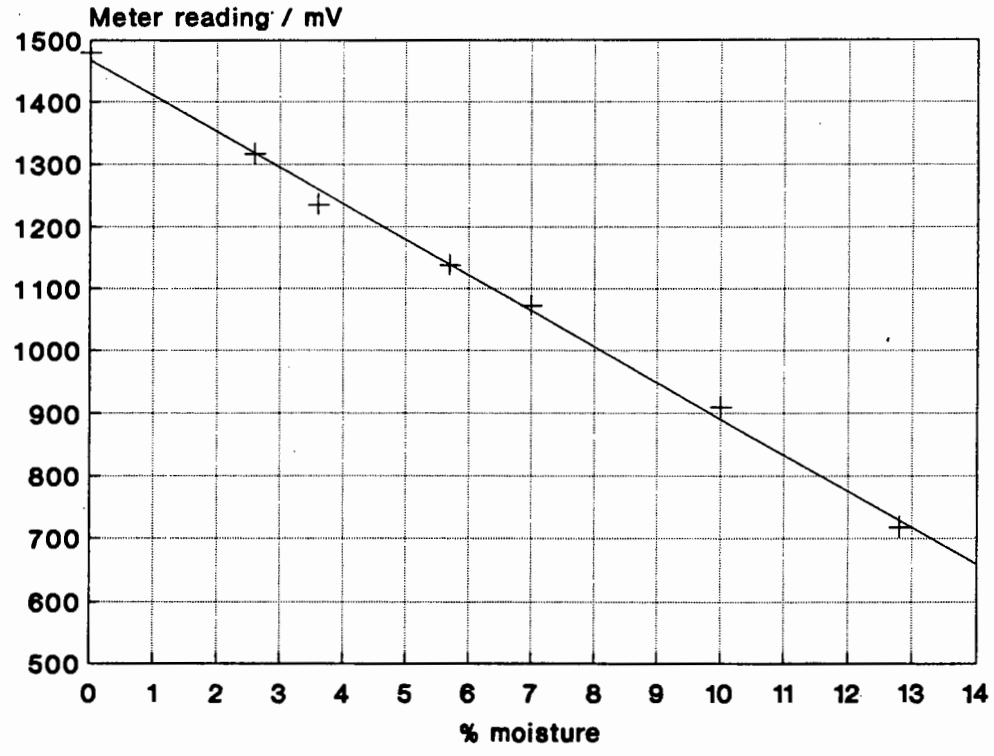


Figure 8.20 Calibration curve for kaolin.

A calibration curve for de-husked whole rice is shown in Figure 8.21. A linear relationship was obtained, as for the other materials above. The slopes of the calibration curves for kaolin and rice were similar. It was possible to use the kaolin calibration curve to measure the moisture content of rice. This is illustrated in Figure 8.22, where the accurate moisture content of rice (as measured by mass loss) is plotted against the values obtained from the kaolin calibration curves.

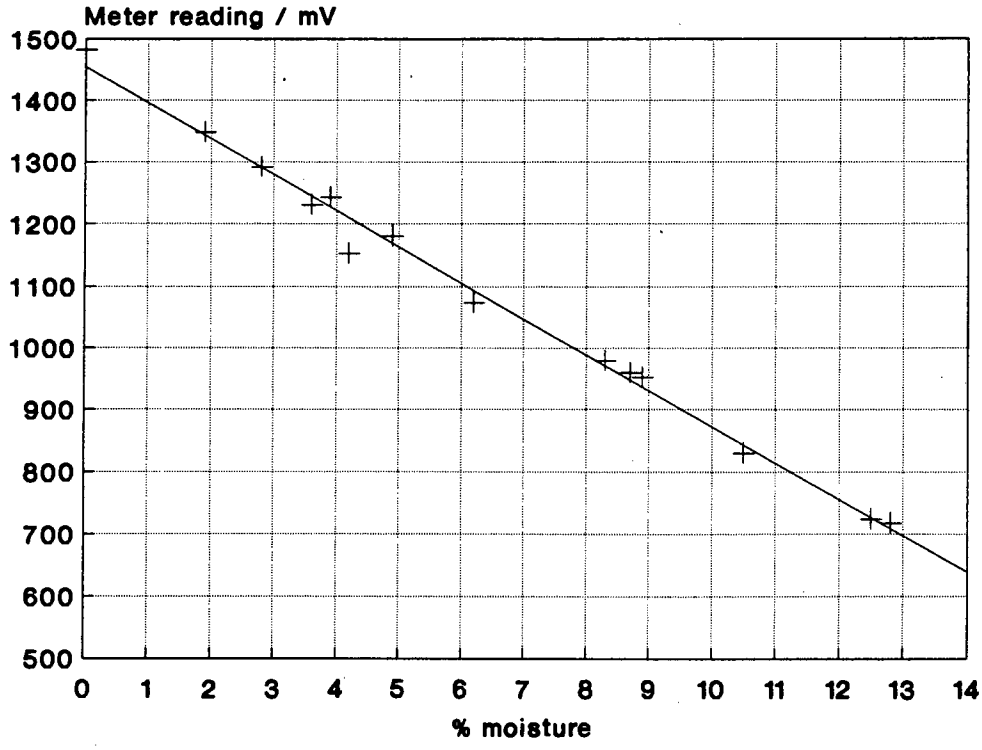


Figure 8.21 Calibration curve for whole rice.

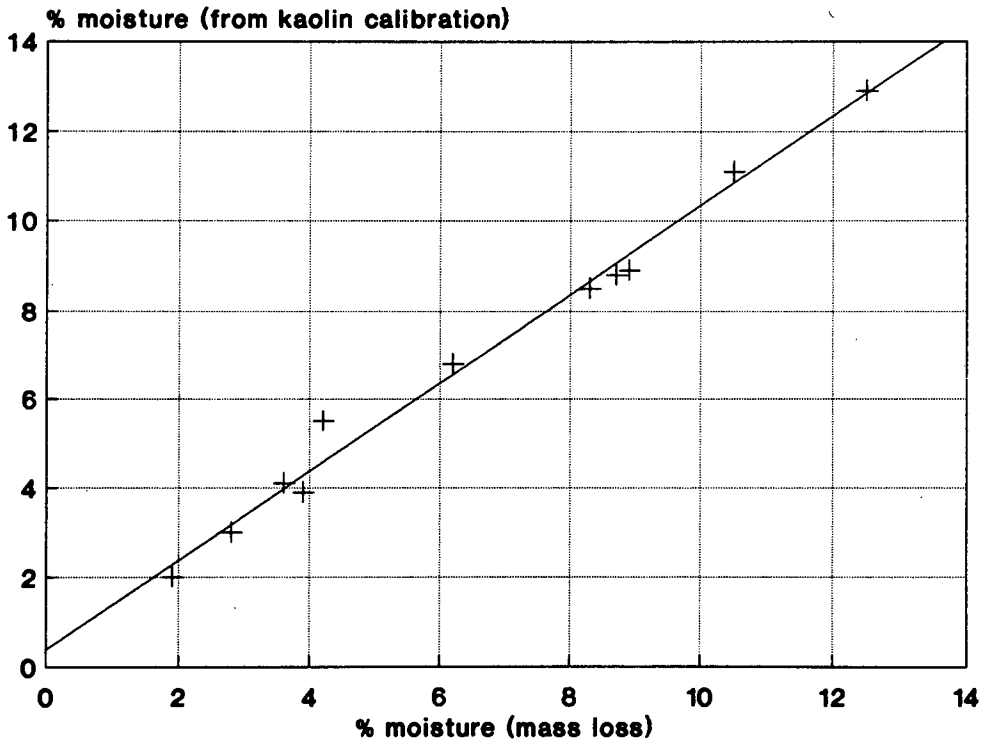


Figure 8.22 Comparison of the moisture content in rice determined by mass loss and calculated from the kaolin calibration curve using the meter.

The rice calibration curve was used to measure the moisture content of other foodstuffs (split peas, whole peas, flour, and couscous). The moisture content was also measured by mass loss. The results are shown in Table 8.2. It can be seen that accurate results were obtained for the split peas and couscous. However, poor agreement was obtained for flour and whole peas. The whole peas are very much larger than the rice grain and the flour is finely ground. However, the precision of measurement was about 1% for the flour and 5% for the whole peas, which indicated that the discrepancy between the two measurements was not due to the packing of the samples in the cell. In general, the relative permittivities of dry foodstuffs, such as grains, are expected to be similar since they contain essentially organic molecules; however other components could be present (*e.g.*, mineral salts) that would affect the microwave absorption measurements and therefore the calibration curve.

Table 8.2 Comparison between the moisture content of food measured by mass loss and the rice calibration curve.

	% moisture	
Sample	From rice calibration	By mass loss
Split peas	11.0	11.0
Whole peas	17.0	14.0
Flour	9.0	13.0
Couscous	7.5	7.7

8.6.4 Conclusion

The present instrument has been shown to give accurate and precise results for the moisture content determination of several samples. The method of presentation of the sample and generation of the calibration curve has been shown to be critical. It has been found that, although for some materials it is possible to use a calibration curve drawn from a different material, in practice each material should be calibrated independently.

The instrument is simple, easy to use, fast, and could also be used in an industrial environment. It also has the advantage of being portable since a microprocessor can be used to store the relevant calibration curve and calculate the percentage moisture content directly.

This type of instrument is well-suited for quality control in the laboratory and on the production line where samples are collected for analysis (off-line sampling).

CHAPTER 9

OVERALL CONCLUSIONS

The objectives of this thesis have been achieved through the development of a wide range of microwave equipment for the chemical laboratory.

The designs of the pressure vessels described in Chapter 2 have proved to be sound and they are now widely used in many research and quality control laboratories in South Africa.

The modified Sharp oven (Chapter 3) is also now used in several laboratories and this simple modification has fulfilled the requirements for a safe laboratory system.

The computer-controlled waveguide (Chapter 4) has been extremely useful for very many investigations and has prompted many new applications in the use of microwaves in the chemical laboratory. Three waveguide systems have been built and are all performing well.

The problem of the limitation in sample size with the requirement for temperature control has been solved by the development of the cylindrical applicator (Chapter 5). The upgraded system using the higher power magnetron, a circulator and the on-line tuning facility (Chapter 8) has increased the potential for such applicators. A larger reactor based on this concept is presently being designed.

The investigation into the design of a suitable applicator for evenly heating several laboratory samples with the facilities to extract the acid fumes efficiently (Chapter 6) has proved to be a difficult task but has, however, helped in the development of the microwave engineering skills required for this type of work. This successful design will certainly lead to a commercial system provided a cost-effective way can be found for manufacturing the rotating choke. Such an instrument would be most useful for many routine sample digestions presently carried out in traditional heating blocks.

In Chapter 7 it was shown that a number of waveguide structures could be simply optimised for irradiating a variety of pressure vessels. These systems might be useful for automatic routine sample digestion since it is easy to introduce and remove the vessels from the applicators. Using computer control, the heating conditions are easily adjusted and reproduced. This approach should be cost-effective since low-power magnetrons are required. It was shown that it was possible to use microwaves with PTFE-lined steel vessels. The system was found to be very sensitive to the load, but adequate power transfer was achieved and the ability to tune the system for specific applications was demonstrated. Interesting observations in the change of power absorption during the heating and pressurization cycles were made. Further research is required to explain these observations. It can be appreciated that apart from providing a technology for the use of strong, durable

pressure vessels for analytical purposes, this development could also provide unique opportunities for investigating many chemical reactions in a very controlled fashion and should be attractive to chemists interested in synthesis work.

The simple modification of a commercial microwave oven with temperature control (Chapter 8) showed that this approach, as has been adopted by many researchers, can be very useful for preliminary investigations. However, better suited equipment can be designed using the more expensive industrial type generators with power control, circulators, and means to measure reflected power. The upgraded version of the cylindrical reactor (Chapter 8) is an example of the latter approach.

Two simple and compact on-line heaters were described in Chapter 8. Other designs should be possible for specific applications and on-line heating with microwaves should become more widespread in the chemical laboratory.

The cavity described in Chapter 8 has been found to be suitable for exciting discharges in several gases. The conditions for each gas was investigated and optimised. The formation of singlet oxygen was successful and these species were found to be efficient for oxidation reactions. This system can be used for analytical applications such as low temperature ashing of samples and for synthesis reactions with organic molecules. Further development of suitable reactors for the different applications needs to be done.

As temperature measurement and control become more important in the laboratory applications of microwave heating, simple and reliable techniques to accomplish these will be required. The gas thermometer described in Chapter 8 provides another practical technique that can be successfully used with liquids.

The development of the moisture meter (Chapter 8), which was prompted by a specific need in industry, has proved to be a relatively versatile and useful analytical tool. Excellent stability, reproducibility, ease of use and low cost make this instrument extremely competitive compared to other commercially available instruments and it is well-suited for a number of quality control applications.

In general, it has been shown that, with some minimum understanding of microwave principles, it is possible to design suitable equipment for a wide range of laboratory applications.

It is concluded that the potential for microwave heating in the chemical laboratory will grow further as more interactions between the chemist and the microwave engineer take place, since it is not possible for chemists to develop all the required skills in microwave heating engineering and for the engineers to involve themselves with all the problems of the chemists. It is also felt that the origins of many of the microwave "special" effects observed by chemists will become clearer when the equipment and instrumentation that is necessary for these investigations is properly designed and applied.

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APPENDIX 1

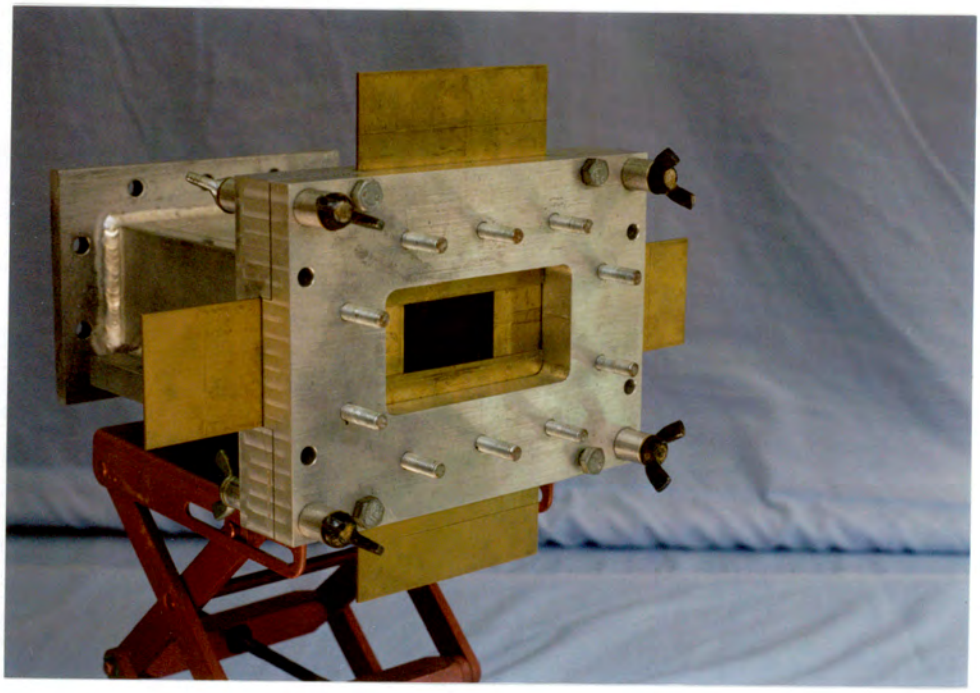
1.2 kW generator

The generator built by Sairem, France, consists of a YJ1540 magnetron capable of delevering 1.2 kW and a thyristor controller for varying the power. The forward power can be set manually and is indicated on a calibrated meter in W. The forward power was calibrated using a matched water load. A 6 kW Philips circulator is mounted on the launch waveguide and a dummy load is used to absorb the reflected power. The circulator is water cooled and a flow monitor on the water circuit (for both circulator and dummy load) is used as interlock to the generator. A diode detector (Model IN23B) mounted at the waveguide section containing the water load and a calibrated meter in W are used to monitor the reflected power.

The generator can be controlled manually from the control box which is separate from the magnetron, high voltage supply and the cooling fan. A computer program written in Turbo Pascal, is used to control the generator and monitor the experiments. The program can be used to set the power and time, monitor the reflected power, temperature and pressure and write these parameters to file. Since the output from the diode detector is not linear, its response was calibrated (by shortening the circulator and varying the forward power) and an equation is used by the program to calculate the accurate reflected power in W.

Variable coupling iris

The variable coupling iris shown below was built from aluminium plates with 1 mm brass sections that can slide between the two halves and provide apertures of varying sizes. After adjustment, the four screws in each corner are tightened to ensure good electrical contact between all the plates and preventing microwave leakages.



APPENDIX 2

Circuit diagram of the multiplexing system (Chapter 6)