MICROWAVE OVEN DIGESTIONS

by

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Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

in the

Chemistry

Program

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THESIS

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TITLE: **MICROWAVE OVEN DIGESTIONS**

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ABSTRACT

MICROWAVE OVEN DIGESTIONS

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Microwave energy for use in sample dissolution during acid digestions was first demonstrated in 1975. Since the first experiments in this type of digestion, the technique has advanced and become the most favored means of sample digestion. The method grew from the use of home microwave ovens with open vessels to the more sturdy laboratory microwave system with closed vessels.

Microwave digestions have become a widely used laboratory practice for heating liquids above their normal boiling points with the use of pressurized vessels. The method is a more efficient means of digestion than conventional methods. Two distinct advantages in the use of microwave digestions are those of decreased time and good reproducibility. In addition, the use of microwave energy approaches ideal sample preparation for analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy and Atomic Absorption Spectroscopy.

These sample preparation ideals would result in the following goals being attained:

1. Conversion of all solid and liquid sample components to a homogeneous aqueous solution. This would help to prevent any obstructions from being caught in the nebulizers of the instruments and permit complete atomization.

2. Elimination of all organic material to prevent combustion problems and help to eliminate background complications.

3. The retention of all elements of interest, especially those that are most volatile, such as lead, mercury, arsenic, and selenium.

4. No addition of any interfering elements or compounds, particularly from the environment or digestion vessels.

5. Adjustment of viscosity and percent dissolved solids within the solution to help with introduction into the instrument.

In this study, efforts were made to facilitate microwave oven digestion method development. Difficulty in digesting several samples acquired through investigations conducted at Youngstown State University were encountered using the manufacturer's suggested method development schemes. Action to enhance digestion completeness and temperature control were undertaken. Electronic devices, including infrared-temperature-to-millivolt, digital-to-analog and analog-to-digital converters, and computational software needed to simplify the methodology were employed. A significant improvement in digestion efficiency and ease of oven operation was effected. The major manufacturer of chemical microwave oven digestion equipment will incorporate the design developed at the Department of Chemistry of Youngstown State University into its next oven model.

ACKNOWLEDGMENTS

I would like to thank my parents, other family members, and friends for their support and encouragement during this endeavor. I also would like to thank Drs. Mincey, Mike, and Spiegel for their efforts in reviewing this document. Finally, I would like to thank the members of the faculty of the Department of Chemistry at Youngstown State University for their years of instruction and inspiration.

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LIST OF SYMBOLS

SYMBOL	DEFINITION
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
AAS	Atomic Absorption Spectroscopy
g	Grams
mL	Milliliters
°C	Degrees Centigrade
P_{abs}	Power Absorbed per Second
C_p	Heat Capacity of Liquid at Constant Pressure
cal	Calories
M	Mass of Liquid being Heated
T	Temperature Rise During Heating
t	Time in Seconds
L	Convective, Conductive, and Radiative Heat Losses
PTFE	Polytetrafluroethylene
psi	Pounds per Square Inch
meq/ohm	Milliequivalents/Ohm
ft-lbs	Foot Pounds
NBS	National Bureau of Standards
V	Volts

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CHAPTER I

Introduction

For years, sample digestion has been a major source of difficulty in trace metal analysis. There are many types of samples and a wide range of techniques that have been developed to dissolve samples.[1-9] As the years have progressed, newer methods have been developed to dissolve different materials.

The process of sample digestion entails the solvation of organic and biological samples and the leaching of metals out of inorganic materials such as soil, sediment, and ores. Though some may not consider it as needing to be dissolved, water must also be digested to guarantee that all metals have been introduced into solution.

Biological samples are difficult to digest. Even though the sample size is small, there may be large amounts of organic materials present. If organics in a sample solution are not completely oxidized during digestion, the samples will behave differently during analysis than standards of a "purely" aqueous nature. If samples and standards are viewed differently, the results of analysis will not be valid. Even though the possibility of incomplete organic oxidation exists, the decomposition method of choice is still dry ashing or wet ashing coupled with hot plate acid digestions.

In the case of inorganic samples the method of choice is hot plate digestion, though on occasion other methods such as fusion can also be used. In fusion, the sample is introduced into a heat

stabilized container along with an acid, such as nitric, hydrochloric, perchloric, or hydrofluoric. This type of digestion allows the acid to leach the heavy metals out of the sample. The leachates are then filtered, diluted, and usually analyzed using either ICP-AES or AAS.

The last type of sample to be considered is water. Aqueous samples can contain small amounts of microscopic sediment. This invisible material can contain significant amounts of metals that could be undetected unless the sample is digested. This digestion is again accomplished by an acid-coupled-hot-plate digestion. At elevated temperatures, a loss of water as vapor and a loss of volatile metal salts may occur. Several metal ions that form volatile salts include mercury(II), arsenic(III), antimony(III),and tin(IV). With this loss, the results one reports could possess a large degree of error.[1]

Some of the processes of sample digestion include open vessel hot plate digestion, fusion, and digestion with Parr Bombs. Hot plate digestions involve the use of single acid or acid mixtures to help the digestion proceed. Problems can arise during these types of digestion, such as films of insoluble substances, lengthy time, incomplete digestions, and loss of volatile salts.[1]

Fusion is the other method of digestion discussed. This method is mainly used to dissolve samples unable to be broken down by simple acid hot plate digestions. There are many types of fusion which include: alkaline; acid; oxidative; reductive; sulphoalkaline. This type of decomposition is employed for samples difficult to digest by other means. The great efficiency by fusion, compared to

decomposition by acids, is due to "the effect of the high temperature, which cannot be achieved in an aqueous solution, and which allows for heterogeneous reactions to proceed at a far greater rate."[1]

Parr Bomb decomposition is a third type, often used in the digestion of organic substances. This consists of a steel bomb that has a Teflon^{R} insert. The substance of interest in the digestion is loaded into the bomb and then it is heated at a very high temperature in an oven. This usually takes a few hours.

One of the latest types of digestion is microwave digestion. Vessels typically employed are constructed of Teflon^{R}. They may be of an open or closed configuration. Parr bombs are even heated using microwave energy instead of the conventional oven. In an article by Nicholson, et al., at the University of Virginia the quote was, " By use of the modified Parr microwave digestion bomb, digestion proceeds rapidly (≤90s) in a sealed Teflon-lined vessel that eliminates contamination or loss from volatilization."[2]

This thesis describes an aid to the development of microwave sample digestion methods by computer controlling the temperature of digestion vessels. This method has been successful and tested extensively.

Statement of Problem

In our laboratories, it was observed that often incomplete digestions of organic materials were encountered after following the microwave digestion procedures suggested by the microwave oven manufacturer. For example, the digestion of leaves resulted in the presence of a white precipitate upon cooling. These digested samples were unsuited for analysis. A simple and effective method of biological sample dissolution needed to be developed.

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Chapter II

History of Decomposition

Hot Plate Dissolution with Acids

The first type of sample dissolution discussed is that of acid dissolution. This method usually involves the use of open vessels and a hot plate for gentle heating. Many acids are available for digestion and include: Hydrochloric acid; Nitric acid; Hydrobromic acid; Hydroiodic acid; Sulfuric acid; Perchloric acid; Phosphoric acid; and some organic acids.

Most of these acids are good oxidizers or hydrolyzers for certain types of materials. Each may be specific for helping the dissolution of biologicals, inorganics, such as ores and minerals, and finally some types of organics. A few of the acids will be discussed in detail.

"Hydrochloric acid is the usual solvent in the analysis of ores and minerals."[3] Following is a list of the advantages of this type of digestion: "volatility, solubility of most of its salts in water, and weak reducing effect on dissolution."[4] There are some problems when employing this acid; one of the major of these is the loss of elements through volatilization. The chloride salts of elements such as germanium (IV), arsenic (III), antimony (III), tin (IV), and mercury (II) can be lost during digestion. Therefore, if the concentrations of these elements are to be determined, another method must be found.

In many cases the concentration of these heavy metal toxins is of interest.

Hydrofluoric acid is used in conjunction with other acids to aid in the complete dissolution of certain samples. Some rocks resist digestion, but they may be more susceptible to hydrofluoric acid than other acids. Hydrofluoric acid should not be used alone, however, because volatile fluoride salts may be lost during digestion. The metal salts that could be lost include tin, titanium, zirconium, and germanium. Hydrofluoric acid is widely used in the dissolution of the silicates.[7]

Another disadvantage of dissolution with hydrofluoric acid is the formation of stable fluoride complexes. These can interfere with the later steps of analysis. It is very difficult to remove metal ions from tightly bound fluoride complexes. If free metal ions are required for determination, the amount of metal detected may be erroneously reduced. Fluorides may also interfere in the photometric determination of the alkaline earth metals. The other problem commonly encountered is that the hydroflouric acid reacts with the glass of an ICP torch introducing significant amounts of silica into the plasma which limits the determination of silicone. This can be remedied with the use of an alumina based torch which is more resistant to hydroflouric acid.[4]

Nitric acid, a strong oxidant, is widely used for its dissolving capabilities with the metals that occur in organic matrices, such as biological samples. Being a strong oxidant, it is also used extensively for the dissolution of metal rich ores. There

is some difficulty using nitric acid to digest samples for gold and platinum determinations. "In general, nitric acid is utilized in analytical chemistry in all cases, where other mineral acids would interfere. Such cases are, for example, the determination of phosphates in a great variety of materials, or the analysis of thorium, rare earth elements, and transuranium elements."[5]

The final acid to be discussed is perchloric acid. Disadvantages with perchloric acid arise from its extreme volatility, its great oxidative powers, and its potential to cause formation of explosive mixtures. A special hood must be used for this type of digestion, because perchloric acid may form explosive perchlorates from materials found within the hood itself. Perchloric acid is often used instead of sulfuric acid and at times is mixed with other acids. The rapid loss of oxidizing power of perchloric acid occurs upon cooling after being heated, and upon dilution. "Perchloric acid has been found useful for the decomposition and determination of the silica dioxide in colimite, dolamite, and magnasite."[6] Recently, the use of perchloric acid has increased in the dissolution of mineral raw materials, metals, and metal alloys. It has taken the place of sulfuric acid and its greater oxidative power makes it more useful than nitric acid.

There are many other acids which could also be discussed, such as sulfuric, phosphoric, iodic, organic, and the various mixtures of acids. All acidic digestions are accomplished from hot plates in different types of vessels. This technique has been widely accepted for over 100 years for the dissolution of samples for analysis.

Below is a list of advantages and disadvantages of hot plate digestions:

Advantages

1. Well accepted techniques in use for well over 100 years.
2. No sample size limit.
3. Easy addition of reagents and samples.
4. Trace metals are unable to leach from polytetrafluoroethylene (PTFE) vessels.
5. Low cost of dissolution.
6. No problem monitoring the digestion.
7. Simple to implement.

Disadvantages

1. Time consuming, and the digestion temperature is restricted to the atmospheric boiling point of the acid used.
2. Loss of acid strength upon heating ex: Nitric (HNO_3) and Hydrochloric (HCl).
3. Increase of maximum detection limit due to concentration of trace impurities in the acid.
4. Loss of volatile elements such as arsenic, selenium, mercury, lead, and cadmium.
5. Constant monitoring to prevent evaporation to dryness of the acids.

6. Health concerns due to fumes from evaporation, and damage to hoods because of the acid's corrosive properties.
7. Use of large amounts of high purity acids, which can be costly.
8. Sample can be contaminated by airborne particles, even if beaker is covered, by the high temperature vapor escaping and being replaced by cool air from outside.
9. Leaching of trace metals if glass is used; if PTFE containers are used they will not be as conducive to heating because of their insulating properties.
10. Danger of certain acids (hydrofluoric can cause severe tissue damage and perchloric can become explosive in the presence of organic material and metals if allowed to go to dryness).

Fusion Dissolution

The second method of sample dissolution is fusion. There are a variety of fusion techniques; two will be discussed. They are alkaline and acid fusion. Fusion takes place at very high temperatures and can be effective in the breakdown of different materials for analysis. The main ingredients for this technique are known as fluxes. These fluxes can lead to water soluble and insoluble products. Platinum and silver crucibles are the vessels most commonly

used in this method. They are usually heated over a gas burner, but the digestion can also be performed in an electric muffle furnace.

Alkaline fusion is usually done in carbonate mixtures, which include sodium bicarbonate; sodium potassium carbonate; potassium bicarbonate. The majority are done in anhydrous sodium carbonate, which melts at 850 °C. A major difficulty is the presence of impurities which may cause problems in later determinations. A blank correction for these impurities must be provided, especially in the determination of chlorine, sulfur, silica dioxide, ferric and aluminum oxides.

Another problem is the decomposition of the vessels in which the fusion takes place. Platinum vessels, over a period of heating, can decompose and lose up to several grams of weight. This would be a severe limitation if platinum was one of the metals of interest.

After the melt has been performed, solvation of the solidified sample must be carried out. This is usually accomplished with various acids. The samples most widely dissolved by this method include glasses, ceramics, and minerals.

One fusion method of particular interest is mineral decomposition. "In recent years borate fluxes have been widely used, in particular lithium borate has provided a flux which does not interfere with the determination of major elements."[7]

Below is a general method reported by M. Thompson and J.N. Walsh in their handbook.[4]

1. *Accurately weigh 0.5 g powdered rock into a platinum crucible.*

2. *1.5 g of anhydrous lithium metaborate is added and carefully mixed (important to have complete mixing)*
3. *Fuse for 30 minutes on Meker burner or in a furnace at 1000 degrees centigrade. Swirl several times.*
4. *Allow to cool to room temperature.*
5. *Immerse crucible in 175 mL of distilled water containing approximately 10 mL of nitric acid. (This is done on a magnetic stirrer)*
6. *In about one to two hours the fused bead will dissolve yielding a clear stable solution.*
7. *Dilute to 250 mL before ICP analysis is performed.*

As is shown by the above method, the time involved is less than that of a normal hot plate digestion, but again the method is fairly involved. If there are many samples involved the time required would be lengthy.

Acid fusion is the next system that will be examined. Acid fusion utilizes either sodium or potassium hydrogen sulfate or pyrosulfates as the flux. It should be noted that it is better to use pyrosulfates than sulfates, as the latter must be converted to pyrosulfate and this can cause spattering onto the crucible lid with the formation of water in the process. This formation of water occurs during the reaction to convert the sulfates to sulfuric acid and on to pyrosulfuric acid. Spattering can cause a loss of sample at the same time.

The crucible used in acid fusion is produced from platinum or quartz. There are problems that arise with decomposition of the

platinum crucible. Since decomposition of the crucible does occur, if platinum is a metal of interest it cannot be used for fusion. Quartz can be substituted, but the cost of quartz is prohibitive to most labs. Other types that could be used, such as gold or iridium are dependable but only resistant to pyrosulfate up to temperatures of 600 °C. Quartz crucibles are the most recommended to prevent foaming, which occurs in the presence of the metallic containers.

Commonly, acid fusion is used in the dissolution of insoluble residues, which contain aluminum, chromium, and titanium oxides. These samples are highly resistant to simple acid digestion.

Following are the advantages and disadvantages of the fusion techniques:

ADVANTAGES

1. Rapid; approximately 15-30 minutes per fusion.
2. Suited for samples resistant to hot plate digestion. Resulting glass can usually be dissolved in nitric acid.
3. Simple.
4. Regular monitoring is not required.

DISADVANTAGES

1. Salts are not highly pure so trace contamination can exist.
2. Increased salt content can clog burners used in flame AA analysis and can cause the ICP torch to be extinguished.

3. Background correction can be difficult.
4. Due to high temperature (400-1000 °C), volatile elements are lost.
5. Sample size between 0.1 and 1.0 grams.
6. Costly with the amount of apparatus needed such as platinum or quartz crucibles and increased amount of electricity needed to run the muffle furnace.
7. Means to remove heat from lab area is needed.

Chapter III

METHODOLOGIES

Basic Principles

Microwave energy is a form of electromagnetic energy that has alternating electric and magnetic fields. The fields, or waves as they are sometimes called, travel at the speed of light. At the frequencies of microwaves, the electric and magnetic fields will complete between 300 to 300,000 million cycles per second, or Megahertz (MHz). A typical microwave oven uses a frequency of 2450 MHz. This translates into a wavelength of 12.2 cm. Microwave energy falls above the visible and infrared light regions of the spectrum and below radio waves.

The principle of this type of digestion is that as microwaves are absorbed by a suitable material its temperature will increase. The velocity at which the material heats depends on the materials dielectric loss factor. The dielectric loss factor indicates the susceptibility of a material at a certain temperature to absorb microwave energy at a certain frequency. The term dielectric loss factor refers to the amount of microwave energy that is lost to the sample and converted to heat.

The distance microwave energy penetrates into the sample is infinite in materials that are transparent, such as a vacuum or teflon, zero in reflective materials like metals, and finite in absorptive materials like water. The larger the loss factor of the

sample the shallower the penetration of the microwave energy, since it is attenuated by absorption as it passes farther into the sample.

Methods of Microwave Radiation Absorption

For liquids there are two methods of microwave absorption that are of interest. They are dipole rotation and ionic conductance.

Dipole rotation is the ability of microwave absorbing molecules to have rotation in response to the microwave electric field. The rotation of a molecule continues until it collides with other molecules. As these collisions occur they cause transfer of kinetic energy. This kinetic energy transfer then causes heating and the sample begins to dissolve. The microwave electric field oscillates several billion times per second and causes the liquid to heat very rapidly in accordance with the number of collisions. The rate of the dipole rotation strongly depends on the viscosity of the liquid. As the viscosity decreases the amount of dipole rotation increases and as the viscosity increases the amount of dipole rotation decreases. The microwave absorption is decreased as the liquid heats and its viscosity decreases.

Ionic conductance is the second method of absorption. Certain liquids contain ions that are dissolved. These ions are able to conduct current. Mineral acids are an example of these types of liquids. The ions that are dissolved enable better conductance of microwave electric energy.

The dissolved ions migrate in the presence of an applied microwave field and this migration will cause collisions with other

substances. This collision of ions raises the kinetic energy of the liquid molecules and the temperature of the liquid is increased.

In microwave energy the sign of the magnetic field changes billions of times each second. The change of sign forces the ions to change direction an equivalent number of times.

Liquids can heat from both dipole rotation and ionic conductance simultaneously. The concentration of ions and their equivalent conductivity will determine the percent contribution by each method. In the case of low ion concentration, the heating conversion will be mainly due to dipole rotation.

The ability of microwave energy to penetrate liquids causes heating throughout the liquid rather than just at the surface. In conventional heating methods the heating is more surface oriented. This can cause an increase in the length of time that it takes to digest a sample.

Microwave heating can be very efficient and is calculated by the following equation:

$$P_{abs} = C_p M \, T/t - L$$

where:

P_{abs} = Power absorbed/second

C_p = heat capacity of liquid at constant pressure, cal/g°C

M = Mass of liquid being heated, grams

T = Temperature rise during heating, °C ($T_f - T_i$)

t = time, s

L = convective, conductive, and radiative heat losses

In most cases heat losses (L) are ignored as they are minimal in the type of closed vessel microwave digestion that is studied here. In open vessel digestion, this heat loss could become a factor, because air currents within the microwave oven may remove heat.

Take water for an example. In a microwave system that is operating at 2450 MHz, and assuming that 600 watts of power (143.3 calories/second) is absorbed by the water, one can calculate the temperature of the water after a certain amount of time. The temperature rise from the previous equation is calculated by the following:

$$T = (143.4 \text{ calories/s})(t)/C_p M$$

It should be noted that this equation is only valid for microwave energy that is absorbed. Most microwave heating ovens provide between 600-700 watts of power, which is equivalent to approximately 8600-10,000 cal/minute. If this energy was applied to a sample that is unable to absorb microwave energy, then no heating would take place, and P_{abs} would be zero.

Sample Preparation Methods

Open Vessel

Open vessel microwave oven digestion can be employed as a means of sample preparation but overall the same problems occur as with the hot plate digestions. There are some advantages over the hot plate digestions. The sample does heat faster since the microwave radiation input is more efficient. The heat capacity of the vessels are similar in both procedures, though the open vessel microwave digestions reach high temperatures faster.

Closed Vessel

Closed vessels are the containers of choice for sample dissolution when using the microwave digestion systems. Because the containers are closed to the atmosphere during digestion, they are not vulnerable to contamination from the air.[8] There are a couple of different vessels that can be used that follow the guidelines for this type of digestion. They are both different in the amount of internal pressure they will reach before the safety relief valve will open. The first is the PTFE-lined container, which is sealed and holds pressures up to 1200 psi. during microwave heating. The problem that exists with this type of vessel is that if the pressure builds up to above the limit a relief mechanism will open. This mechanism will not reseal after the pressure drops below the limit of the vessel. This results in the sample having to be reprocessed.

The second type of vessel is one that is made only of PTFE and these vessels can also be sealed. Some vessels of this type have been designed without a pressure relief valve, posing a great deal of danger to the operator of the microwave oven. The vessel of choice was made from Teflon PFA (see Figure 1) with a volume of 120 mL and was capable of maintaining pressures up to 120 psi. These vessels were equipped with a pressure relief valve to prevent any danger to the operator (see Figure 2). They also had the ability to reseal after the pressure dropped below the limit of the vessel. This prevented loss of the sample and the need to repeat the procedure. Below are a list of advantages and disadvantages of microwave oven digestion:

ADVANTAGES

1. Digestions can be done 4-100 times faster than comparable hot plate digestions.
2. Temperatures of up to 270 °C are possible.
3. Able to use samples of 1.0-2.0 g for most materials.
4. Acids that are utilized in the digestions will not lose strength due to vaporization of the active components.
5. No sample contamination from airborne particles.
6. Elements which are volatile are maintained in the sealed vessel.
7. Digestions can be programmed and left unattended freeing the time for other duties.
8. The generation of fumes is eliminated.

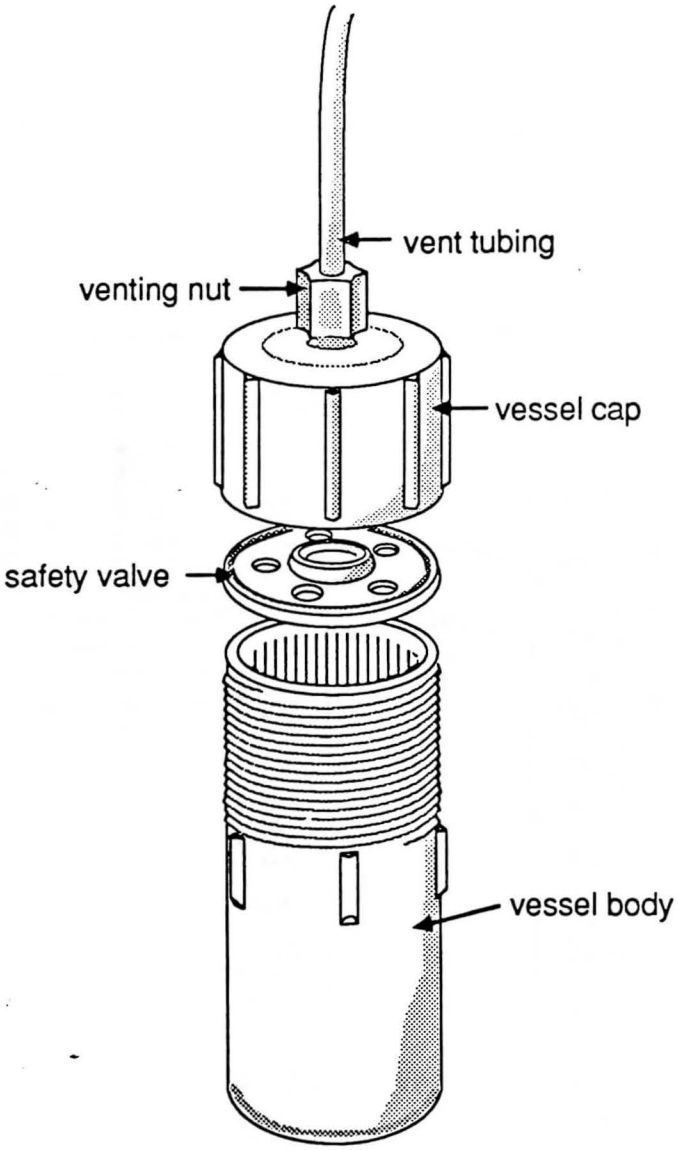
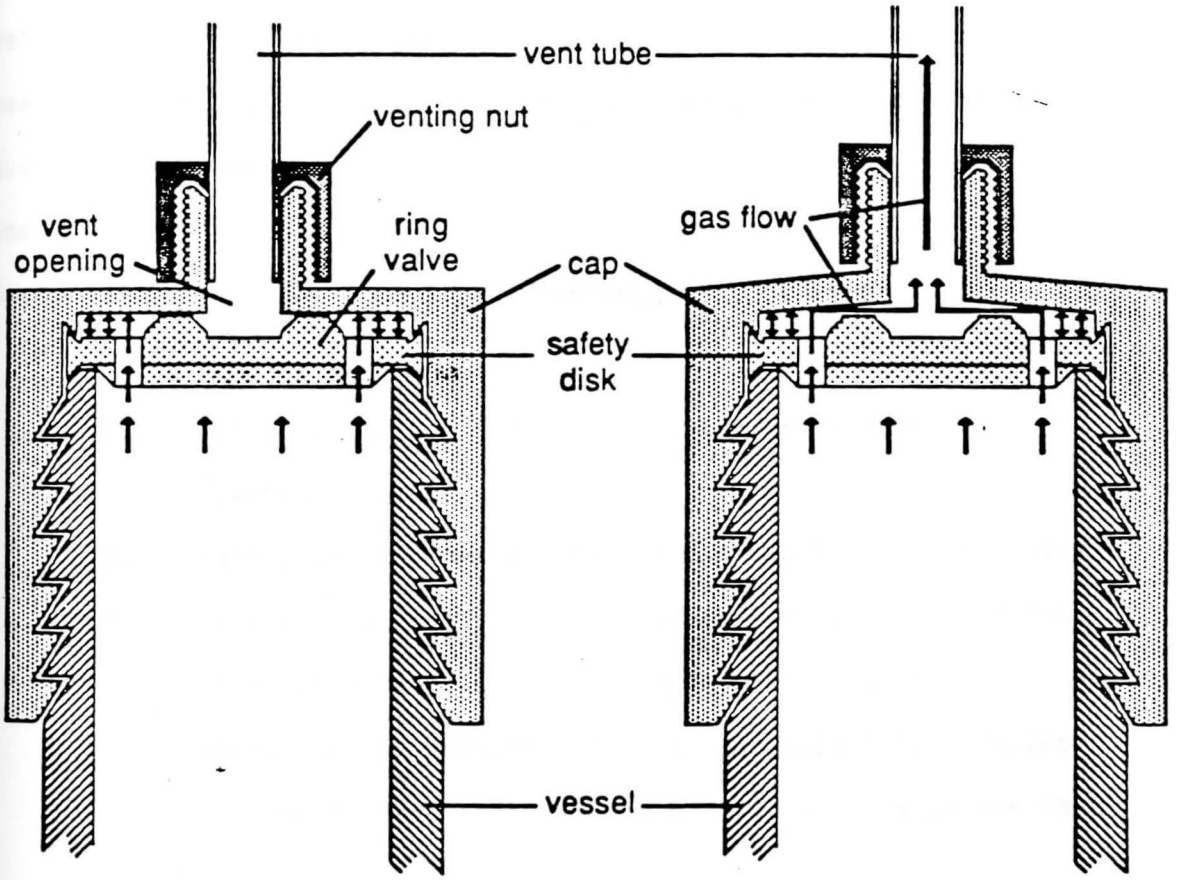

vent tubing
venting nut
vessel cap
safety valve
vessel body

FIGURE 1

Cutaway view of vessel cap and safety pressure relief valve assembly, sealed and venting



At pressures below 120 PSIG, ring valve remains sealed against cap.

Excess pressure forces top of cap to distort (shown exaggerated), breaking the seal at the ring valve, and exhausting the pressurized gas.

FIGURE 2

9. Dangerous acids are contained to the vessel eliminating the hazard of exposure to laboratory personnel.
10. Perchloric acid is often not needed due to the generation of higher temperatures during acid digestion with nitric and hydrofluoric acid.
11. Relief valve will open if pressure limit is exceeded, but will reseal when safe pressure is reached.
12. System can be set up with robotics, freeing up more of the technician's time.
13. Teflon PFA is translucent so digestion progress can be observed.

DISADVANTAGES

1. It is a relatively new technique and few studies are completed using it.
2. Cleaning and assembling the vessels can be time consuming.
3. Some elements, such as chlorine, osmium, and rhodium can diffuse into Teflon^{R} on long exposure to elevated temperature and pressure causing contaminations. Teflon^{R} PFA helps to reduce this problem as it is less porous than PTFE.
4. Refractory inorganic and organic samples occasionally need to be ashed or fused to prepare them for digestion or prepared in quartz containers or they may not completely dissolve.
5. Microwave digestion systems are moderately expensive.

Chapter IV

Materials and Instrumentation

Chemicals Used

Table 1 lists all the reagents and standards used in this study. Any dilution of digestates were performed using ASTM class 1 water. This water has been deionized to 18 megohm resistance and is essentially free of metal ions. All digestions were performed using microwave digestion techniques. The samples that were used for analysis and the digestion experiments contained citrus leaves purchased the National Bureau of Standards.

Equipment

1. CEM MDS 81-D Microwave oven - The microwave oven that has been specially fitted to accommodate an acid digestion. The sealed Teflon^{R} vessels were produced to withstand pressures up to 120 psi. The inside of the microwave oven was lined with teflon to prevent corrosion in the event that acid fumes were released into the cavity. The microwave had a 600 watt magnetron. Electronic relay control of the magnetron was effected by a digital programming board.
2. CEM capping station - This part of the system was set up to torque the digestion vessels at 12 ft-lbs.

3. CEM Digestion Vessels - Teflon^{R} PFA vessels that were tooled to withstand 120 psi. before the safety valve in the cap vented the vessel.
4. Omega OS-500 infra-red to millivolt converter - This was used to sense the wall temperature of the digestion vessel and represent this temperature as a voltage. One millivolt was equal to 1 °C.
5. Houston Instruments X-Y recorder - This was used to plot the temperature progress of the digestion.
6. Apple IIE personal computer - This was used to digitally monitor and control the temperature of sample digestion within the microwave oven. A listing of the monitor and control programs occurs in appendix 1.
7. Interactive Microware, Inc. ADALAB Data Acquisition System - This was used to take the readings from the Omega OS-500 and convert them to a meaningful number for the computer to use. In addition, a magnetron control relay signal was sent from this system. The ADALAB board was able to communicate with intelligent instruments and computers that have parallel or serial input/output capabilities. There were four different subsystems that are associated with the board. They were the analog to digital converter, digital to analog converter, digital to parallel input/output, and real-time clock/timer subsystems. The analog to digital converter was able to read voltages with a 0.025% precision and accuracy of 0.1%. It was equipped with internal zeroing which enhanced the accuracy of the readings. The

subsystem could take up to 20 voltage readings per second, and the ability to do dual slope integrations helped to smooth out noisy signals. The digital to analog converter was just as accurate as its opposite. The subsystem had jumper selectable voltage ranges of ±4V, ±2V, ±1V, or ±0.5V and had a conversion rate up to 50,000 conversions per second. The digital and parallel input/output subsystem had 8 bit input 8 bit output or 16 bit bidirectional bits that were individually selectable as input or output bits. The ability also existed for versatile handshaking signals and had interrupt and enable circuitry. The real-time clock/timer subsystem has a 32 bit countdown timer which was able to be set for any amount of time from 10 microseconds to 100 minutes. There was also the two 16 bit timer/counters that could be configured as an interval timer, event counter, pulse generator, square wave generator, or shift register.

TABLE 1

REAGENTS USED IN THE EXPERIMENTATION

Acid	Concentration	Manufacturer
Nitric	6 Molar	GFS
Hydroflouric	48% by wgt.	GFS
Hydrochloric	6 Molar	GFS
Sulfuric	95-98% by wgt.	GFS

NOTE: all acids were double distilled from vycor
Produced by G.F. Smith, Columbus, Ohio

Standards	Lot Number	Manufacturer
Citrus Leaves	#1572	NBS

NOTE: Purchased through National Bureau of Standards,
Washington, D.C.

CHAPTER V

EXPERIMENTAL

This thesis has described several means of sample digestion. It has reported on several methods and has examined the advantages and the disadvantages of each. It has also given some preliminary background on the method that will be further discussed in this section. The prime point of this thesis is to demonstrate the ability of microwave radiation, under proper control, to more completely digest samples and therefore deliver more accurate results than with conventional digestion techniques.

The project was a direct result of a joint study between the Chemistry and Biology Departments. The samples were made up of different matrices and needed to be dissolved for analysis for metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Atomic Absorption Spectroscopy (AAS) using a graphite furnace. The two methods used to perform the metals analysis will not be discussed in the body of this paper. The ICP-AES was used to do a screening on the samples and the AAS was used to analyze any samples that fell below an elements detection limit of the ICP-AES. This analysis could be time consuming so a method was needed to dissolve the samples quickly. The method also had to be valid and in some way verified against a known control. The microwave oven was utilized, and to verify the analysis, National Bureau of Standards (NBS) controls that closely matched to the sample matrices were used.

The first samples to be analyzed were from the Biology Department. These samples consisted of caterpillar larvae and cherry leaves. Difficulty was encountered when cherry leaves and chemically similar NBS citrus leaves were digested. When these leaves were digested for a time of 2 minutes at 100% power and 10 minutes at 40% power with 10 mL of nitric acid and 3 mL of hydrofluoric acid (see Figure 3), as suggested by CEM, a white precipitate, revealing an incomplete dissolution, occured.

Nitric acid was the acid first employed in the digestions performed in this study. The use of other acids was explored, but the microwave digestion still resulted in samples that were still not completely dissolved. The other acid used was a small amount of hydrofluoric acid which helped dissolve any material resistant to nitric acid. The boiling points of the acids at atmospheric pressure are found in Table 2 along with the concentrations involved. Table 3 contains the temperatures that the certain acids of choice need to reach to attain a safe internal pressure of 100 psi. in a sealed vessel. One means of obtaining a more complete digestion could be to control the actual temperature within the digestion vessel (see Figure 4), thus maintaining the highest possible digestion temperature without vessel venting.

MICROWAVE APPLICATION NOTE FOR ACID DIGESTION

Sample Type: Citrus Leaves (NBS SRM 1572)
Tomato Leaves (NBS SRM 1573)

Summary:

This method provides for the acid dissolution of citrus leaves and tomato leaves in a closed Teflon* PFA vessel using microwave heating for analysis by spectroscopic or wet chemical methods.

Required Equipment:

MDS-81D Microwave Instrument, Teflon PFA Vessels (120 ml size) with pressure relief valve, Digestion Turntable, Capping Station.

Reagents:

Hydrofluoric Acid (48%)
Nitric Acid (70%)
Hydrogen Peroxide (30%)

Method:

1. Transfer 0.5 g of powdered sample into a vessel. Add 10 ml of nitric acid and 3 ml of hydrofluoric acid. Place a safety valve and cap on the vessel and then tighten cap using the Capping Station. Place the vessel in the turntable and attach a venting tube.
2. Repeat step 1 until the turntable contains 12 vessels.
3. Turn the MDS-81D exhaust on to the maximum fan speed. Activate the turntable so that it is rotating.
4. Program the instrument for 2 minutes time and 100% power in program 1, and 10 minutes time and 40% power in program 2. Depress the START key and allow the sample mixtures to heat.

* Teflon is DuPont's registered trademark for its fluoropolymer resins.

CEM Corporation • P.O. Box 200 • Matthews, NC 28106 • (704) 821-7015 • Telex 802118

5. Allow the sample solutions to cool to room temperature and vent each vessel.
6. Open the vessels, add 5 ml of hydrogen peroxide and swirl.
7. Place the open vessels in the turntable and heat at 100% po the solution volume has been reduced to 3 ml (approximately minutes).
8. Allow the solutions to cool to room temperature, filter if and transfer to appropriate containers.

NOTE: This procedure is a reference starting point for sample dig using the MDS-81D and may need to be modified or changed to the required results on your sample.

CAUTION: Manual venting of CEM closed vessels should only be perfor the vessel contents are at or below room temperature to av potential for chemical burns. When venting vessels, it is mended that hand, eye, and body protection be worn.

FIGURE 3

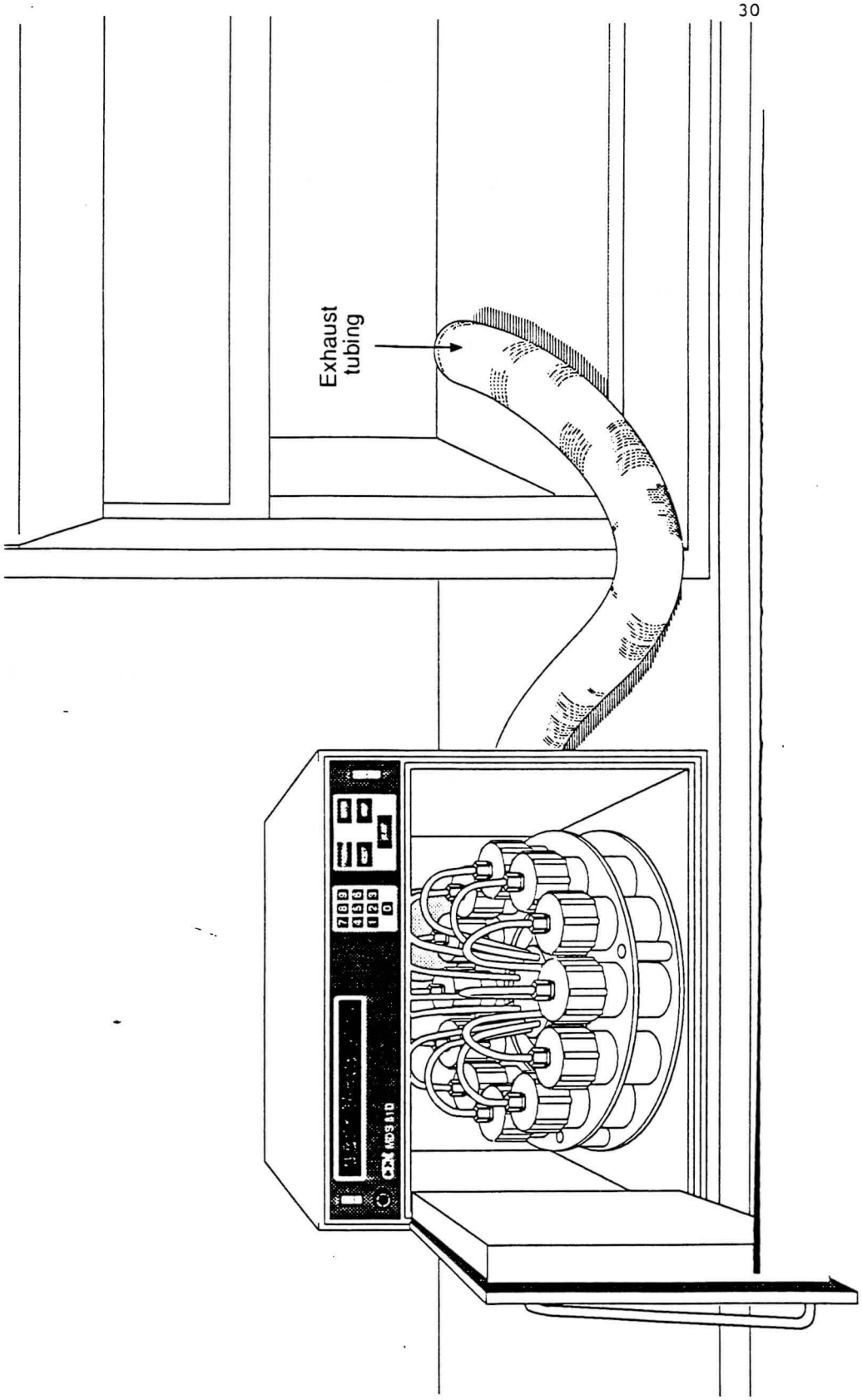


FIGURE 4

TABLE 2

BOILING POINTS OF ACIDS AND ACID MIXTURES

AT ATMOSPHERIC PRESSURE

ACID	CONCENTRATION	BOILING POINT (°C)
Hydrochloric	37 Weight Percent	110
Hydrofluoric	49 Weight Percent	108
Nitric	70 Weight Percent	120
Aqua Regia	(HNO_3:HCl, 1:3, v/v)	112
Sulfuric	98.3 Weight Percent	338
Phosphoric	85 Weight Percent	150

TABLE 3

ACID AND ACID MIXTURE TEMPERATURES RECQUIRED TO GENERATE 100 PSIG. IN A SEALED VESSEL

ACID	CONCENTRATION	TEMPERATURE (°C)
Hydrochloric	37 Weight Percent	140
Hydrofluoric	49 Weight Percent	175
Nitric	70 Weight Percent	190
Aqua Regia	(HNO_3:HCl, 1:3, v/v)	146

TEMPERATURE CONTROL of MICROWAVE DIGESTIONS

These experiments in microwave oven temperature control were performed using an Apple IIE computer with an ADALAB board installed to do the digital controlling. A program, supplied by IMI and termed Quick Soft I/O, was modified so the microwave magnetron could be turned on and off under computer control to effect an operator-specified vessel temperature. The overview of the system is represented in Figure 5.

As the figure shows, the path that was used in the experiment started at the infra-red probe where the temperature of the outside wall of all digestion vessels was read. The temperature then was changed into a voltage reading by the IR/MV converter. The next step was to amplify these readings, which were then fed to the Apple IIE computer and the ADALAB board. To find the maximum temperature existing on the "average" vessel, the IR/MV converter was monitored 200 times at 50 msec. intervals. The maximum voltage reading encountered within these 200 readings was used to calculate a corresponding vessel temperature. This temperature was compared to the operated selected control temperature. If the temperature was below that specified, a digital high was maintained on a 5 V relay that permitted the microwave oven magnetron to remain on. Once the selected temperature was reached a digital low sent from the computer/ADALAB board to the 5 V relay and turned off the magnetron. Once the temperature of the wall of the hottest vessel fell below a selected value the magnetron would be reactivated. A constant temperature of digestion was effected in this manner. Settings on the

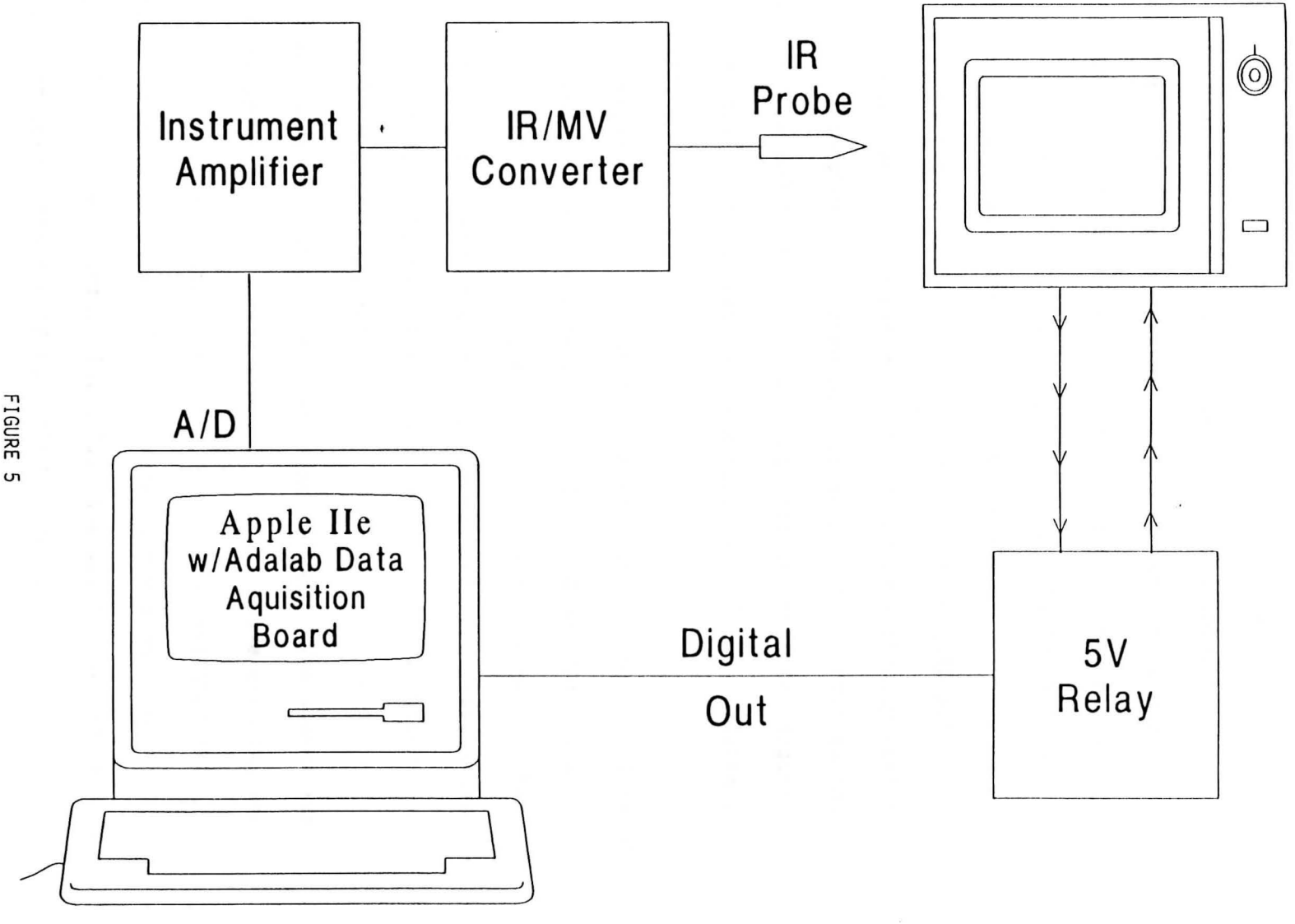

Instrument Amplifier
IR/MV Converter
IR Probe
A/D
Apple IIe w/Adalab Data Aquisition Board
Digital Out
5V Relay

FIGURE 5

front panel of the microwave oven would have maintained the magnetron in a constant on mode.

An infra-red probe was used to judge the temperature inside the vessels. The probe was trained on the vessel as it went by on the attached turntable (see Figure 6). The probe was mounted to the side of the microwave oven using a buret clamp . A small hole was drilled into the side so as to be able to train the probe at the bottom of the vessel. No leakage of microwave radiation was detected with a microwave radiation leak detector, (Radio Shack).

The temperature probe, IR/MV converter, the ADALAB A/D converter, and computer program were calibrated by initially heating water to its atmospheric pressure boiling point. A variable in the program could be modified to instruct the computer that the digital reading received for this temperature should be 99.8 °C. Calibration ocurred daily.

The system worked incident free except for the small problem of lag time. The way that the problem was discovered was that an X-Y recorder was used to plot the progress in the sample vessels. The problem came to light when the recorder showed that the temperature typically "overshot" the specified value (see Figure 7). Often venting of the vessels resulted.

The remedy to this problem took some thought. The answer was to ramp the power setting on the front of the microwave oven instead of starting it at one hundred percent. The optimum settings were determined to be as follows: The microwave oven was able to go through a three-stage program. Initially, the first stage was set at sixty percent power, the second at eighty percent, and the third at

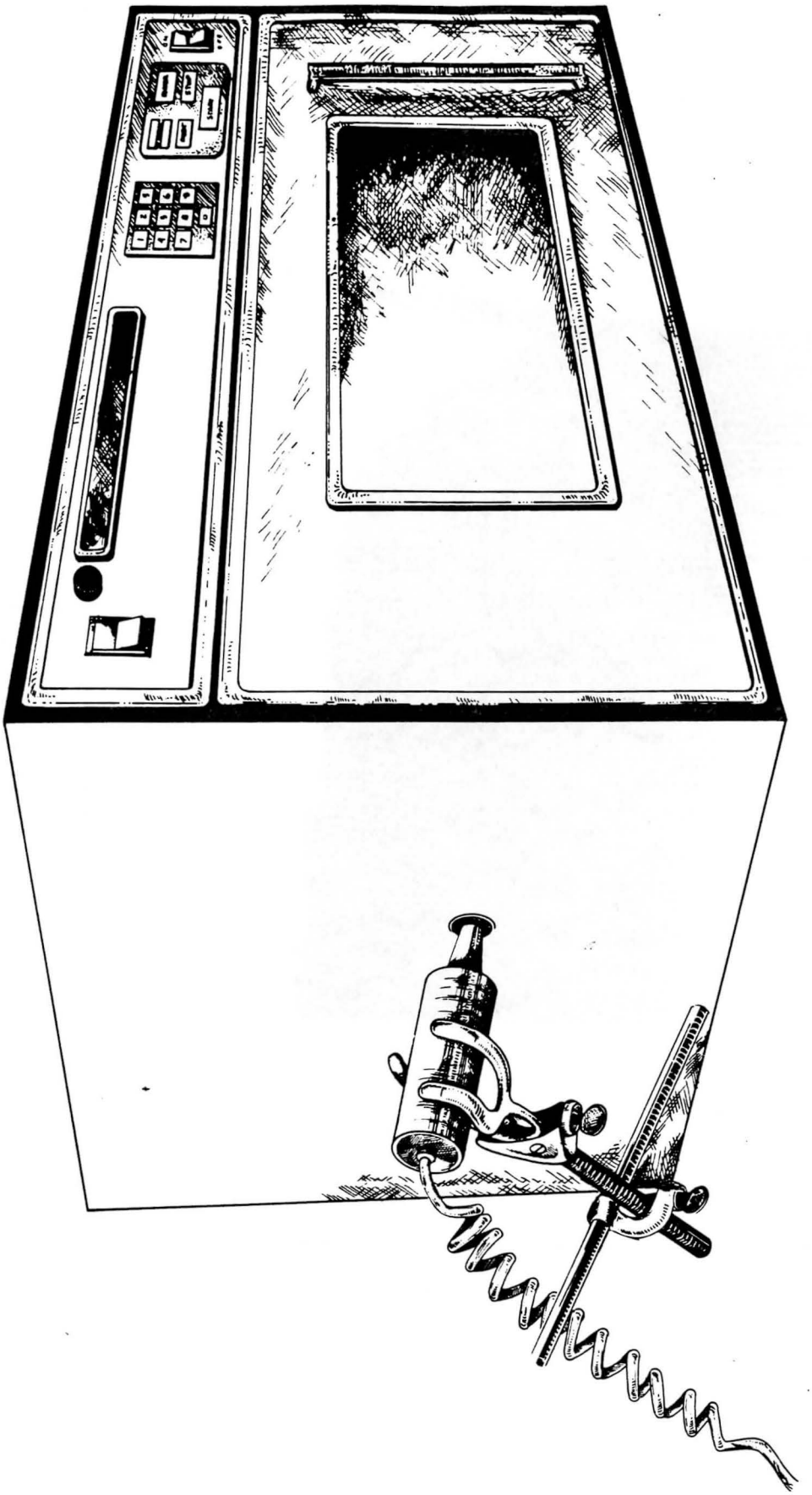


FIGURE 6

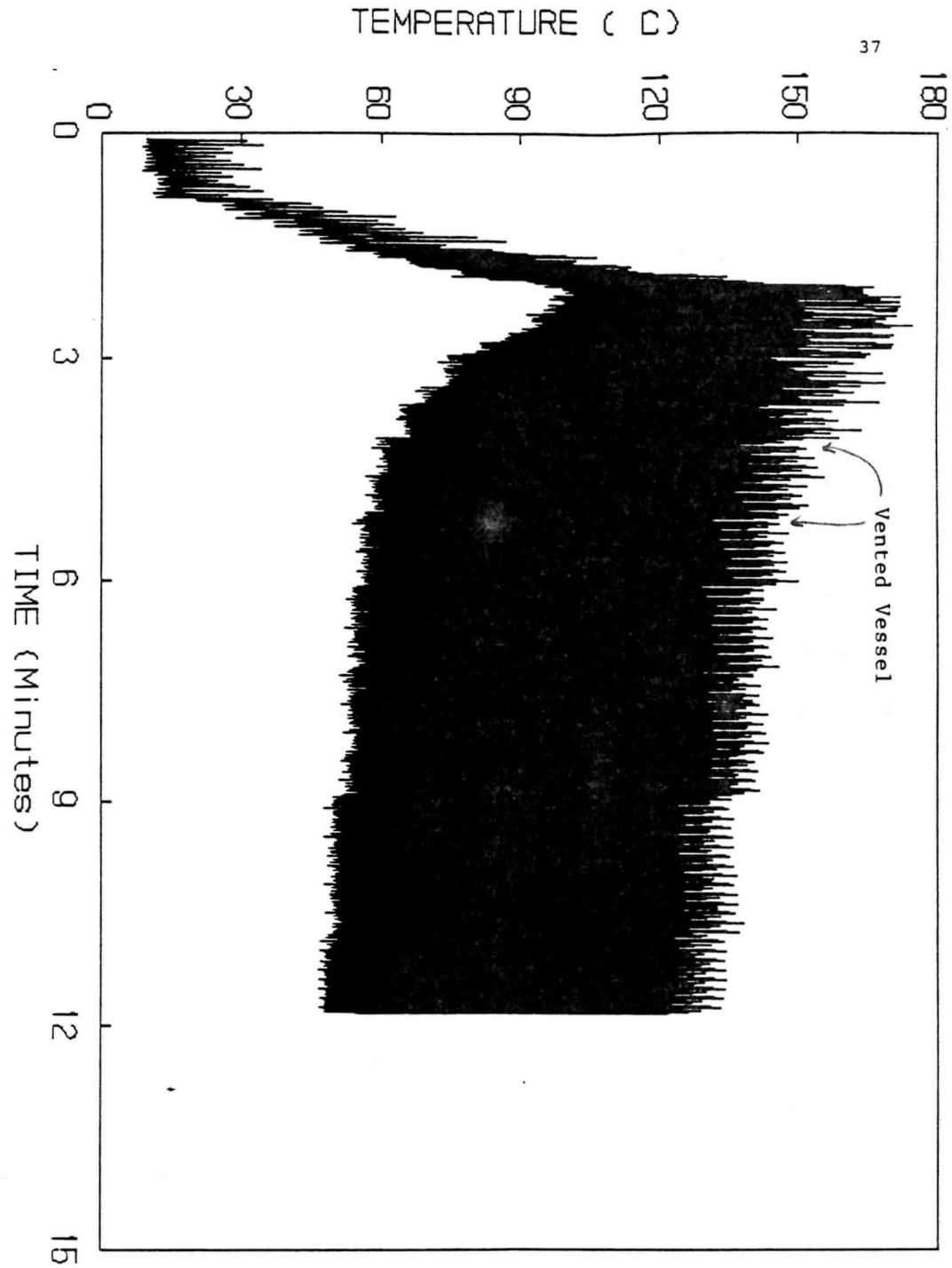

TEMPERATURE (C)
0
30
60
90
120
150
180
0
3
6
9
12
15
TIME (Minutes)
Vented Vessel

FIGURE 7

one hundred. The digestion was begun and the X-Y recorder was turned on. The ramping was done for two minutes in stages one and two with stage three set for the length of time needed for dissolution. The program proceeded and the outcome looked good until the first vessel vented a couple of minutes into the third program. The determination was made that the programs were heating the samples too fast and the programs had to be changed to heat the samples at a slower rate. After experimenting with the microwave on many samples the final program was decided on. This program started the ramping at a lower power of thirty percent, went to sixty percent in the second stage, and then was set at one hundred percent in the final step. This program worked much better than any of the other trials and was adopted by our laboratory as an acceptable means of sample digestion.

Another discovery was made by looking at the plots from the X-Y recorder. This discovery involved the integrity of the vessels. During the constant temperature runs it was noticed that the pen was not always reaching the same level for each individual vessel. This would not normally have been a problem if each of the vessels had only a slightly different internal temperature (see Figure 7). By looking at this plot the evidence shows that the temperature swings are far greater than they should have been. By further studying this phenomenon it was discovered that when the temperatures started to get erratic the smell of nitric acid fumes was evident. Through other trials it was determined that the lower temperatures evolved from weakened vessels. These vessels could no longer hold the pressure generated by the acids under the experimental conditions.

After several hundred trials the constant temperature programs succeeded as evidenced by the plot in Figure 8. The overall consistency of the temperature throughout the program proved that the computer was able to control the magnetron. The vessels did not vent as the temperatures did not exceed the temperature needed to reach above the 120 psig. pressure of the acid.

The next step involved the verification as to the validity of using this method to do sample preparation. This was accomplished by using the aforementioned controls from the NBS. These controls were guaranteed to be within a certain percentage of the value that was given by the National Bureau of Standards. If the controls that were digested compared to the specific values for the metals of interest, then the biologic samples would be analyzed and the values would be reported. The controls were digested in groups of six to determine if the reproducibility was acceptable. Through the trials that were performed, it was determined that the digestions were reproducible and that they matched closely to the assayed results (see Table 4).

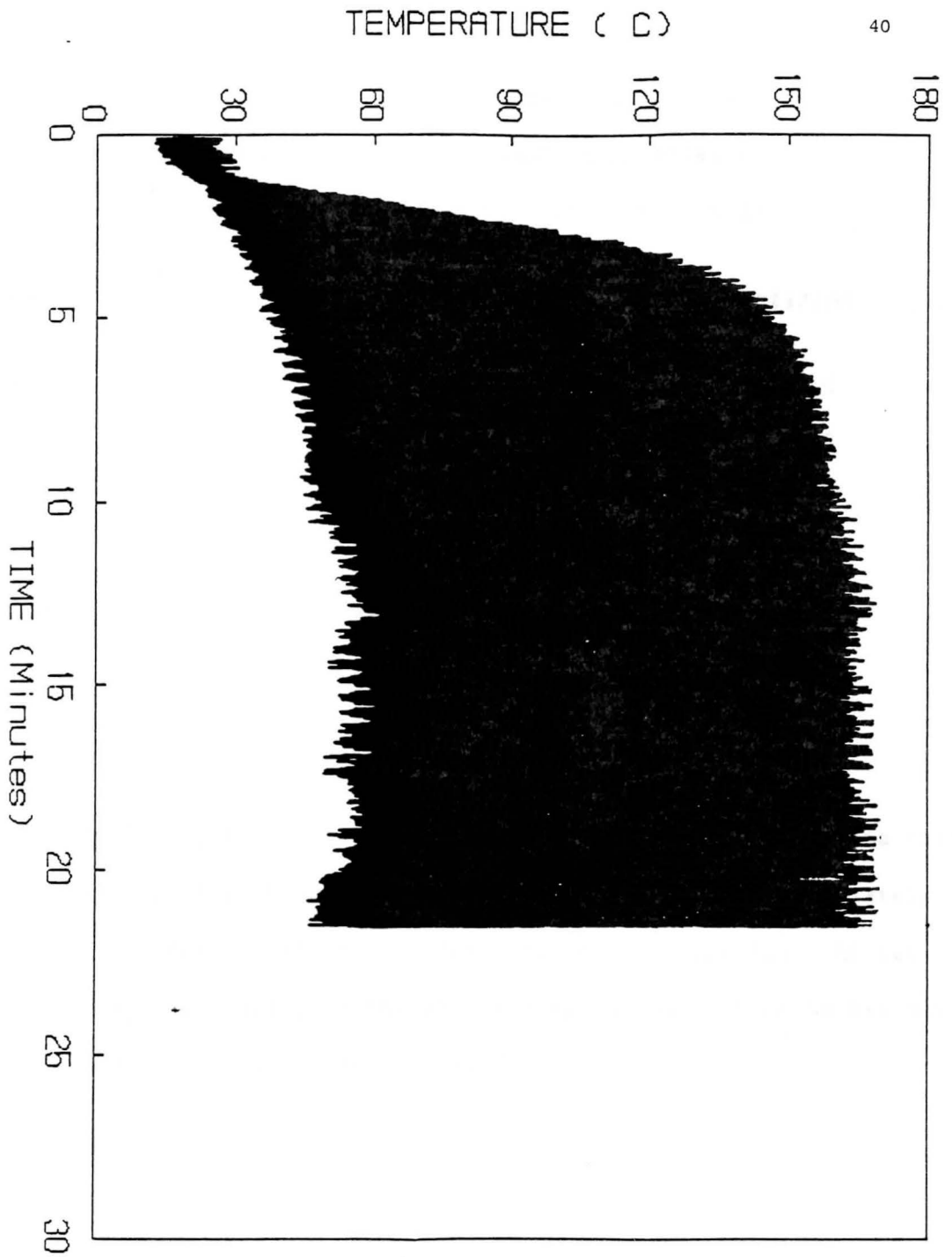

TEMPERATURE (C)
0
30
60
90
120
150
180
0
5
10
15
20
25
30
TIME (Minutes)

FIGURE 8

TABLE 4

COMPARISON OF ICP EMMISION SPECTROMETRY ANALYTICAL DATA FROM NBS 1752 CITRUS LEAVES BY CONSTANT TEMPERATURE MICROWAVE OVEN DIGESTION METHOD AND CERTIFIED VALUES

Element	*1752 Citrus Leaves*	*NBS Certified Values*
Ca wt %	3.17 ± 0.06	3.15 ± 0.10
Mg wt %	0.57 ± 0.02	0.58 ± 0.03
Ba µg/g	22 ± 1	21 ± 3
Mn µg/g	24 ± 2	23 ± 2
Zn µg/g	29 ± 2	29 ± 2
Cu µg/g	15 ± 2	16.5 ± 1.5

Sample digestions then preceded with confidence. The time that was saved overall enabled the analysis to be done almost immediately following the sample digestion. This proved the point that through the increased efficiency of the sample preparation, approximately one-half of the time of analysis was saved.

CHAPTER VI

RESULTS AND CONCLUSIONS

In this study, Constant Temperature Microwave Oven Digestion has been examined as a possible means of digesting samples. It was found to be a viable alternative to the normal inefficient sample digestion procedures currently described. In addition, the capability of monitoring the temperature of all vessels being heated was a considerable aid in sample digestion method development.

The ability to control the temperature by computer appreciably reduced the number of times vessel venting occured. With venting occuring less often, sample throughput was increased, since samples contained in vented vessels had to be discarded. Sample throughput was increased by a factor of two although the time for each individual digestion series was substantially increased.

The second finding in this research was that a more complete digestion was achieved. The microwave digestion had no visibly detected undigested material and this is a advantage to the analyst in the lab. The fact that there is less undigested material improves the overall performance of the instrument. The reduced levels of organic matrix causes samples and controls to be more similar under instrumental analysis. Accuracy and precision of the technique, whether ICP-AES or AAS, was increased.

The ability to determine when a digestion vessel cannot maintain the 120 psi specified pressure was an unanticipated result of considerable significance. With the expense of vessels, a tendency

exists to use vessels past their useful life. The inability of a vessel to remained sealed during a digestion was immediately noted. Sample throughput was increased by reducing the number of samples discarded due to venting.

It is believed that microwave oven digestion offers a successful alternative to the problems associated with the other types of digestion offered. It is faster than most other techniques with minimum contamination and volatile metal salt loss. The addition of constant temperature control dramatically facilitates digestion method development. Sample throughput can be significantly increased. CEM, the major manufacturer of laboratory microwave digestion systems, will incorporate this capability in the next generation of ovens it produces.

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APPENDIX 1

```
3  REM  ENABLE ANALOG HANDSHAKE
5  POKE 36259,1
10  LOMEM: 24576:D% = 0: PRINT  CHR$ (4)"BLOAD TIMOBJ1,A$370"
20 P = 0
2000  REM  MICROWAVE OVEN CONTROL ROUTINE
2001  PRINT
2002  PRINT "THE CORRECTION FACTOR (FAC) MAY NEED TO BE ADJUSTED ON A DAI
     LY BASIS.  IT'S VALUE IS DEFINED ON LINE 2150 OF THIS PROGRAM."
2004  PRINT
2010  PRINT "THIS PROGRAM MAY BE HALTED BY TYPING AN S"
2030  INPUT "WHAT TEMPERATURE DO YOU DESIRE? (RECOMMENDED MAX = 150 DEGRE
     ES CELSIUS)";TEMP
2049  PRINT
2080  PRINT "TEMPERATURE= "TEMP" DEGREES CELSIUS"
2105  INPUT "IS THIS CORRECT? (Y OR N)";YN$
2106  IF YN$ = "Y" GOTO 2120
2107  IF YN$ = "N" GOTO 2030
2120  FOR N = 1 TO 300
2125  & AIO
2130  IF D% > MAX THEN MAX = D%
2135  NEXT N
2150 FAC = .37
2155 IRTEMP = FAC * MAX
2156 MAX = 0
2157  IF IRTEMP >  = 190 GOTO 14900
2160  PRINT "THE PRESENT TEMPERATURE= "IRTEMP" DEGREES CELSIUS"
2161  IF P = 1 GOTO 2170
2162  IF IRTEMP > TEMP - 10 GOTO 3000
2164  IF IRTEMP <  = TEMP - 5 GOTO 2120
2170  IF IRTEMP > TEMP GOTO 2190
2180  IF IRTEMP < TEMP GOTO 2250
2190 D% = 1: & DOO
2195  FOR X = 1 TO 1000: NEXT
2200  IF  PEEK ( - 16384) < 128 GOTO 2120
2210  GOTO 15000
2250 D% = 0: & DOO
2260  FOR X = 1 TO 1000: NEXT
2270  IF  PEEK ( - 16384) < 128 GOTO 2120
2280  GOTO 15000
3000 D% = 1: & DOO
3005  PRINT IRTEMP
3007  FOR F = 1 TO 5000: NEXT F
3008 P = 1
3010  GOTO 2170
14900  PRINT "THE TEMPERATURE IS TOO HIGH"
15000 D% = 1: & DOO
15010  END
```