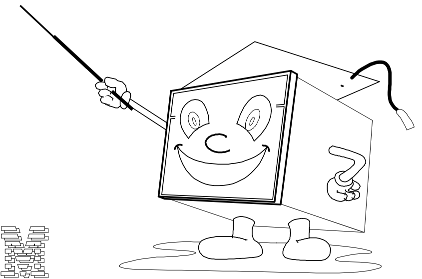
Microwave Heating:
Theory and Practice

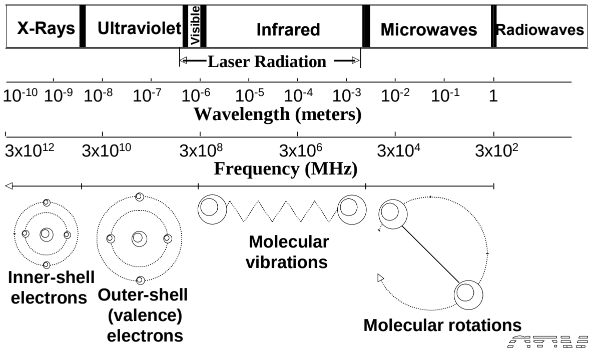


Based on Lecture Prepared by Dr. Lois B. Jassie

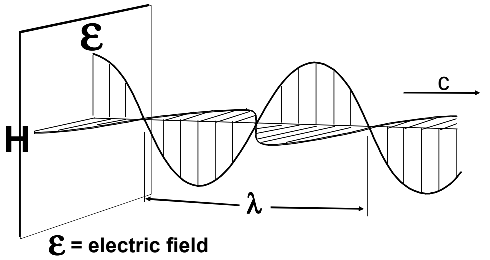
Characteristics of Microwave Energy

- **Microwaves are electromagnetic radiation between the far IR and radio waves**
- **Microwaves are nominally between 1 mm and 100 cm in length (*e.g.*, 2450 MHz wave is 12.25 cm)**
- **Microwave energy is non-ionizing, low photon electromagnetic radiation at the powers used**
- **Microwave radiation causes molecular (particle) and ionic motion and dipole rotation**
- **Microwave energy does not cause a change in molecular structure**

Electromagnetic Spectrum



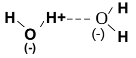
A Microwave



ε = electric field
H = magnetic field
λ = wavelength (12.2 cm for 2450 MHz)
c = speed of light (300,000 km/s, 3.00 x 10⁸ m/s)

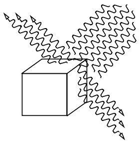
Microwave Energy *versus*
Other Electromagnetic Energy

Radiation Type	Typical Frequency (MHz)	Quantum Energy (ev)
Gamma Rays	3.0×10^{14}	1.24×10^{6}
X-Rays	3.0×10^{13}	1.24×10^{5}
Ultraviolet	1.0×10^{9}	4.1
Visible Light	6.0×10^{8}	2.5
Infrared Light	3.0×10^{6}	0.012
Microwaves	2450	1.013×10^{-5}
Radio	1	4×10^{-9}

Chemical Bond Type	Chemical Bond Energy (ev)
$H-OH$	5.2
$H-CH_3$	4.5
$H-NHCH_3$	4.0
H_3C-CH_3	3.8
$PhCH_2-COOH$	2.4
	0.21

Material Interaction With Microwaves

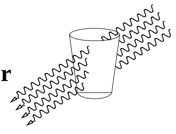
Conductor



Reflective

Metals reflect microwave energy and do not heat.

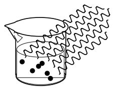
Insulator



Transparent

Numerous materials are transparent to microwave energy and will not heat but can be good insulators.

Dielectric



Absorptive

These materials absorb microwave energy and are heated.

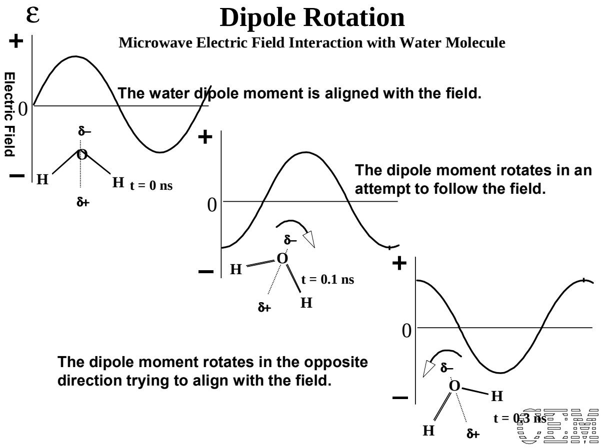
Liquids (mineral acids, solvents) heat rapidly when exposed to microwave energy. Absorption of microwave energy occurs by two mechanism:

Dipole Rotation
Ionic Conduction

Sources of (Internal) Heat
(*via* Energy Transformations)

- **Molecular Rotation**
- **Conformational Changes**
- **3-Dimensional Distortion**
- **Ion Flow Enhancements**
- **Liquid Structure Dissipation**

Dipole Rotation
Microwave Electric Field Interaction with Water Molecule

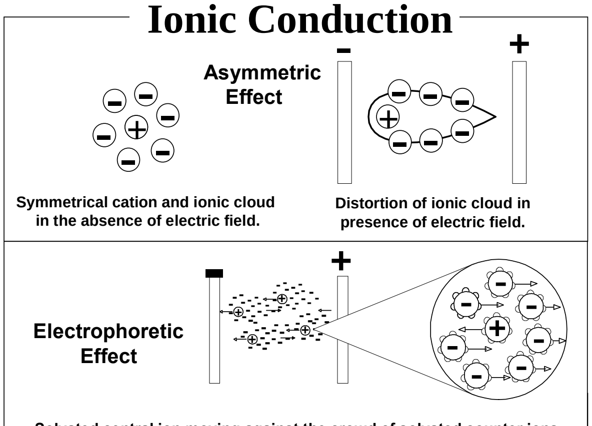


The water dipole moment is aligned with the field.

The dipole moment rotates in an attempt to follow the field.

The dipole moment rotates in the opposite direction trying to align with the field.

Ionic Conduction



Symmetrical cation and ionic cloud in the absence of electric field.

Distortion of ionic cloud in presence of electric field.

Solvated central ion moving against the crowd of solvated counter ions

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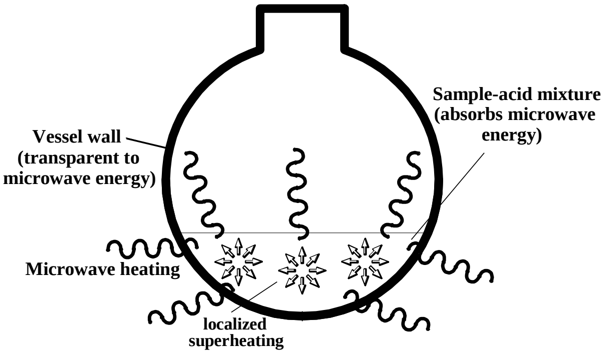
Schematic of Sample Heating by Microwaves



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Has this ever happened to you?

You try to make you coffee in the morning by heating the water in the microwave and when you add the coffee it boils all over the Counter top?

Explanation {Superheated}: Under microwave heating water boils at 105°C until nucleated to boil at 100°C.

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Superheated Temperatures of Solvents Irradiated with Microwave Energy

Solvent	Boiling Point, °C **	Superheated Temperature, °C	Temperature Difference, °C
Water	**100**	**105**	**5**
1-butanol	117	138	21
2-butanol	98	127	29
tert-butanol	83	112	29
methanol	65	84	19
2-propanol	82	108	26
1-pentanol	136	157	21
2-pentanol	119	135	16
tert-pentanol	120	115	13
1-heptanol	176	208	32
ethylene glycol	196	216	20
acetone	56	89	89
ethyl acetate	77	102	33
chloroform	61	89	25
diethyl ether	35	60	28
tetrahydrofuran (THF)	67	103	36
acetonitrile	**82**	**120**	**38**
cyclohexane	155	186	31
methyl ethyl ketone (MEK)	80	110	30

Reference: Majetich, G.; Neas, E.; Hoopes, T. *Journal of Chemical Education*, 1994

*** In 1 liter flask; ** B.P. at 760 mm. Handbook of Chemistry and Physics, CRC Press, Inc.**

Factors That Influence Solution Heating

Physical Properties of the Solution
- **Viscosity**
- **Temperature**
- **Polarity**
- **Heat Capacity**
- **Dielectric**

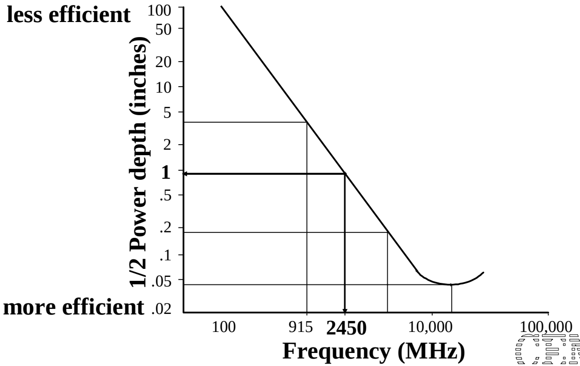
Ion Characteristics (conduction only)
- **Concentration**
- **Charge**
- **Size**
- **Mobility**

Wavelength

Factors that Affect Materials Heated with Microwaves

- ◆ **Angle of incidence of radiation**
- ◆ **Frequency**
- ◆ **Dielectric Constant**
- ◆ **Impedance**
- ◆ **Loss Mechanisms**
- ◆ **Mass and Molecular Size**
- ◆ **Magnetic Properties**

Variation of Penetration with Frequency for Water at 25°C



Dipole Moment

CCl_4	0
CO	0.10
HCl	1.08
H_2S	1.10
C_3H_8O	1.66
HF	1.82
H_2O	1.85
CH_3Cl	1.87
HNO_3	2.17
HCN	2.93
CsF	7.87

Handbook of Chemistry and Physics, 60th Edition, CRC Press,1980.
Table E-66*, Gas phase molecule

Dissipation Factor
Tangent delta

Ratio of the sample's dielectric loss (loss factor), *E"* to its dielectric constant, *E'*

Tangent δ = *E"/E'*

E"	**Loss factor is a measure of the sample material's ability to convert electromagnetic energy to thermal energy (heat).**
E'	**Dielectric constant is the sample material's ability to store the microwave energy.**

Effect of Increasing NaCl Concentration on the Dissipation Factor

Molal Concentration	Tangent δ (x 10^{-4})
0.0	1570
0.1	2400
0.3	4350
0.5	6250

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Effect of Temperature on the Dissipation Factor of Water

Temperature, °C	Tangent δ (10^{-4})[a]
1.5	3100
5.0	2750
15.0	2050
25.0	1570
35.0	1270
45.0	1060
55.0	890
65.0	765
75.0	660
85.0	547
95.0	470

[a] measurement at 3000 MHz and 25° C

Selected Physical and Dielectric Constants of Organic Solvents

Solvent	BP	VP	E'	Dipole Moment	tan δ x10^{-4}
acetone	40	436	8.93	1.14	
methanol	**56**	**184**	**20.7**	**2.69**	**6400**
tetahydrofuran	65	125	32.7	2.87	
hexane	**69**	**120**	**1.88**	**<0.1**	
ethyl acetate	77	73	6.02	1.88	
ethanol	**78**	**-**	**24.3**	**1.69**	**2500**
acetonitrile	82	89	37.5	3.44	
2-propanol	82	32	19.9	1.66	6700
1-propanol	97	14	20.3	3.09	~2400*
iso-octane	99	49	1.94	0	
water	**100**	**760**	**78.3**	**1.87**	**1570**
MIBK	116	20	13.11	-	
DMF	153	2.7	36.71	3.86	
DMSO	189	0.6	46.68	3.1	
ethylene glycol	**198**	**-**	**41.0**	**2.3**	**10,000**

note: data from Burdick & Jackson Laboratories Solvent Handbook. BP at 760 torr, VP (torr) at 25°C; e' at 20 °C; dipole moment at 25 °C. * at 10 °C (E.Peterson, IMPIsymposium, 1989). Tan δ values from von Hippel, MIT Presss, 1954.

Thermal and Microwave Characteristics of Laboratory Container Materials

Material	Melting Point (°C)	Maximum Service Temperature (°C)	Tangent δ (x10^{-4})
Water			1570
Sodium chloride (0.1 molal)			2400
Polysulfone	<190	160	760
Phenol/formaldehyde	dec	120-190	519
Bakelite (asbestos filled)	dec	200-218	438
Nylon 6/6	253	102	128
Glass (Corning 0800)	>1000	---	126
Glass (Borosilicate)	>1080	---	12-75
Ceramic (depends on type)	---	---	6-50
Polypropylene	168-171	100-105	57
Polymethylmethacrylate	115	76-88	57
Porcelain (4462)	---	---	11
Polystyrene	242	82-91	3.3
Polyethylene	120-135	71-93	3.1
Kel-F, CTFE	198-211	199	2.3
Polymethylpentene	240	175	---
Tefzel, TFE+CE	271	200	2.0
Halon, (P)TFE	>320	260	1.5
Teflon®, FEP	252-262	204	---
Teflon®, PFA	302	260	1.5
Polycarbonate	241	121	0.7
Quartz, fused	>1665	---	0.6

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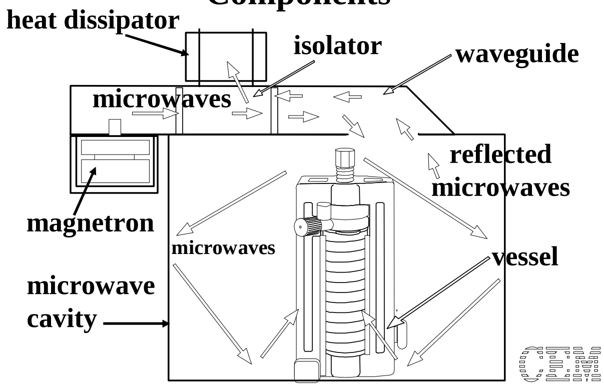
Components of a Microwave System

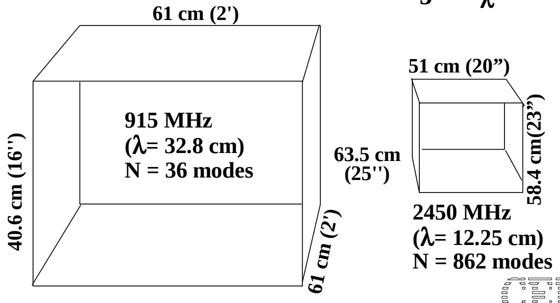
- Magnetron
- Waveguide
- Cavity
- Circulator
- Turntable
- Wavelength Attenuator Cutoff
- Duty Cycle

Schematic of CEM Microwave Components



Heating Efficiency of Microwave Cavities

$$N = \frac{8\pi}{3} \circ \frac{V}{\lambda^3}$$


61 cm (2')

40.6 cm (16'')

61 cm (2')

915 MHz
(λ= 32.8 cm)
N = 36 modes

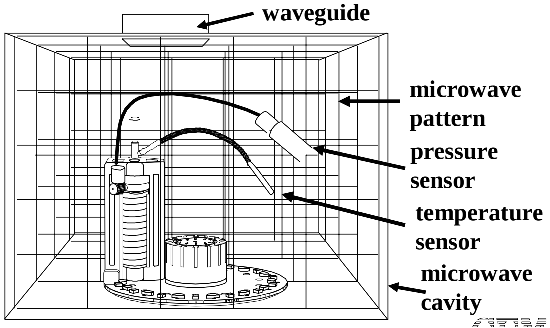
51 cm (20”)

63.5 cm
(25'')

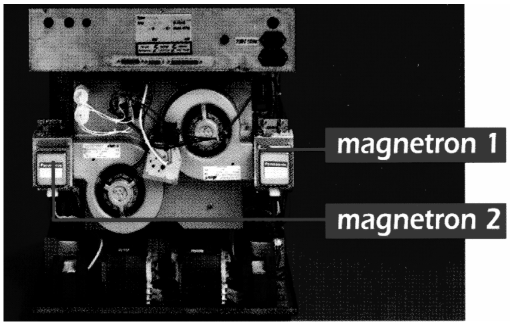
58.4 cm(23”)

2450 MHz
(λ= 12.25 cm)
N = 862 modes

Schematic of Microwave Pattern Interaction with Pressure Vessels

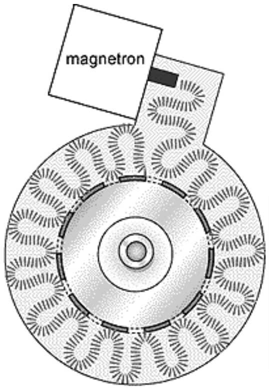


Double Magnetron Design



Dr. S. Leikin

CEM Microwave Components



Cycling the Magnetron

Controls the power to obtain average power level

Duty Cycle = $\frac{\text{length of time magnetron is on}}{\text{time base}}$

Time base = 60 Hz (60 times/sec)

Examples

1. **500 W on a 1000 W unit (50%) with a 60 Hz time base the magnetron goes on 30 times/sec and off 30 times/ sec. In 10 min at 50% power, a MW field is created 18,000 times and gives the appearance of continuous power**
2. **500 W on a 1000 W unit (50%) with a 1 sec time base has the magnetron on 0.5 sec and off 0.5 sec. In 10 min heating at 50%, a field is created 600 times**

Calibration of a Microwave Oven

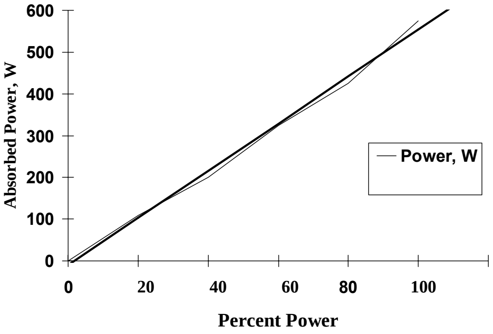
- **Weigh 1 kg of ~ 23°C DI water in a plastic vessel**
- **Measure initial temperature of the water (T_i) to ±0.05 °C**
- **Irradiate 1 kg of water for 2 minutes at three different power settings (e.g., 100%, 50% and 25%).**
- **Measure final temperature of water (T_f), ±to 0.05 °C with stirring; use highest temperature**
- **Repeat twice more with new sample of room temperature water in room temperature container**
- **Calculate unit power according to the formula**

$$\text{Power} = \frac{K \times Cp \times M \times \Delta T}{t} \qquad \Delta T = (T_f - T_i)$$

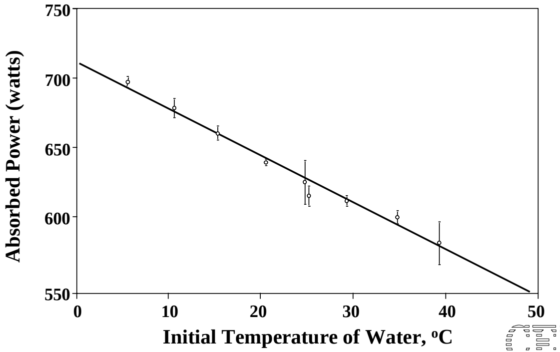
for 1000 g water and 120 s, the equation becomes

$$\text{Power (watts)} = 34.85 \times \Delta T$$

Linearity of Proportional Power

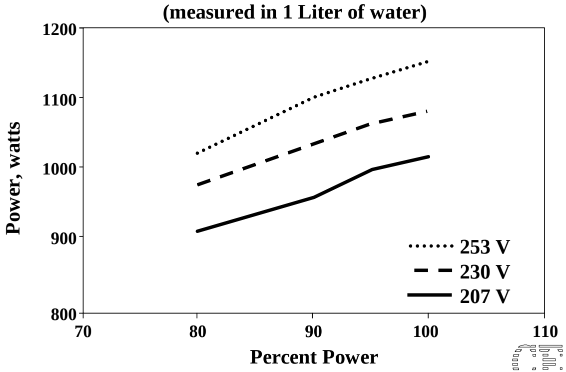


Water Starting Temperature and the Measurement of Full Power



Effect of Changes in Line Voltage on Absorbed Power

(measured in 1 Liter of water)



Sources of Error in Microwave Calibration

Method Dependent
- **Vessel Material- heat loss, absorption of MW**
- **Vessel Configuration- height and diameter**
- **Engineering Design- cavity dimensions, exhaust fan, hot spots**
- **Electrical- line voltage, power supply (capacitor)**

Measurement Dependent
- **Temperature- accuracy and size of Δ T**
- **Starting Temperature of Water**
- **Properties of Water- dielectric of dissolved ions and heat capacity**
- **Irradiation Time**
- **Low Power- errors greater than at high wattage**

Absorbed Microwave Power in Multiple Vessels

Number of Vessels	Thermister	Digital Thermometer		Mean
1	989 ± 13	963 ± 5	967 ± 2	973 ± 8
2	965 ± 12	991 ± 30	997 ± 15	984 ±19
5	982 ± 5	995 ± 10	986 ± 17	991 ± 6
$\bar{X}$	979 ± 12	983 ± 17	986 ± 17	982 ± 9

- uncertainty is expressed as one standard deviation
- range of uncertainty is 0.4% to 3%
- MDS-205 at 100%, starting water temperature 23 ± 2 °C, 12/3/90

Microwave Hardware Design

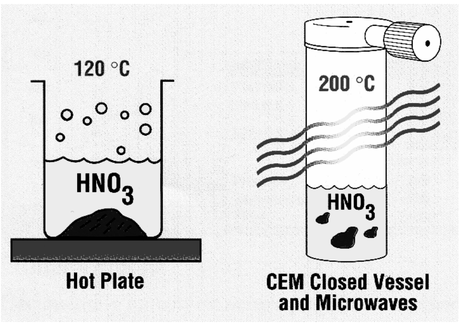
Objectives of Sample Preparation

- Ability to prepare multiple samples
- Ability to monitor and control reaction conditions
- Ability to achieve rapid sample throughput
- Automation

Problems

- Uniform distribution of energy to multiple samples
- Temperature and pressure monitoring in MW
- Strong microwave-transparent vessels
- Relief mechanism must be microwave immune

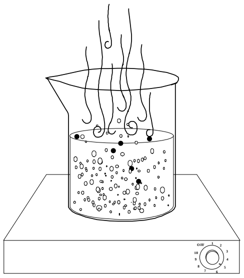
Microwave Closed Vessel *vs.* Open Vessel (Hot Plate)



Classical Digestion Approaches

Open Vessel on Hot Plate

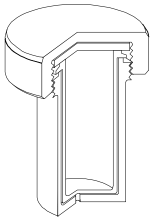
- Easy to Use
- Low Capital Cost
- Slow
- Labor Intensive
- Easily Contaminated



Classical Digestion Approaches

Closed Vessel

- Raise reagent temperature above boiling
- Sealed environment
- Limited sample size
- Pressure build up difficult to control



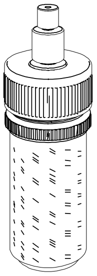
Organic Samples

Matrix, Size, and Reagents

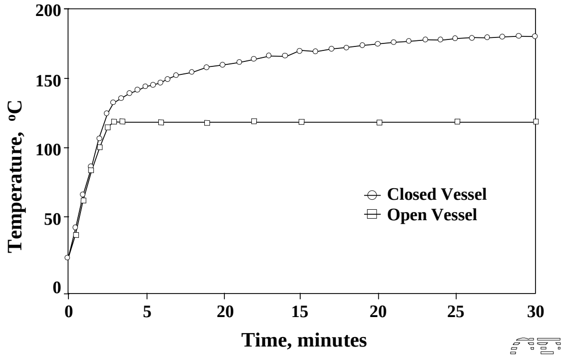
Generate high gas volume during dissolution. Sample size helps determine method.

> 0.5 g
Open Vessel

< 0.5 g
Closed Vessel



Temperature Curve for Open Vessel and Closed Vessel Microwave Heating



12 each 120 mL PFA vessels, 19 mL HNO_3 per vessel, 648 W power

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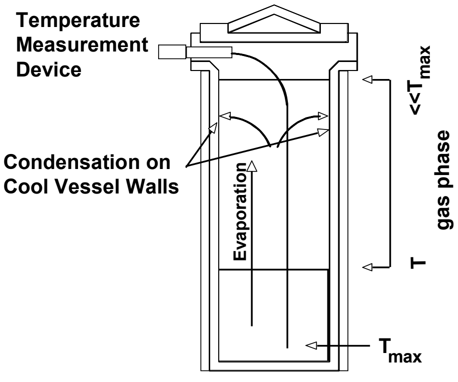
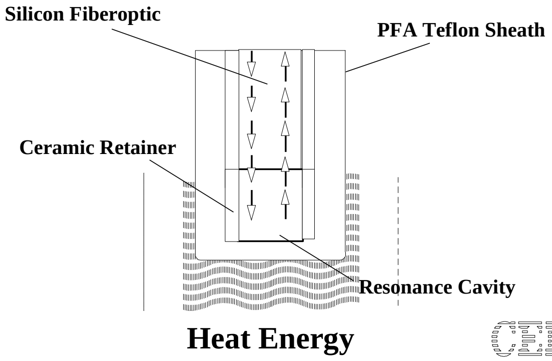
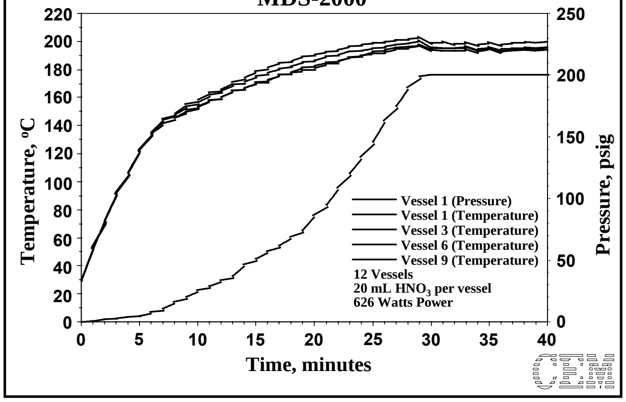


CEM RTP-300 Plus Probe



Temperature-Pressure Curves

MDS-2000



Heating of Acids in a Microwave Cavity

Thermodynamic Basis of Measurement

$$P = \frac{(K)\,(Cp)\,(m)\,(dT)}{t}$$

P, power absorbed by sample in watts, W (W=joule/sec)
K, conversion factor for thermochemical calories to W =4.184
Cp, heat capacity, thermal capacity, specific heat, cal/g/C
m, mass of the sample in grams, g
dT, final temperature minus initial temperature, $dT=(T_f - T_i)$
t, time in seconds

Estimate T_f from

$$T_f = T_i + \frac{(P)\,(t)}{(K)\,(Cp)\,(m)}$$

Estimate time to reach T_f

$$t = \frac{(K)\,(Cp)\,(m)\,(dT)}{(P)}$$

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Microwave Sample Preparation

How to Control The Digestion ?

Reaction Chemistry and Mechanisms

Reagents (*e.g.*, Acids) and Temperature
Decomposition Rate
Separation or Oxidation *vs*. Explosion
Extent of Extraction

Distribution

Contamination of Reaction Environment
Loss of Analyte

New Available Mechanism

Unique T and P Capability for Chemical Reactions
Retention of Elements Evaporated by Microwave Only

Why these concepts are so important?

- **Temperature and pressure relationships are unique in microwave equipment**
  - **They are not predictable from convection and conduction data tables**
- **Boiling points of many solvents are elevated and not standard under MW conditions**
- **Non-classical relationships exist in closed vessels**
- **These unique conditions aid in specific technology and applications**

Goal:

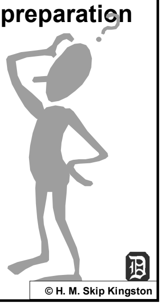
Achieve Control of Sample Preparation/ Decomposition/Extraction/ (and post reaction sample manipulation) Using Unique Mechanisms (& apparatus)

Control of

- **Reaction Chemistry**
- **Microwave Energy Transfer**
- **Microwave Reaction Mechanisms**
- **Equipment Configuration and Operation**
- **Reaction Environment**

Key Unique Technical Advantages of Microwave Energy Application

- Microwave enhanced chemistry is unique
- Key technical advantages in sample preparation
  - Unique relationships
  - Chemical reaction control
  - Standardization
  - Clean chemistry and its strategic effect
  - Applications
- Microwave Technologies



Quantum Absorption of Microwave Energy is Predictable and Controllable

Fundamental Relationship

$$P_{absorbed} = \frac{KC_p m \Delta T}{t}$$

Used to Predict Temperature

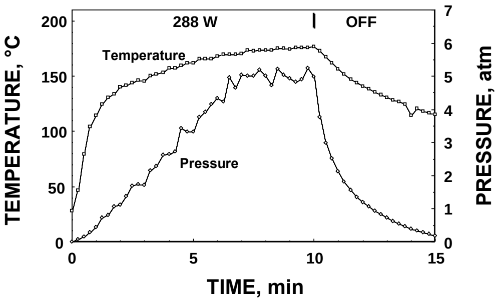
$$T_f = T_i + \frac{P_{absorbed} \cdot t}{K \cdot C_p \cdot m}$$

Deviation from Ideal Conditions

$$T_f = T_i + \frac{P_{absorbed} \cdot t}{K \cdot C_p \cdot m} - \text{Heat Loss}$$

Dependent on Equipment Configuration

Final Microwave Heating Profile of 16 mL of Nitric and Hydrofluoric Acids (5:3 v/v). What is happening? Why do they appear this way?



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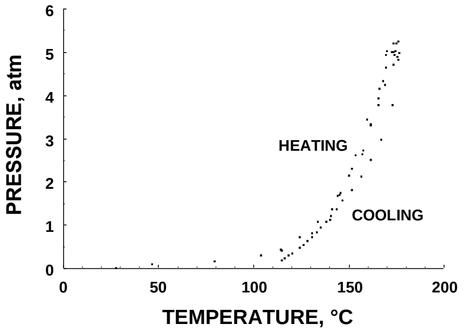
Temperature and Pressure Profile of 16 mL of Pure Nitric and Hydrofluoric Acids (5:3v/v) Only No Sample Present



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Example: Vapor Pressure Nitric Acid

Temperature, °C	Pressure lb/in ^{2}	P, atm
133	180	12.3
165	380	25.9
192	630	42.9
219	995	67.7
256	1565	107
285	2245	153
313	2945	200

Reference
Journal of Research of the National Bureau of Standards, vol. 30, Feb. 1943, p 110.

Conventional Open Vessel on a Hot Plate

At Atmospheric Pressure
HNO_3, maximum (boil point) T ~ 120 °C, w/continual heat loss

Conventional Steel Jacketed Bomb in an Oven

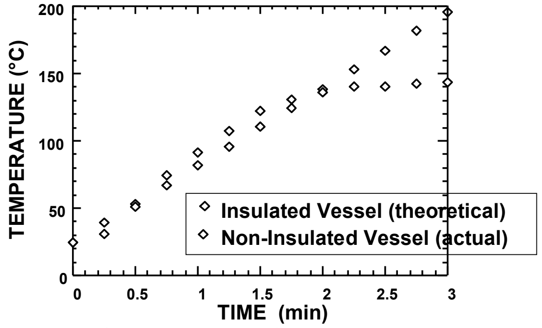
Bomb Reaches Thermal Equilibrium with Oven
Liquid and Gas Phases Both at Final Temperature
HNO_3 at 180°C, Pressure ~ 40 atm

Microwave Closed Uninsulated Vessel (All PFA)

Pressure is Limited by Heat Loss in Vapor Phase
HNO_3 at 180 °C, Pressure ~8 atm

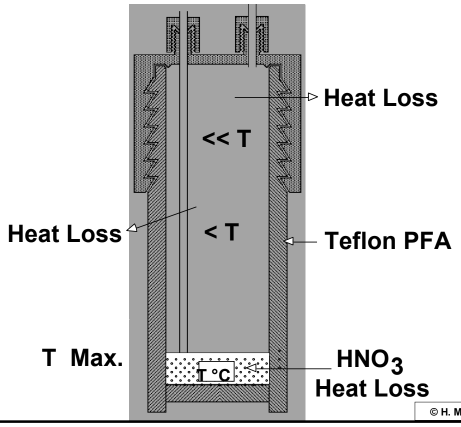
This Condition Results in a
"Sustained Dynamic Non-Equilibrium"

Temperature in an Insulated and Non-Insulated Vessel During the First Three Minutes



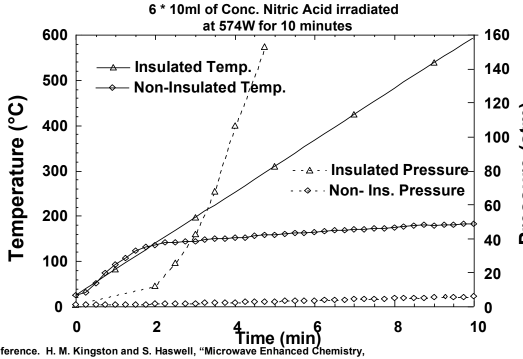
Reference. H. M. Kingston and S. Haswell, “Microwave Enhanced Chemistry, Chapter 3, ACS Professional Reference Book, ACS Washington DC, 1997.
U.S. Patent # 5,883,349 , Kingston “Method and Apparatus for Microwave Assisted Chemical Reactions’, March 16, 1999
C/MAC, Duquesne University

Vessel During Microwave Heating



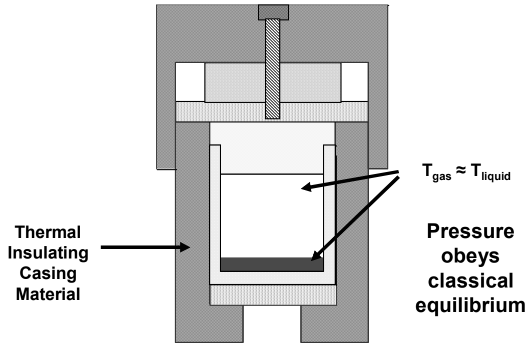
Comparison of Reaction Conditions in Insulated and Non-Insulated Vessels

6 * 10ml of Conc. Nitric Acid irradiated at 574W for 10 minutes



Reference. H. M. Kingston and S. Haswell, “Microwave Enhanced Chemistry, Chapter 3, ACS Professional Reference Book, ACS Washington DC, 1997.
U.S. Patent # 5,883,349, Kingston “Method and Apparatus for Microwave Assisted Chemical Reactions’, March 16, 1999
C/MAC, Duquesne University

Insulated Microwave Bomb



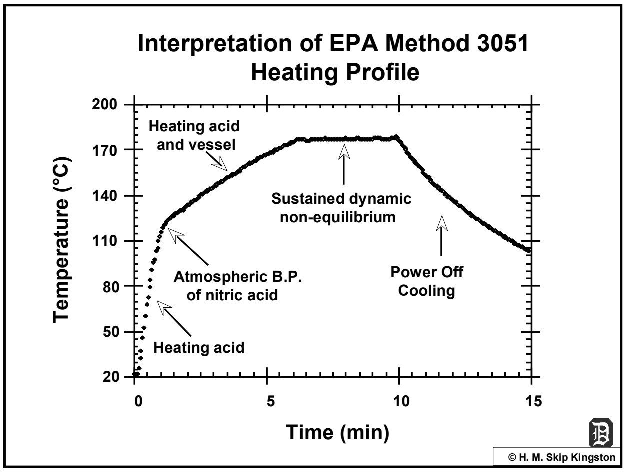
Summary

- PV = nRT
  - V and R are constants
  - If either T or n are reduced, P is reduced
- Microwave systems are not in equilibrium and heat loss reduces both n (the number of gas molecues) in the gas phase and the T (temperature) of the gas phase as the gas phase collides with the energy transparent vessel walls, which are being cooled externally

---

Heat Loss from the Microwave Bombs

	Temperature			
	Non-Insulated Vessle		Insulated Vessle	
	PFA Vessel (Savillex ™)		High Pressure (PARR ™)	
Reagent	Inside	Outside	Inside	Outside
H_3PO_4/HNO_3	132°C(60 mL)	92°C (Bottom)	>200°C	47°C (Side)
HNO_3/HCl	78°C(120 mL)	72°C (Bottom)	>200°C`	44°C (Bot.)



Interpretation of EPA Method 3051 Heating Profile

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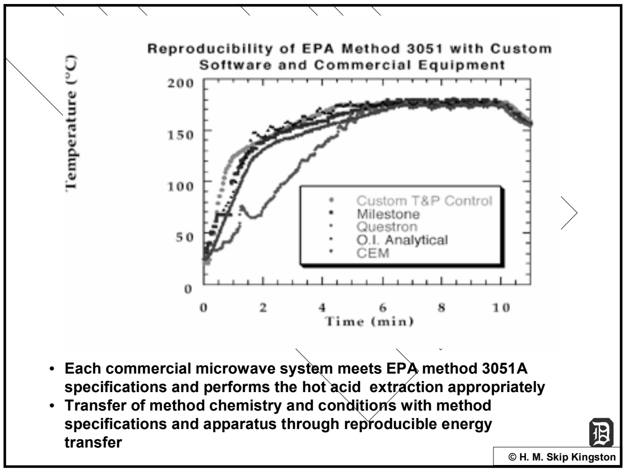

Reproducibility of EPA Method 3051 with Custom Software and Commercial Equipment

- Each commercial microwave system meets EPA method 3051A specifications and performs the hot acid extraction appropriately
- Transfer of method chemistry and conditions with method specifications and apparatus through reproducible energy transfer

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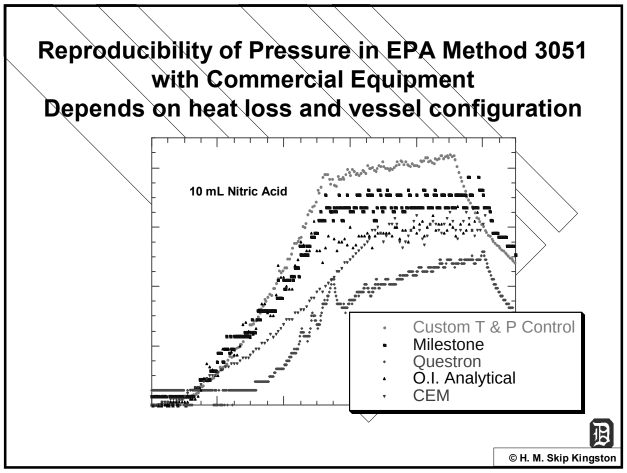

Reproducibility of Pressure in EPA Method 3051 with Commercial Equipment Depends on heat loss and vessel configuration

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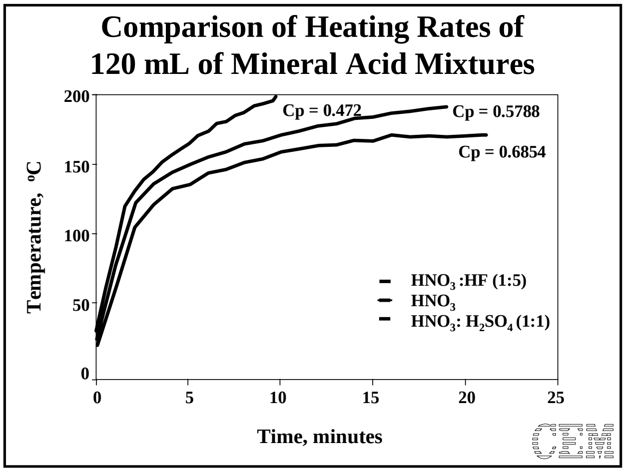
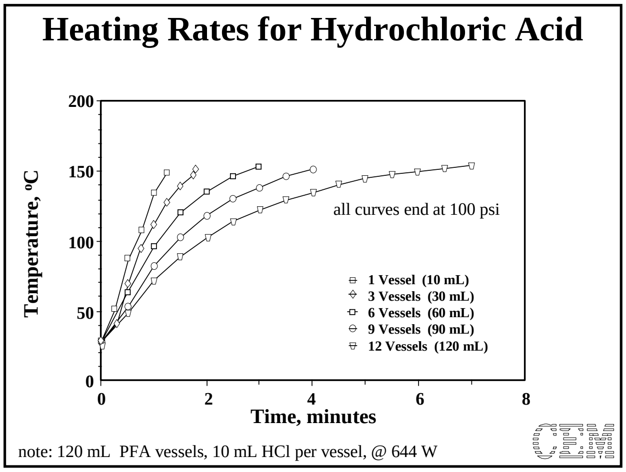
Absorption Efficiency

Absorption Efficiency, % = <u>Av Power *, W x 100</u>
Input Power, W

*** measured in the first 90 seconds**



Comparison of Heating Rates of 120 mL of Mineral Acid Mixtures

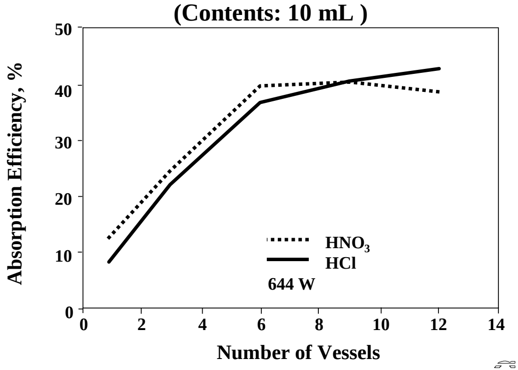


Heating Rates for Hydrochloric Acid

note: 120 mL PFA vessels, 10 mL HCl per vessel, @ 644 W

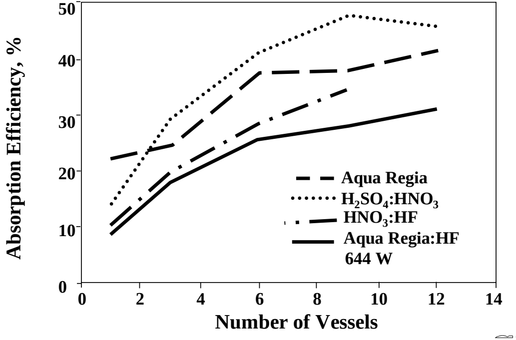
Absorption Efficiency of Individual Acids as a Function of the Number of Vessels

(Contents: 10 mL)



Absorption Efficiency of Mixed Acids as a Function of Number of Vessels

(Contents: 10 mL)



Mineral Acid Decomposition of Matrices

Biological Samples

$$C_2H_4 + 12HNO_3 \xrightarrow[\text{mwave}]{\text{heat}} 12NO_2\uparrow\ 8H_2O + 2CO_2\uparrow$$

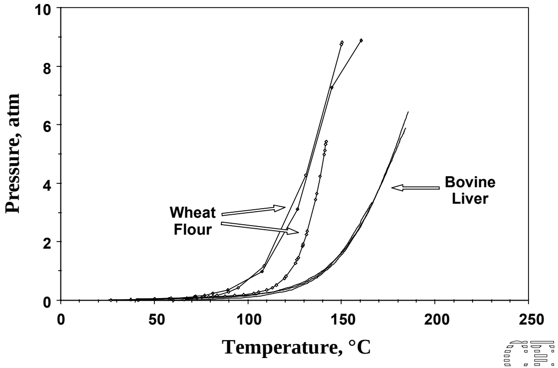
Geological Samples

$$SiO_2 + 4HF \xrightarrow[\text{mwave}]{\text{heat}} 2H_2O + SiF_4\uparrow$$

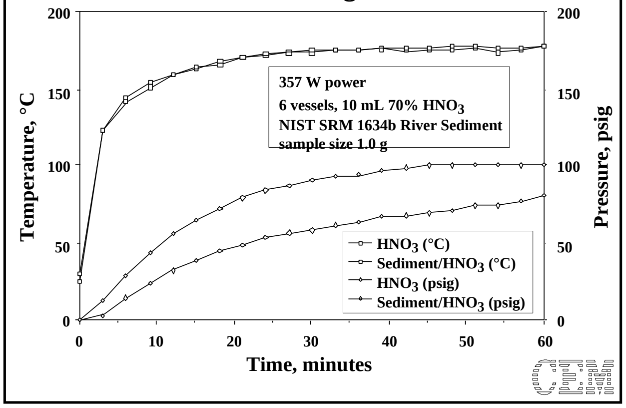
Metals

$$Cu + 2HCl \xrightarrow[\text{mwave}]{\text{heat}} H_2\uparrow + Cu\ Cl_2$$

Predicted Decomposition Curves Showing Transition Temperatures for Real Materials



Temperature and Pressure Curves for River Sediment Digestion



Safety in the Analytical Laboratory Using Microwave Decomposition

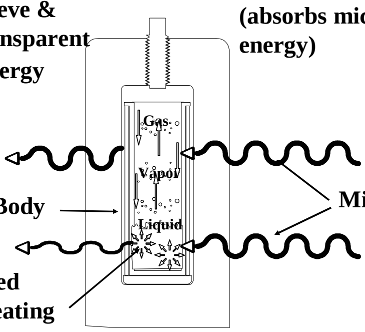
Radiation
- Leak Detection
- Safety Interlocks
- Wavelength Attenuator Cutoffs
- Remote Operation

Pressure
- Vessel Construction
- Safety Release Devices
- Software

Temperature
- Materials and Construction Design
- Fiber Optic Thermometer

Chemistry
- Acid Choice
- Matrix Composition

Sample Heating by Microwaves



Liner, sleeve & frame transparent to MW energy

Sample-acid mixture (absorbs microwave energy)

Vessel Body

Microwaves

Localized superheating

Volatile Elements and MW Heating in Closed Systems

Normal Heating

- Solvated ions (Cl^-, F^-) in solution have no vapor pressure
- At elevated temperatures, vapor pressure of Cl^- and F^- metal salts is much higher than acid vapor pressures

Reduced Pressure (vacuum)

- Solution vaporization temperatures appear to decrease as volume decreases; accompanying boiling points and acid vapor pressures decrease as well
- Final solution temperature of 3 mL is < 60°C. B.P. of volatile salt is never reached

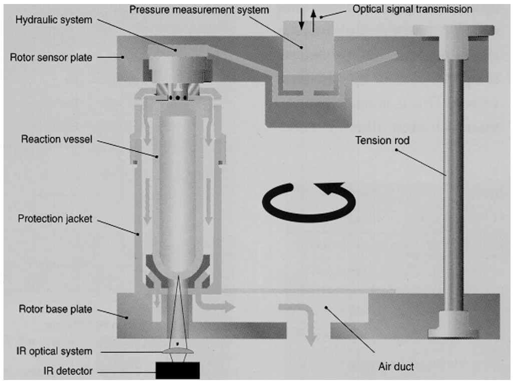
Link, D. D., Kingston, H. M. *Anal. Chem*. 72(13), July 1, 2000, p 2908

Safety in Microwave Digestion Systems

"Laboratory Microwave Devices are Chemical Reaction Systems"

- Microwave digestion systems are general purpose systems. Reactants and reaction conditions are not specified and are often unknown in some cases.
- Microwave digestion systems are designed to meet electrical, mechanical and chemical safety standards, as well as safety factors specific to microwave heating
- Microwave digestion systems that have a means of cooling (air flow or liquid) remove heat from outer jacket and can moderate reaction rates
- Microwave digestion systems do not control pressure directly (*i.e.*, no control or check valve or back pressure regulator).

Multiwave: Temperature and Pressure Control



Mechanical and Radiation Safety

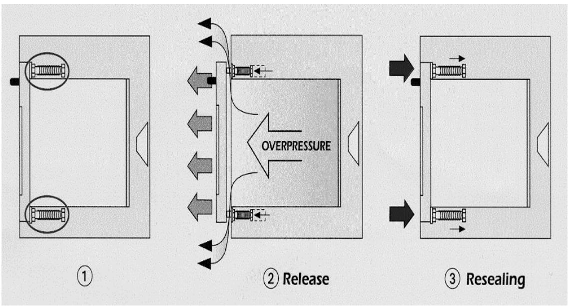
Mechanical

Door- positive button release; interlock monitoring system
Latches- safety interlocks; separate circuitry
Thermal Switches- prevent magnetron overload, door interlocks compromised
Exhaust-variable speed fan; corrosion resistant plastic hose
Inlet/Outlet Ports- stainless steel wavelength attenuators
Isolator-patented reflected power circulator
Teflon Coated Stainless Steel Cavity- < 5 mw/cm^2 leakage

Radiation

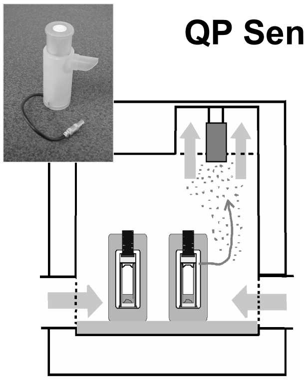
Mirowave Leakage Detectors- survey meters

Pressure Release Door



Dr. S. Leikin

QP Sensor



- QP “Quality Pressure” chemical sensor monitors acid vapors within the microwave cavity
- Once past a preset value, the QP will adjust power to the unit, preventing exothermic reactions

Dr. S. Leikin

Pressure Can be Dangerous

Vessels

Construction- molding, machining
Design- threaded, pressure seals, edges
Materials- plastic, polymers, glass, metal rotors, and frame construction

Safety Devices

Relief disks
Relief diaphragms, membranes
Compression devices
External relief valves

MARS 5 Digestion System Hardware & Software Safety Features

Hardware (integral software)

ReactiGuard^{TM}: sensor disables magnetron in case of disruptive event in the cavity

Turntable sensor: senses stop-software override restarts rotation

TempGuard^{TM} (optional): IR temperature sensor to prevent vessels overheating

SafetyLock Door: positive button release, spring-loaded metal door (burps when vessel vents violently)

Safety Switch: shuts down magnetron in case of overheating

Isolator: shunts reflective MW energy to dummy load, prevents magnetron from overheating

---

MARS 5 Digestion System Hardware & Software Safety Features

Software

Temperature: 0-300 °C (jacketed); 0-260 °C (Thermo-Optic) automatic default at 210 °C

Pressure: sensed 200 times/minute- control to 800 psi, and monitor to 1500 psi; sensor drop > 20psig/5 sec shuts off MW power

AutoLoad^{TM} sensing: checks power to maintain 90% on rate

Chemical Safety Concerns at High Temperature

Mineral Acids

Perchloric.....	**Dangerous hot** **Explosive with potassium** **Decomposes to Cl_2 gas**
Sulfuric......	**Dehydrating agent**
Hydrofluoric..	**Biological irritant/poison**
Aqua Regia....	**Nitrosyl chloride gas irritant**

Alkaline Hydroxides

NaOH, KOH, LiOH..... Caustic, dehydrating, biological irritants

Peroxides

Hydrogen.....	**Potent oxidizer**
Organic Ethers..	**Explosive**

Organic Solvents

toxcity; explosiveness; flammability; noxiousness; volatility

---

Unique Hazard of Metal/Alloy Acid Digestions in a Microwave Unit

- **Metals with negative reduction potentials liberate hydrogen gas; e.g., Pb^{2+}, Sn, Ni, Zn, Cr, Fe^{2+}, Mn^{2+}, Mg, Na, Li**
- **Samples sealed in air**
- **Potentially flammable/explosive mixtures may form where metals mixtures’ activation energy to ignite is very low**
- **Interaction of metal particles and strong magnetic field can generate sparks**

Example: **Titanium metal shavings, 0.1g in HCl:HF, 10:5 mL**
2 ACVs with Temperature and Pressure control

Digestion program	1	2	3
power	80	80	80
pressure	100	150	200
run time	10	30	30
TAP	5	20	20
temp, °C	180	180	180

note:After 3 min, cover was blown off non-control vessel

How to Avoid Forming Potentially Dangerous Hydrogen Mixtures During Microwave Acid Digestion of Metals/Alloys

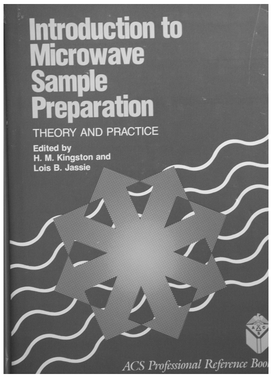
- **Seal closed digestion vessels in inert gas atmosphere**
  - ***e.g.*, glove-box under nitrogen or argon**
- **Purge vessel with nitrogen or argon after addition of acid**
- **Purge microwave compartment with inert gas (argon or nitrogen) when open vessels are used**

Compounds Unsuitable for Closed Vessel Microwave Acid Digestion

- **Explosives (TNT, nitrocellulose, *etc*.)**
- **Propellants (hydrazine, ammonium perchlorate, *etc*.)**
- **Pyrophoric chemicals**
- **Hypergolic mixtures (nitric acid with phenol, triethylamine, or acetone)**
- **Animal Fats (glycerol esters undergoing nitration to nitroglycerin)**
- **Aviation Fuels (JP-1)**
- **Acetylides (compounds of acetylene)**
- **Glycols (ethylene glycol, propylene glycol, *etc*.)**
- **Perchlorates (potassium, ammonium)**
- **Ethers (Cellosolve, *etc*.)**
- **Lacquers**
- **Alkanes (butane, hexane, *etc*.)**
- **Ketones (acetone, methyl ethyl ketone, *etc*.)**

Microwave Sample Preparation Techniques

- Acid digestion for atomic absorption (AA), emission (ICP) and mass spectroscopy
- Hydrolysis of proteins and peptides for amino acid Analysis
- Polymer dissolution for molecular weight determination by gel permeation chromatography (GPC)
- Acid digestion of reinforced composites for gravimetric determination of fiber content
- Solvent extraction for gas and liquid chromatography
- Sample drying and moisture determination
- Organic synthesis reactions
- Dry ashing

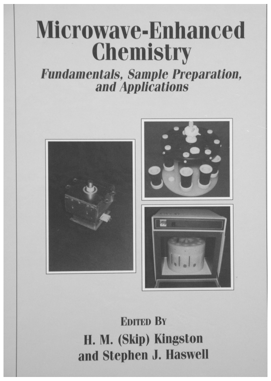


Introduction to Microwave Sample Preparation

THEORY AND PRACTICE

Edited by
H. M. Kingston and
Lois B. Jassie

ACS Professional Reference Boo



Microwave-Enhanced Chemistry

Fundamentals, Sample Preparation, and Applications

Edited By
H. M. (Skip) Kingston
and Stephen J. Haswell