


When Microwaves Left the Kitchen

How a Modern Convenience Made
the Transition into the Laboratory

The image is a composite. The left side shows several glass test tubes in a rack, illuminated with a warm, orange glow. The right side is a dark background with a white spectral plot showing a sharp peak and a broader, lower-intensity peak.

J.P. Northrop
Anton-Paar USA

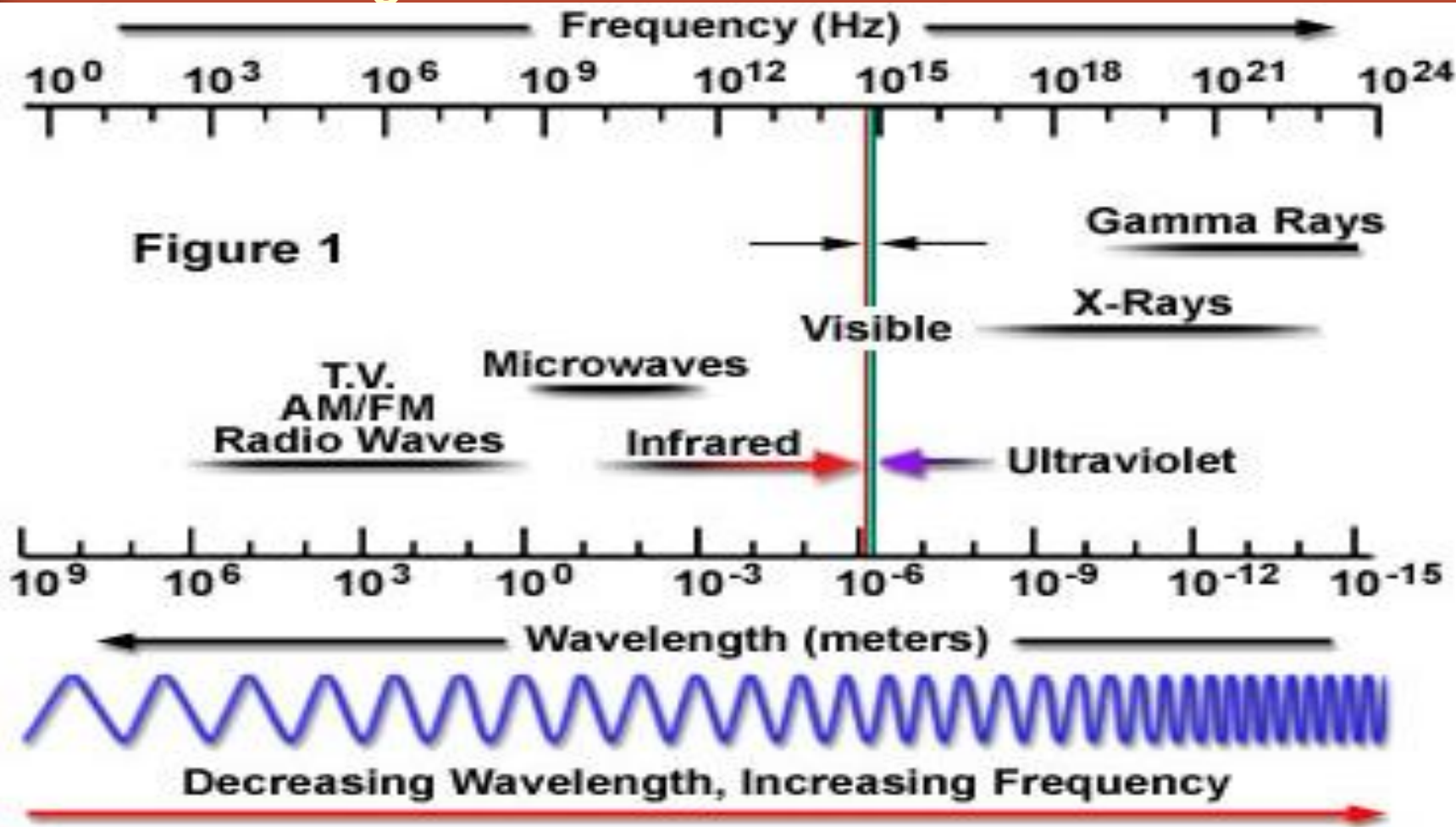
The Modern Microwave

- “Discovered” by Dr. Percy Spencer of Raytheon Labs – 1946.
- Started domestic use around the mid-1970s.
- Typically for heating food and beverages.
- Uses electromagnetic waves in the Ultra-High, Super-High, and Extremely-High Frequency range (0.3 GHz to 300 GHz)



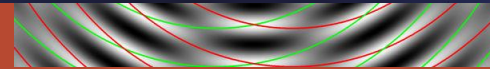
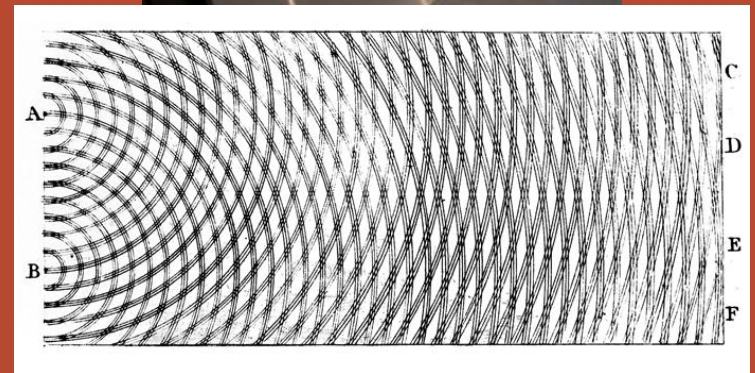
Principles

- Time to go in the “WABAC Machine”



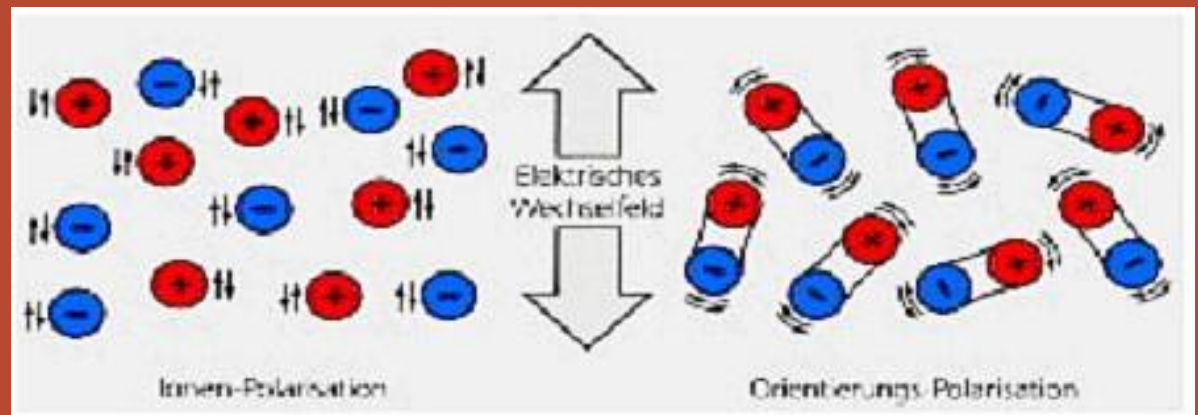
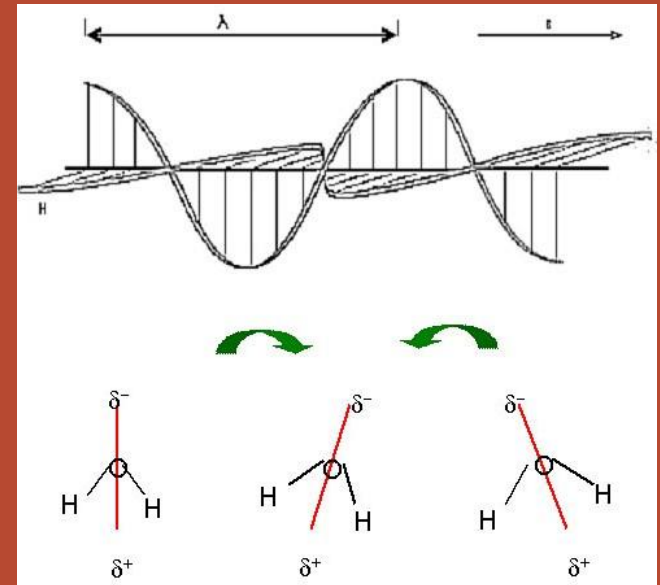
Property of Electromagnetic Waves

- Show similar properties as light
 - Diffraction
 - Interference
 - Refraction
 - Reflection
- Microwaves
 - Reflected by non-polar metals
 - Pass through Ceramics and Glass
 - Are typically absorbed by organic materials



Microwave Heating

- One of two typical ways:
- Dipole Moments
- Ionic Solutions



As a result . . .

- Not all solvents are good for use in a microwave:

Poor	Medium	Good
Chloroform	Water	Methanol
Dichloromethane	Acetonitrile	Ethanol
CCl ₄	Acetone	Propan-2-ol
n-Hexane	Ethylacetate	1-Butanol
Toluene	Tetrahydrofurane	Ethylene glycol
Xylene	DMF	

No More Hard Science

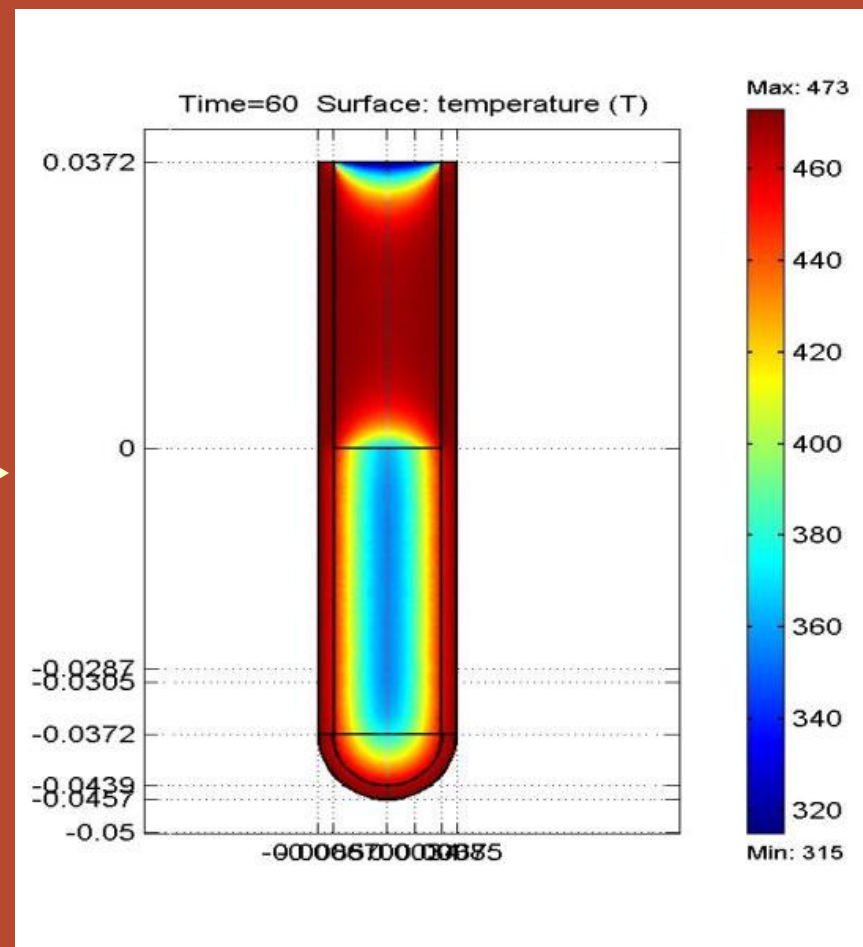
- Application in the typical lab

Heated Reactions

- Old ways are unpredictable and dangerous (fire, oil bath, etc.)
- More modern ways were safer (hot plate with positive feed back control, heating mantle, etc.)
- Traditional heating gives the same problem:

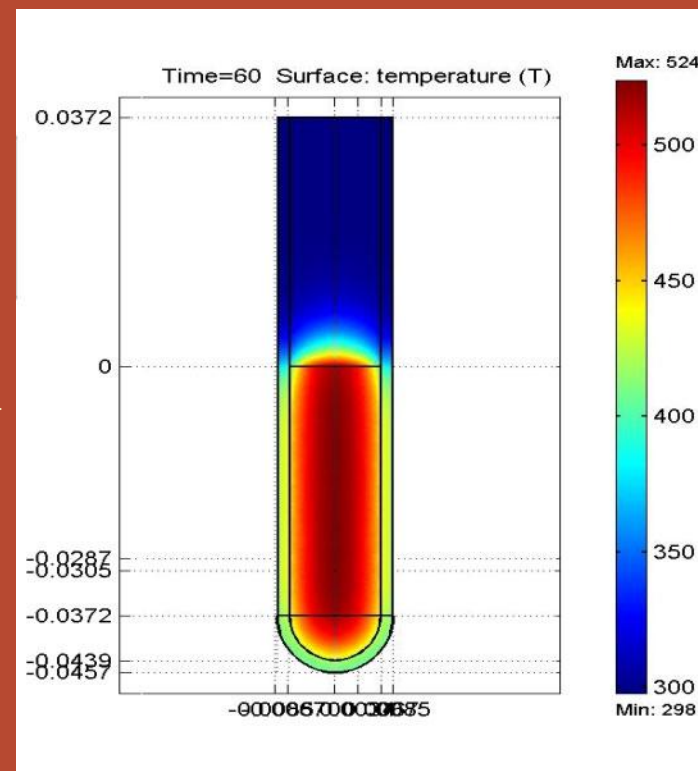
Conventional Heating

- Heating only at the surface



Microwave Heating

- Much Faster and More Uniform Heating



Higher Temperatures

- Under normal conditions, temperatures are limited to boiling point of solvent.
- Close the system, however . . .
- Higher temperatures means . . .

Open vs Closed Vessels

- One last time, I swear:

$$k = A \times e^{\frac{-E_a}{RT}}$$



Increasing temperature

80 °C	90 °C	100 °C	110 °C	120 °C	130 °C	140 °C	150 °C	160 °C
8 h	4 h	2 h	1 h	30 min	15 min	8 min	4 min	2 min



Decreasing reaction time



That great, but . . .

What's in it for me (the scientist)?

Uses for the Scientist

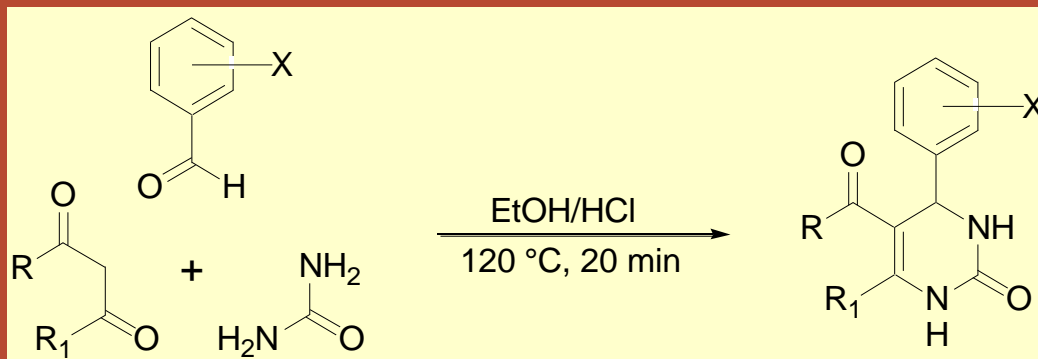
- Synthesis
- Environmental
- Material Testing
- Petroleum
- Geochemistry
- Food and Beverage Testing
- Defense and “Homeland Security”

Types of Synthetic Reactions

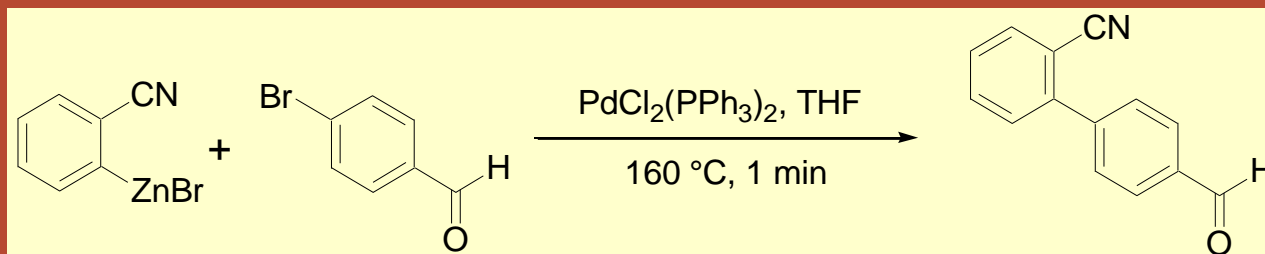
- Suzuki Reactions
- Heck Couplings
- Negishi Couplings
- Sonogashira Couplings
- Ester Hydrolysis
- Methylamination on Merrifield Resins
- Newman-Kwart Rearrangement
- Near Critical Water Reactions

Model Reactions

1) Biginelli Multicomponent Reaction

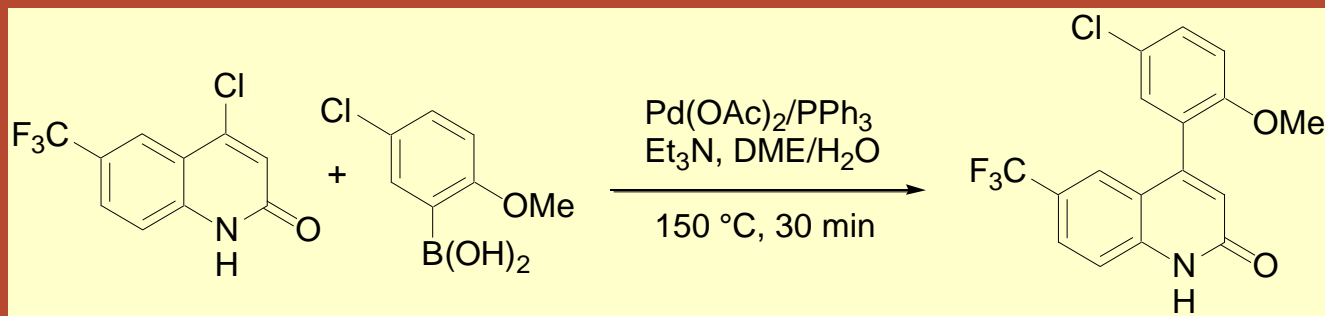


2) Negishi Coupling

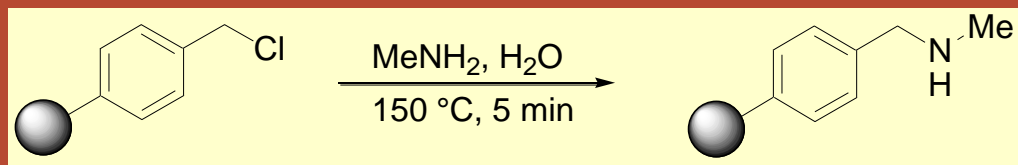


Model Reactions

3) Suzuki Cross-Coupling



4) Solid Phase Synthesis

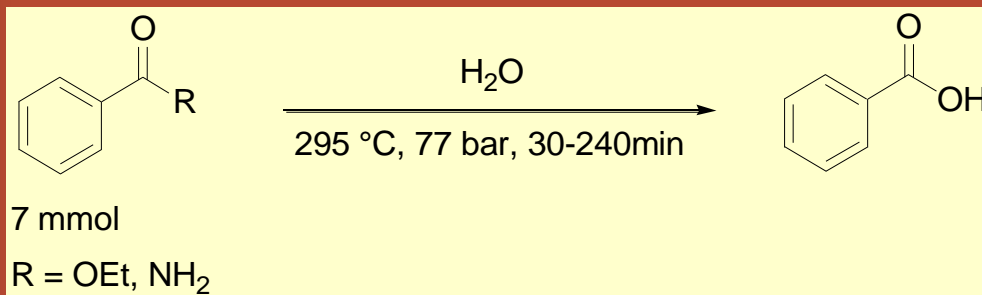


T. N. Glasnov, W. Stadlbauer, C. O. Kappe

J. Org. Chem. **2005**, 3864-3870

Model Reactions

5) Near Critical Water Chemistry



➤ Ester/Amide Hydrolysis

- ✓ NCWC at temperatures >250°C and pressures >40 bar
- ✓ easily accessible with Rotor 8 SXQ80
- ✓ conditions can be maintained up to 4 hours
- ✓ enabling development of new reaction pathways
- ✓ Green Chemistry approach

J. M. Kremsner, C. O. Kappe

Eur. J. Org. Chem., **2005**, 3672-3679

Environmental

- EPA Methods 3015A, 3050B, 3051, 3052, and 3546
- Digestion of Soils to determine metal content.
- Extraction of Soils for SVOC analysis

Extraction Applications

Samples

BCR 392 – sewage sludge

Industrial Soil – naturally contaminated [1]

Extraction procedure

Sample weight: 300 – 500 mg

Extraction solvent 1 (BCR 392)	20 mL cyclohexane-acetone 6:4 (v/v) (for residue analysis, Promochem)
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Extraction solvent 2 (Contaminated soil)	25 mL <i>n</i> -hexane-acetone 7:3 (v/v), (UniSolv, Merck)
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Instrument parameters

Temperature program for extraction solvent 1

Temperature [°C]	Ramp [min]	Time [min]	Fan
120	0	25	1
0	0	15	2

Temperature program for extraction solvent 2

Temperature [°C]	Ramp [min]	Time [min]	Fan
120	2	20	1
0	0	15	2

Results

BCR 392 (n= 3, values in ng g⁻¹)

Compound	Certified value	Found value Multiwave 3000
PCB 28	100 ± 10	88.3 ± 15.5
PCB 52	79 ± 9	81.0 ± 14.0
PCB 101	134 ± 11	132.4 ± 9.2
PCB 153	288 ± 18	275.3 ± 15.4
PCB 180	313 ± 24	302.8 ± 10.5

Industrial Soil (n=8, values in ng g⁻¹)

Compound	Found value Soxhlet	Found value Multiwave 3000
Octachlorostyrene	201.7 ± 13.9	201.4 ± 7.8
PCB 28	349.5 ± 22.8	308.0 ± 17.3
PCB 52	389.2 ± 21.7	357.7 ± 7.0
PCB 101	279.8 ± 37.2	266.2 ± 22.2
PCB 138	471.9 ± 107.1	422.2 ± 29.8
PCB 153	380.9 ± 129.4	346.6 ± 47.1
PCB 180	316.5 ± 141.4	306.7 ± 63.6

Material Testing

- Digestion of fabrics
 - Silver in woven material for odor suppression
- Polymer Manufacturing
 - Extraction of copolymers to determine quality
- Lead in Paint
 - CPSC

Polymer Digestions

Samples

100-200 mg BCR 680 – Polyethylene (high level)
 100-200 mg BCR 681 – Polyethylene (low level)
 100-200 mg unknown Plastic A
 100-200 mg unknown Plastic B
 100-200 mg unknown Plastic C

Digestion program:

Step	Power [w]	Ramp [min]	Hold [min]	Fan
1	300	5	5	1
2	500	2	7	1
3	800	5	10	1
4	0	0	15	2

The highest temperature achieved during digestion was 217°C, measured with the IR sensor at the vessel surface. The resultant solutions were clear without any precipitates. For the unknown plastic samples "A", "B" and "C" it was necessary to lower the sample weight (<200 mg) to reach complete digestion under the current digestion conditions.

Results (n = 6)

Sample	Elem.	Value Obtained [mg/kg]	Certified value [mg/kg]	Recovery [%]
BCR 680 (high level)	Cd	141.8 ± 6.3	140.8 ± 2.5	100.7
	Pb	117.7 ± 5.5	107.6 ± 2.8	109.3
BCR 681 (low level)	Cd	19.1 ± 0.4	21.7 ± 0.7	88.0
	Pb	13.9 ± 0.8	13.8 ± 0.7	100.7

Results (Unknown Plastics; Interlaboratory Cross-Check)

Sample	Elem.	Value Obtained [mg/kg]	Group Mean* [mg/kg]
Unknown Plastic A	Cd	49.3 ± 3.7	44.5 ± 3.7
	Pb	195 ± 28	171 ± 16
Unknown Plastic B	Cd	10.6 ± 1.8	9.8 ± 1.1
	Pb	56.0 ± 8.9	57.1 ± 8.2
Unknown Plastic C	Cd	< 0.2	< 1**
	Pb	1.156 ± 85	1.144 ± 22

Extraction of Polybrominated Flame Retardants

Samples

- ▶ Polyethylene (PE) and polystyrene (PS) pellets with a diameter of 2-3 mm, containing a final concentration of approx. 2% of DecaBDE as the sole brominated flame retardant.
- ▶ Same materials as above, but containing approx. 0.5% of DecaBDE.
- ▶ Pellets from both materials were used for further experiments without any additional pre-treatment.
- ▶ The precise concentration of DecaBDE was determined via microwave-assisted oxygen combustion and subsequent IC analysis.
- ▶ Sample weight: 250 mg

Step	Temp, °C	Ramp, min	Hold, min	Fan
1	125	10:00	40:00	1
2	0	00:00	20:00	3

IR limit: 125 °C

Magnetic stirrer: level 2

Microwave-assisted extraction

Sample	Recovery, %
PE, 2% DecaBDE	95.1 ± 1.3
PS, 2% DecaBDE	91.1 ± 1.3
PE, 0.5% DecaBDE	92.4 ± 1.4
PS, 0.5% DecaBDE	84.5 ± 1.1

(n = 4)

Soxhlet extraction

Sample	Recovery, %
PE, 2% DecaBDE	73.4 ± 4.9
PS, 2% DecaBDE	70.8 ± 4.6

(n = 4)

Geochemistry

- Digestion of soil samples
 - Determination of trace components
 - Platinum Group Metals
- Dating by determination of trace metals by radio isotopes

Geochemical Applications

Sample

SRM 120C Phosphate Rock
Sample weight: 200 – 300 mg

Power Program:

Step 1:

	Power [W]	Ramp [min]	Hold [min]	Fan
1	1400	10	35	1
2	0	---	15	3

Step 2:

	Power [W]	Ramp [min]	Hold [min]	Fan
1	1400	10	20	1
2	0	---	15	3

Results

Constituent	Cert./Rec.* value %	Recovery %
Al ₂ O ₃	1.30 ± 0.04	98.6 ± 1.6
CaO	48.02 ± 0.17	98.0 ± 1.8
Fe ₂ O ₃	1.08 ± 0.03	99.1 ± 0.6
K ₂ O	0.147 ± 0.004	100 ± 3
MnO	0.027 ± 0.002	99.2 ± 1.1
Na ₂ O	0.52 ± 0.02	102 ± 3
P ₂ O ₅	33.34 ± 0.06	102 ± 1
TiO ₂	0.103 ± 0.006	99.3 ± 5.7
V ₂ O ₃	0.016 ± 0.002	95.1 ± 2.9
SrO	0.1*	109 ± 2
ZnO	0.009*	103 ± 2

n=3

Petroleum Industry

- Digestion of crude oil
 - Determination of nickel and vanadium
- Extraction of different components
- Determination of sulfur content

Petroleum Applications

Samples

150 mg	Lubrication Oil (Oil_1)
150 mg	Fuel Oil (Oil_2)
150 mg	Crude Oil (Oil_3)
150 mg	Residual Fuel Oil (Oil_4) (Ref. Material 1618 NBS)

Reagents

7 mL HNO ₃ (suprapure)
1 ml HF (suprapure)
2 ml H ₂ O ₂ (suprapure)

Temperature program:

	Power [W]	Ramp [min]	Hold [min]	Fan
1	900	0	2	1
2	600	0	15	1
3	900	0	15	1
4	0	0	15	3

Results:

Elements	Oil_1 [µg/g]	Oil_2 [µg/g]	Oil_3 [µg/g]
V	7,8 ± 1,3	44,8 ± 0,7	29,1 ± 1,3
Ni	75,7 ± 4,9	22,7 ± 4,2	14,8 ± 1,5
Al	---	---	10,1 ± 0,1
Si	416 ± 88	348 ± 36	---

n=5

Elements	Oil_4 [µg/g] Meas. Values	Oil_4 [µg/g] Ref. Values
V	418,7 ± 3,5	423,1 ± 3,4
Ni	75,6 ± 1,2	75,2 ± 0,4
Al	---	---
Si	452 ± 88	---

n=5

Food and Beverage Testing

- Digestion of food stuff
 - Determination of metals
- Drying
 - Evaporation of Water
- Extraction
 - Determination of vitamins and minerals

Food and Beverage

Samples

500 mg Bovine liver BCR 185
 500 mg Mussel Tissue BCR 278
 500 mg Lobster TORT 2

Reagents

2 mL HNO₃ (subboiling, 65 %)
 2 mL H₂O₂ (suprapur, 30 %)
 0.5 mL HCl (suprapur, 30 %)
 5.5 mL H₂O (ultra pure)

Program:

	Power [W]	Ramp [min]	Time [min]	Fan
1	1400	---	20	1
2	0	---	15	2

Bovine Liver BCR 185

(n = 6)

Element	Found value	Certified value
As [µg/kg]	23 ± 5	24 ± 3
Cd [µg/kg]	302 ± 5	298 ± 25
Cu [mg/kg]	183 ± 5	189 ± 4
Hg [µg/kg]	42 ± 6	44 ± 3
Mn [mg/kg]	8.99 ± 0.22	9.3 ± 0.3
Pb [µg/kg]	484 ± 15	501 ± 27
Se [µg/kg]	532 ± 81	446 ± 13
Zn [mg/kg]	143 ± 6	142 ± 3

Mussel Tissue BCR 278

(n = 6)

Element	Found value	Certified value
As [µg/kg]	5680 ± 350	5900 ± 200
Cd [µg/kg]	360 ± 6	340 ± 20
Cu [mg/kg]	9.40 ± 0.46	9.60 ± 0.16
Hg [µg/kg]	190 ± 5	188 ± 7
Mn [mg/kg]	7.2 ± 0.4	7.3 ± 0.2
Pb [µg/kg]	1791 ± 160	1910 ± 40
Se [µg/kg]	1690 ± 100	1660 ± 40
Zn [mg/kg]	76 ± 4	76 ± 2

Forensics

- Acid digestions of tissues for heavy metal poisoning.
- Extraction of biological material from solid matrices.
- Trace metal determination in biological samples.

Forensic Samples

Digestion procedure

Samples: 200 mg BCR 397 – Hair
 200 mg nails (no RM available)
 2 mL Clin-Rep®-Whole Blood Control
 5 mL Clin-Rep®-Urine Control

Reagents: 1 ml HNO₃ (subboiling)
 2 ml H₂O (ultra pure)
 2 ml H₂O₂ (suprapur)
 0.5 ml HCl (suprapur)

	Power [w]	Ramp [min]	Hold [min]	Fan
1	1400	0	30	1
2	0	0	15	2

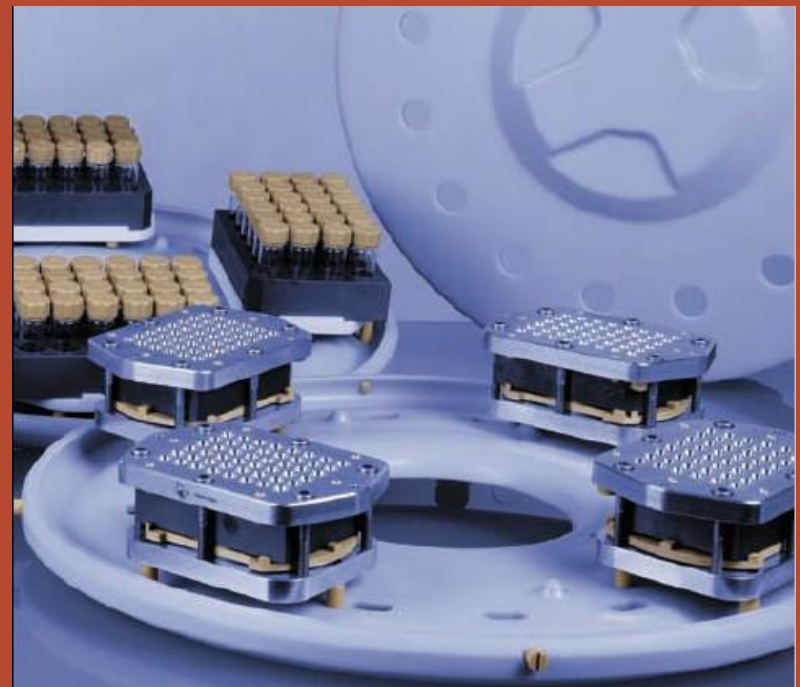
Results (N = 5)

Sample	Elem.	Found value [µg/g]	Certified value [µg/g]
BCR 397	Cd	0.518 ± 0.006	0.521 ± 0.024
	Pb	33.6 ± 0.2	33.0 ± 1.2
Hair	Se	1.94 ± 0.05	2.00 ± 0.08

Sample	Elem.	Found value [ng/ml]	Certified value [ng/ml]
Urine Control	As	141 ± 3	(135)
	Cd	22.5 ± 0.2	(22)
	Cr	42.3 ± 1.3	(44.1)
	Pb	67.7 ± 0.9	(68)
Whole Blood Control	Cd	5.30 ± 0.05	(5.4)
	Cr	10.9 ± 0.3	(11.2)
	Pb	238 ± 3	(235)

Biology and Biochemistry

- Reactions on DNA
 - 96 well block format reactors for parallel reactions
 - (Big Pharma) is doing Suzuki Reactions on DNA
- Protein Hydrolysis



Protein Hydrolysis

Liquid Phase Hydrolysis of BSA:

5 mg Bovine Serum Albumin suspended in 15 ml 6 M HCl + NorLeu as internal standard

Step	Temp [°C]	Ramp [min]	Hold [min]	Fan
1	150	5	30	1
2	0	0	15	3

Max. power 500 W, IR limit 140 °C

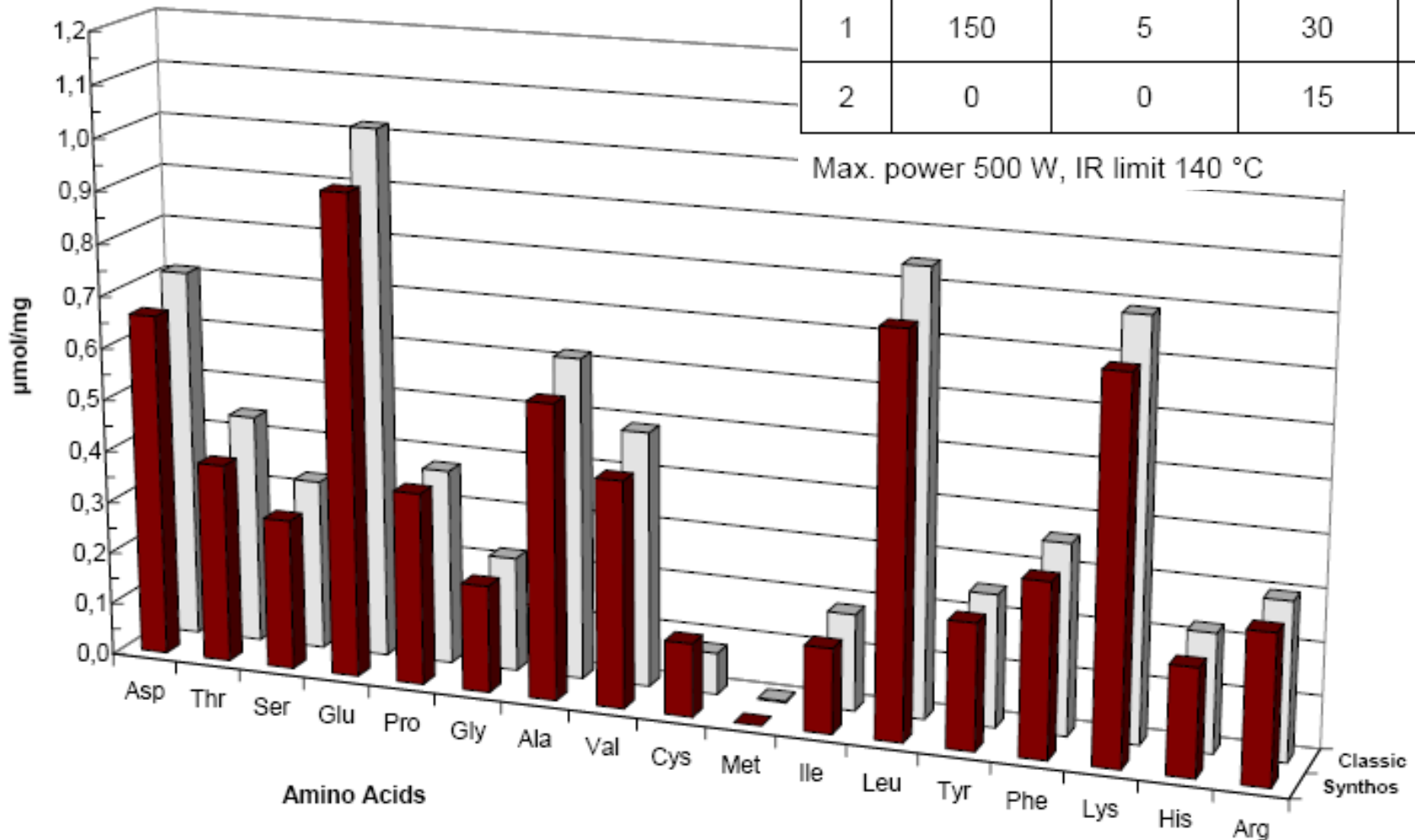


Figure 5. Liquid Phase Hydrolysis of Bovine Serum Albumin

Protein Hydrolysis

Gas Phase Hydrolysis of BSA:

2 mg lyophilized Bovine Serum Albumin + NorLeu as internal standard

Step	Temp [°C]	Ramp [min]	Hold [min]	Fan
1	130	5	30	1
2	0	0	15	3

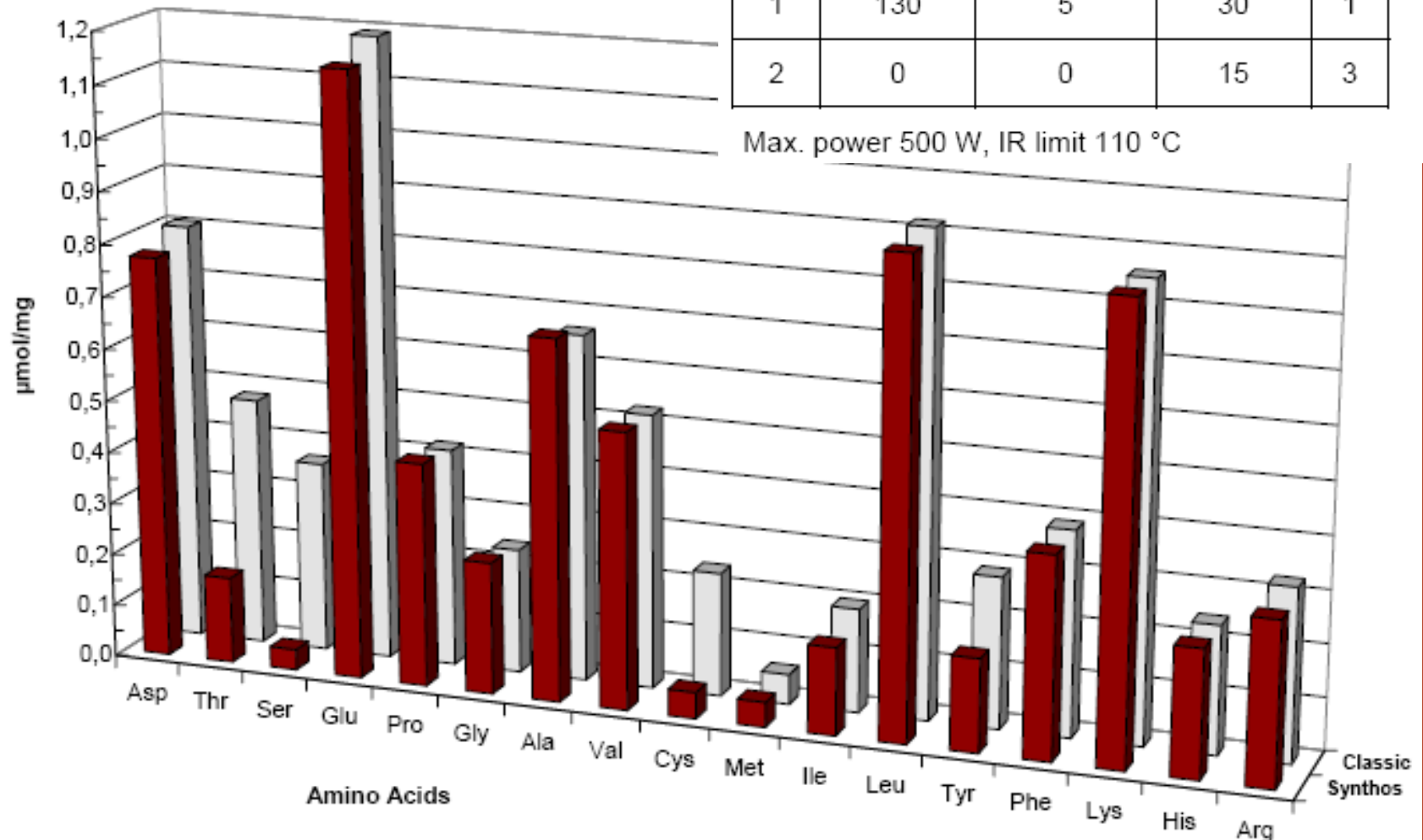


Figure 6. Gas Phase Hydrolysis of Bovine Serum Albumin

The “Complete” Scientific History of Laboratory Microwaves Systems

- First patent was filed in the 1960s.
- Domestic use in the 1970s.
- Industrial use for environmental labs and material testing during the 1980s.
- Pharmaceutical use in the late 1990s/early 2000s.
- Where are you going to take the technology tomorrow?

For More Information

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