Microwave Digestion of Complex Samples including Oils and Polymers

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Why Do We Digest Samples?

- Its all about the analysis (ICP-OES & ICP-MS)
- Measurements take time
- Signal must stay constant during the measurement
- The analyzer needs homogeneity
- The solution is a solution…

Why Pressurized Digestion?

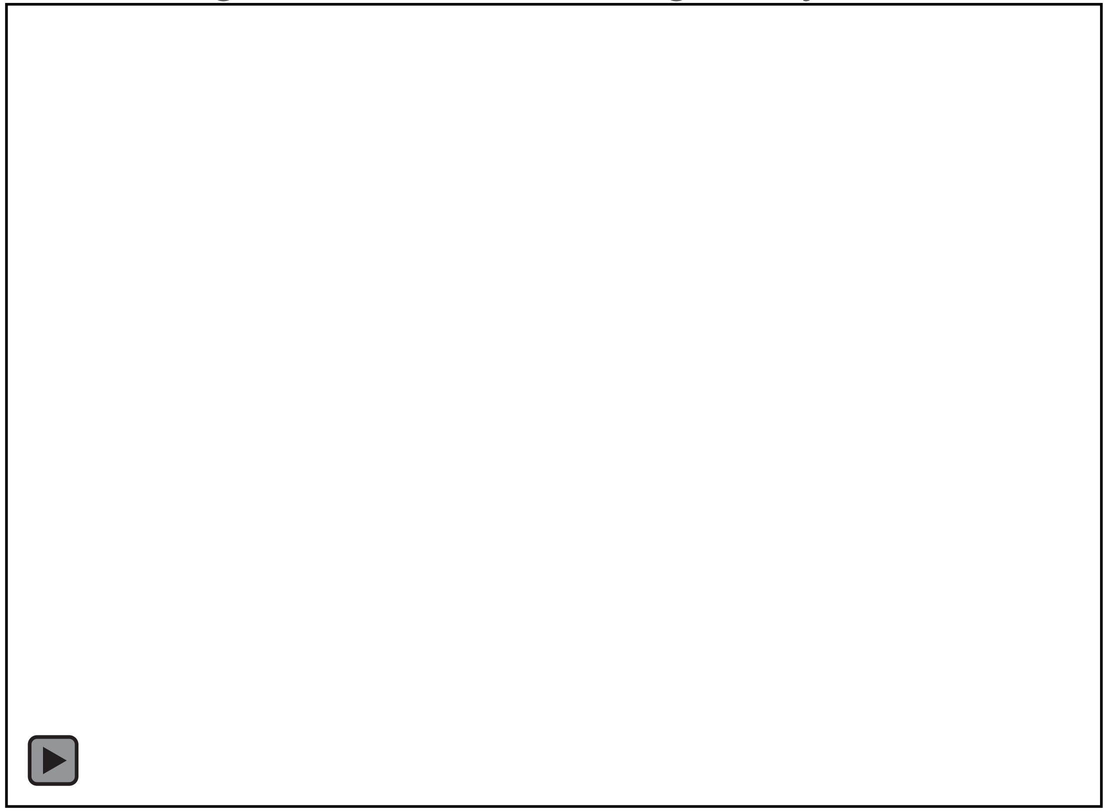
- Elevate acid temperatures above boiling point
- Oxidative potential of reagents is higher at elevated temperatures
- Digestion is faster and more complete
- Can use nitric acid for most oxidations
  - Super acid at 200 °C
  - Cleaner blanks because only 1 reagent
- Will not go to dryness like hot plate/block
  - No worries of analyte loss

Why Microwave?

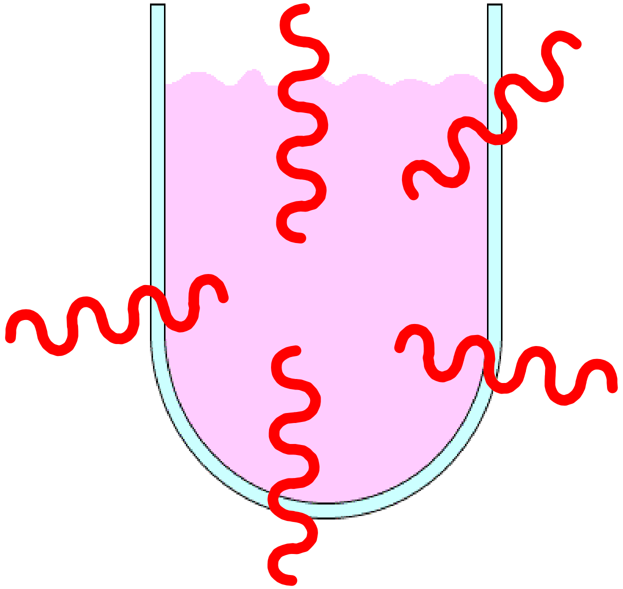
- Rapid heat up time (instantaneous heating)
- Active control of samples
- Reproducibility of conditions
- High throughput
- Rapid cool down
- Only the sample and reagent is heated
- Energy Efficient

Microwave vs. Thermal Heating

- Thermal (Conductive) Heating
  - Energy transferred through vessel then dissipated throughout the digestion
  - Hot Plate remains on after completion of the digestion, risk of heating to dryness.



- Microwave Heating
  - Vessel wall transparent to energy
  - Direct activation of molecules in the solution
  - Localized Superheating maximizes heat transfer
  - Upon reaction completion, energy addition stops, sealed container holds sample for when you are ready to work with it.



Heating Isn't Everything

Organic Samples

- Acid Type
- Sample Size
- Heating Programs
  - Ramp to Temperature
  - Pre-Digestion
  - Hydrogen Peroxide
  - Char Step
- Digestion Vessel

Inorganic Samples

- Acids
- Sample Matrix
- Analytes of Interest
- Heating Programs
- Step-wise Approach

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Samples

Organic Samples

- Plant and Animal Tissue
- Oil and Oily Waste
- Paint and Paint Chips
- Foods
- Nutraceuticals
- Pharmaceuticals
- Polymers
- Graphite Resins Composites

Inorganic Samples

- Soils
- Ores
- Ceramics
- Catalysts
- Metal Alloys
- Ash
- Water

Organic Digestions

- Target temperatures between 180°C and 210°C
- Start with small (0.1 g) samples and increase slowly to 0.5 g if needed
- Elevated temperatures eliminate the need for other oxidants such as peroxide and perchloric acids (less risk of contamination)
- A pre-digestion step will help prevent exothermic reactions

Predigestion

Mixed Foods

Microwave Digestion of
Salami

Procedure

Weigh 0.5 g of the sample into the digestion vessel. Add 10 mL of HNO_3. Gently swirl the mixture and wait approximately 15 minutes before closing the vessel.

Notes

The addition of Conc. HCl (0-4 mL) is appropriate for the stabilization of Ag, Ba and Sb, and high concentrations of Fe and Al in solution. The amount of HCl will vary depending on the matrix and the concentration of the analytes. The addition of HCl may, however, limit the techniques or increase the difficulties of analysis.

Recommended Equipment	Recommended Vessels	Reagents
MARS 6 MARS 6 iWave	EasyPrep EasyPrep Plus MARSXpress MARSXpress Plus	HNO_3

Max Sample Weight	Sample Type	Control Type	Method Type
0.5 g	Organic	Ramp to Temperature	One Touch

Heating Program

Stage	Temp (°C)	*Ramp (mm:ss)	Hold (mm:ss)	Pressure (psi)	* Power (W)	Stirring
1	210	20:00	15:00	800	900-1050	Off

* Ramp times and power may vary depending on the type and number of vessels.

Results

Sample was clear, colorless, and particle free upon dilution to 50 mL.

General Precaution

a) This procedure is a reference point for sample digestion using a CEM system and may need to be modified or changed to obtain the required results on your sample.
b) If using a vessel other than the recommended choice, adjust sample size and pressure limit to values appropriate for the vessel chosen.
c) The control / reference vessel must contain the largest and most reactive sample.
d) Manual venting of CEM vessels should be performed when wearing hand/eye/body protection and when the vessel contents are at or below room temperature to avoid the potential for chemical burns. Always point the vent hole away from the operator.
e) If programming as One Touch, the ramp time and power will be automatically determined based on the number and type of vessels detected.

- Digest up to 40 mixed food samples
- Total digestion time 35 min
- Ready for further processing in under an hour
- Resulting digestate will be clear and colorless

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Inorganic Digestions

It's all about the chemistry!

Acids

Nitric Acid

- Oxidizing acid
- Starting acid for organics
- Most nitrates are soluble
- Compatible with most analytical techniques
- Can be obtained in high purity
- May passivate certain metals (Al, Cr, Ti)

Hydrochloric Acid

- Not an oxidizing acid
- Good complexing agent
- Stabilizes Hg (can be added post-digestion)
- Useful for Fe, Al, In, Sb, Sn, Rh, Au
- Problem with Ag precipitation as AgCl
- May interfere with ICP/MS and GFAA

Acids

Hydrofluoric Acid

- Dissolution of silicates
- F- is a powerful complexing anion (Refractory elements, Sb, Sn, Mo)
- Volatilization of Si as SiF_4
- Formation of insoluble fluorides (Group IIA, Rare Earth elements, ICP Internal Standards)
- Complex with H_3BO_3
- Safety Hazard!
- HF resistant transport systems for ICP/AA

Sulfuric Acid

- High boiling point (340°C)
- Elevation of boiling point in acid mixtures
- Strong dehydrating agent (Charring)
- Opens aromatic rings
- Formation of insoluble sulfates (Pb & Ba)
- High viscosity may cause analytical problems
- Matrix-match calibration standards

Acid Mixtures

• $HCl:HNO_3$ (3:1)	Precious metals (Aqua Regia)
• $HCl:HNO_3$ (1:3)	Soils, fertilizers (Reverse aqua regia)
• $HNO_3:HCl:HF$	Alloys, ores, silicates, ash
• $H_3PO_4:H_2SO_4$	Aluminum oxide
• $HNO_3:H_2SO_4$	High molecular wt. organics

Acid Mixtures – Difficult Applications

“Austin’s Cocktail” (“Piranha” Solution)

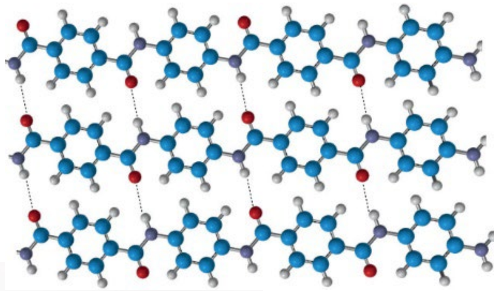
- **4.5 mL H_2SO_4 : 4.0 mL HNO_3 : 1.5 mL H_2O_2**
  260°C – used for digestion of polybenzimidazole (PBI) fiber

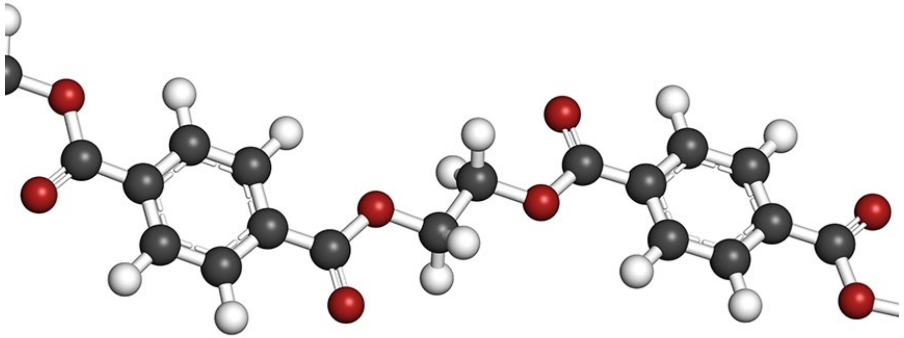
- Add 20°C – will digest Cr_2O_3 & $NiCr_2O_4$ (eliminates $HClO_4$)

- Add HF (280°C) – will digest SiC

- Add HCl (280°C) – will digest B_4C (eliminates HF for analysis of Boron)

Polymer/Plastics & Oil Samples





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Polymers and Plastic Samples

- Why is Metals Analysis Important
  - Metals that are used as catalyst in the production or that are introduced in the process can cause performance issues in materials
  - Pb, Be, Cd, V, Ni, and Fe are most prevalent elements analyzed

- Traditional Methods
  - Heat Muffle Furnace and Digest Ash in Weak Acid
    - Long time for analysis
    - Loss of volatile elements
  - Hot Plate/Block With Sulfuric Char Step
    - Tedious with several stages: Sulfuric, then cool, then add several nitric additions
    - Sulfuric acid is viscous and not friendly to use for ICP or ICP-MS
    - Sulfuric acid is often referred to as a “dirty” acid (higher blank values)

EasyPrep Plus Vessels Can be Used for these Sample Types

- Lighter Fraction Oils
- Waste oil
- Polymers such as nylon and PP
- Mixed Oil and Waste Stream Samples
- Cannot digest difficult polymers without use of H_2SO_4

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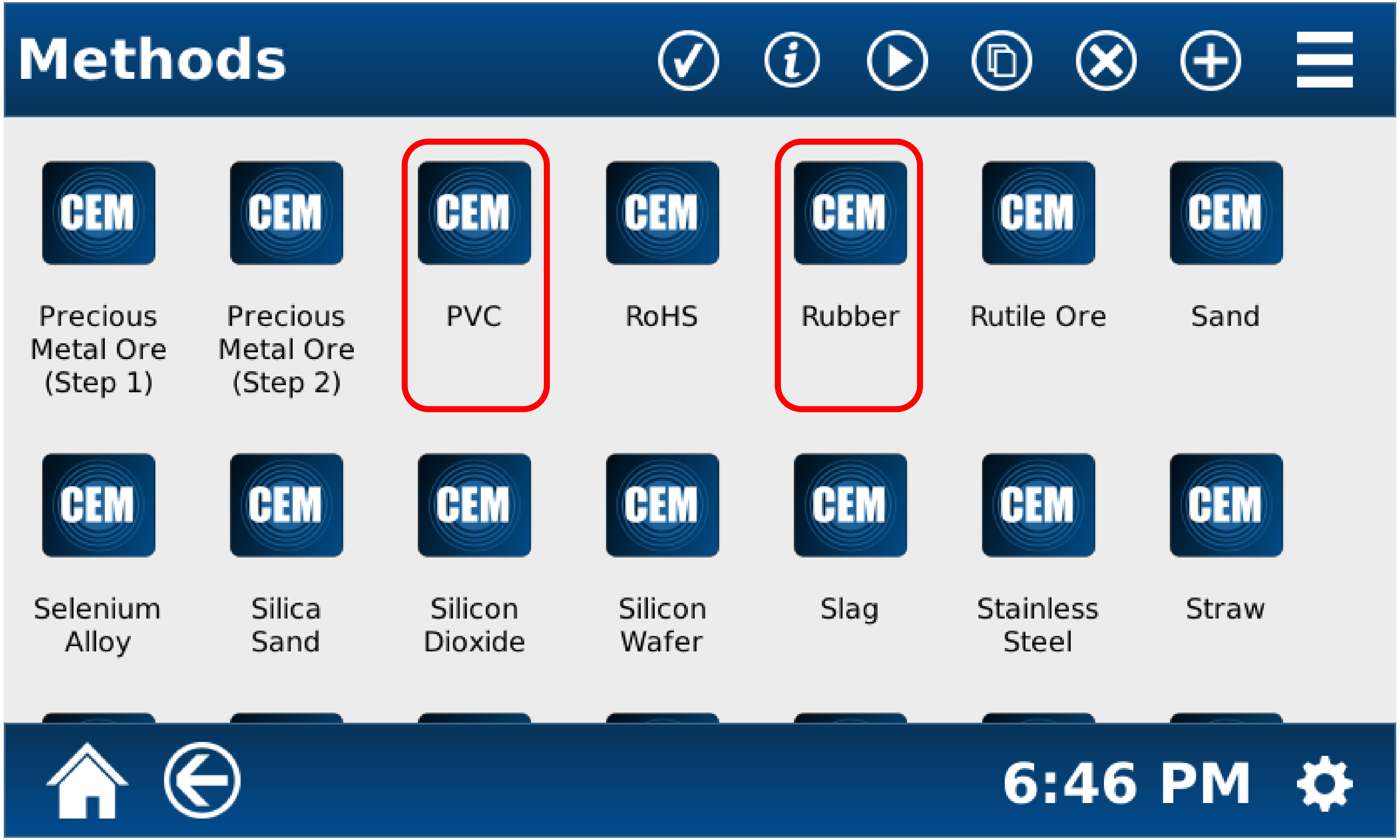
iPrep Vessels Allow For Digestion of Most Samples in Nitric Acid Only

- Digest moderate to very difficult polymers
  - PET, ABS, Kevlar, Bunker Oil
- Highly Aromatic Compounds
- Flame Retardant Materials
- Samples Requiring Highest Temperatures (250 °C) to digest

- Sample sizes of 0.25 – 0.5 g possible

Choose Appropriate One Touch Method



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Some Materials (Polymers) May Require Char Step

Procedure:
Sample Weight: up to 2 g
Stage 1 Reagents: 5 mL conc. H_2SO_4
Stage 2 Reagents: 10 mL HNO_3

Let cool to approximately 80 °C, Uncap and add nitric acid recap and run stage 2 heating

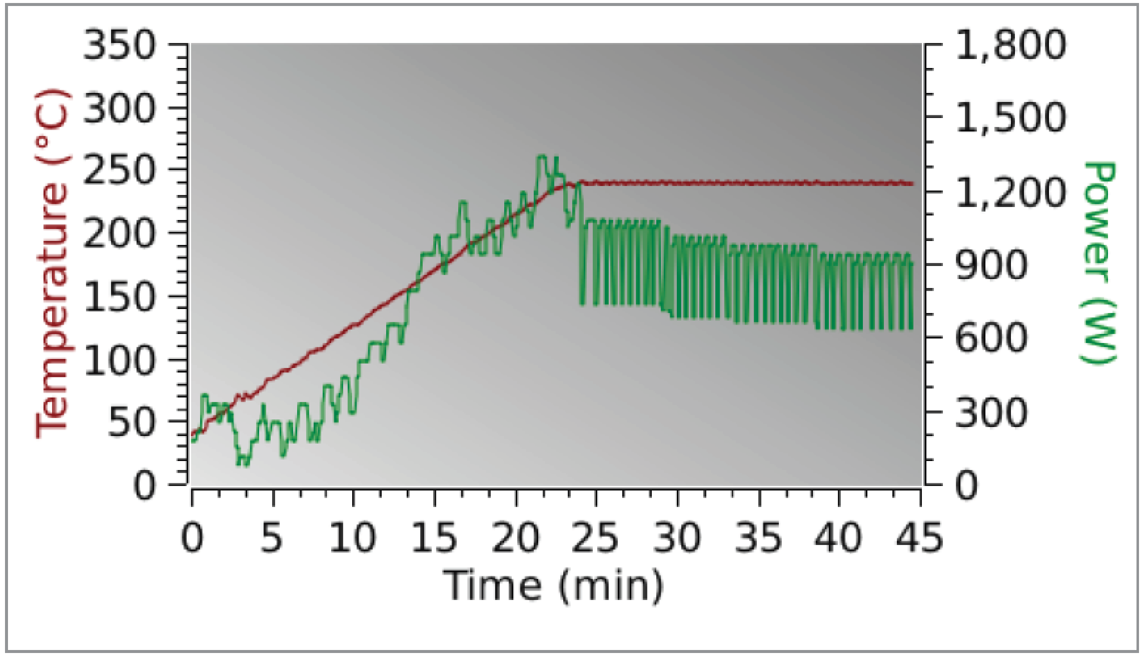
Stage	Acid	Ramp (mm:ss)	Temp (°C)	Hold (mm:ss)
1	H_2SO_4	15:00	260	15:00
2	HNO_3	10:00	200	10:00

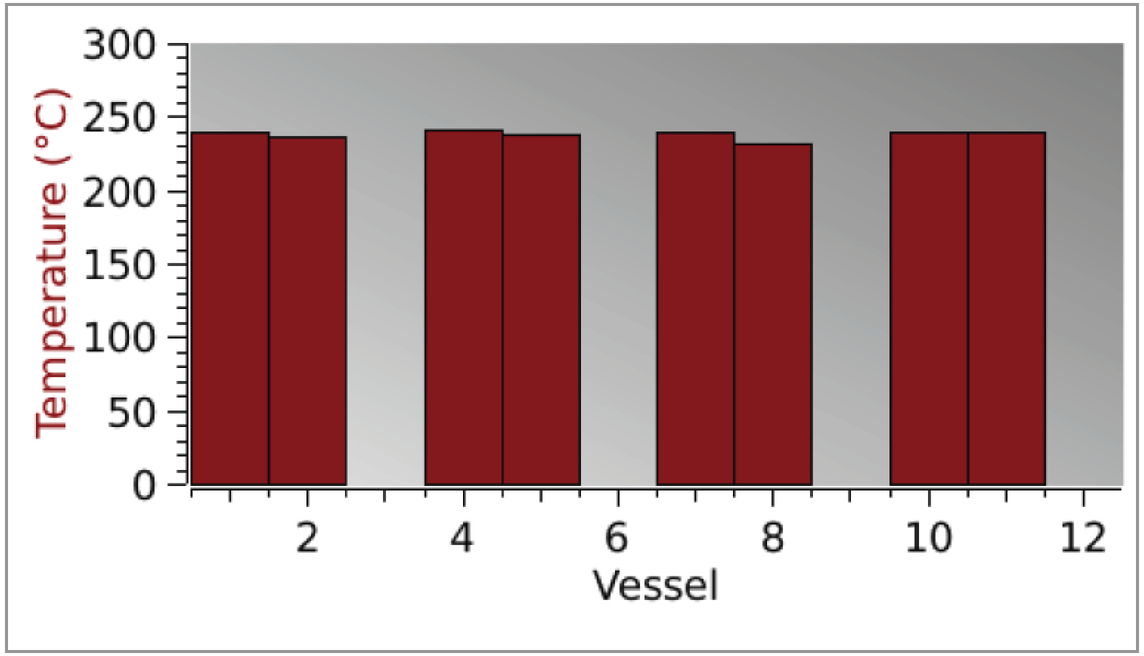
Temperatures and Times For Various Polymer Samples

Sample Type	Final Hold Temperature (°C)	Total Digestion Time (min)
LDPE 680K, 681K	220	40
NIST SRM 2855 (HDPE)	200	45
PVC	230	40
PP	210	40
PET	250	60
Bunker Oil	250	60

Sample sizes were approximately 0.5 g each except PET is 0.25 g
10 mL concentrated HNO_3 added to each sample

Power and Temperature Graph For Mixed Samples





Conclusions

- Microwave closed vessel digestion speeds decomposition
  - Samples that take hours on a hot block can take minutes in the microwave
  - Some samples will not digest without microwave pressurized digestion
- Methods are different for organic and inorganic sample types
  - Organics = oxidation and destruction of the carbon matrix
  - Inorganics = optimize acids for sample matrix and analytes
  - For inorganic samples, total matrix digestion with HF may not always be necessary for analyte recovery
- Method notes exist for hundreds of sample matrices
- For more information visit cem.com/microwave-digestion

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Thank You

Questions?