Microwave Digestion of Organic and Inorganic Samples Including Lithium Battery Materials

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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

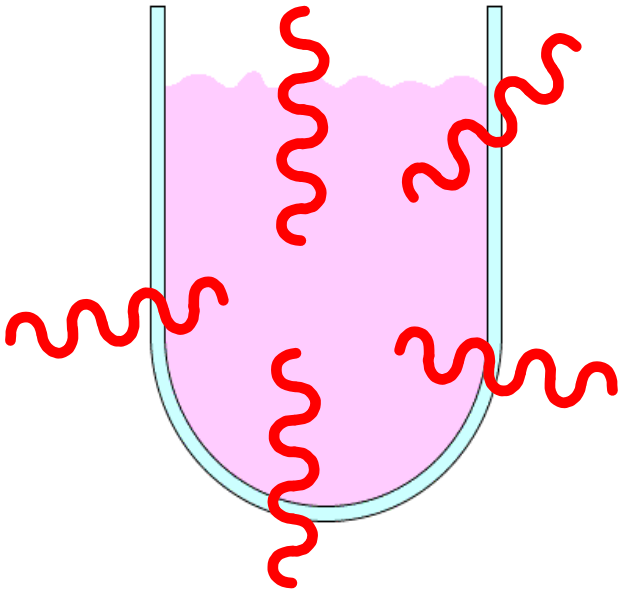
Why Microwave?

- 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

Samples

Organic Samples

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

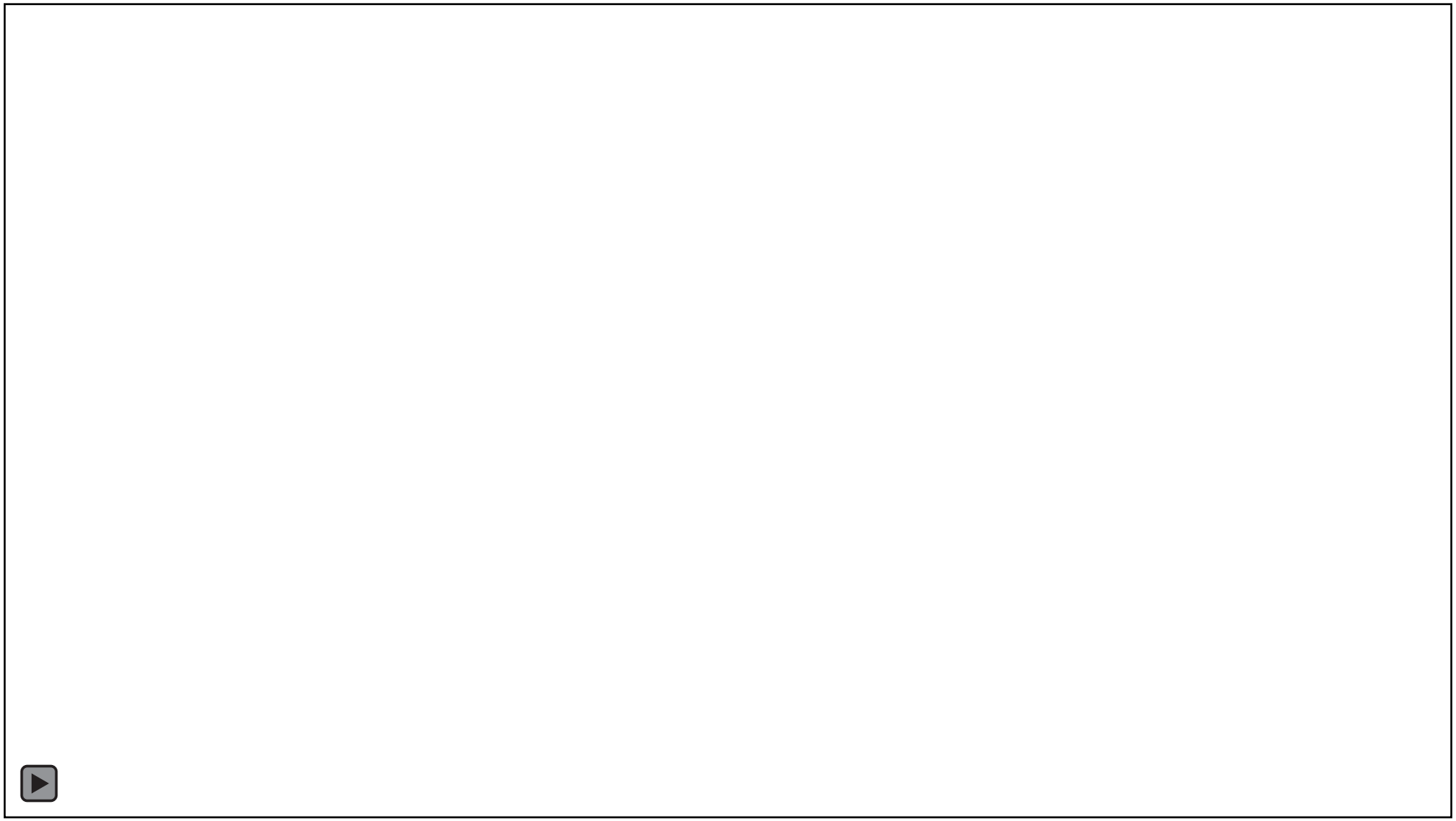
Inorganic Samples

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

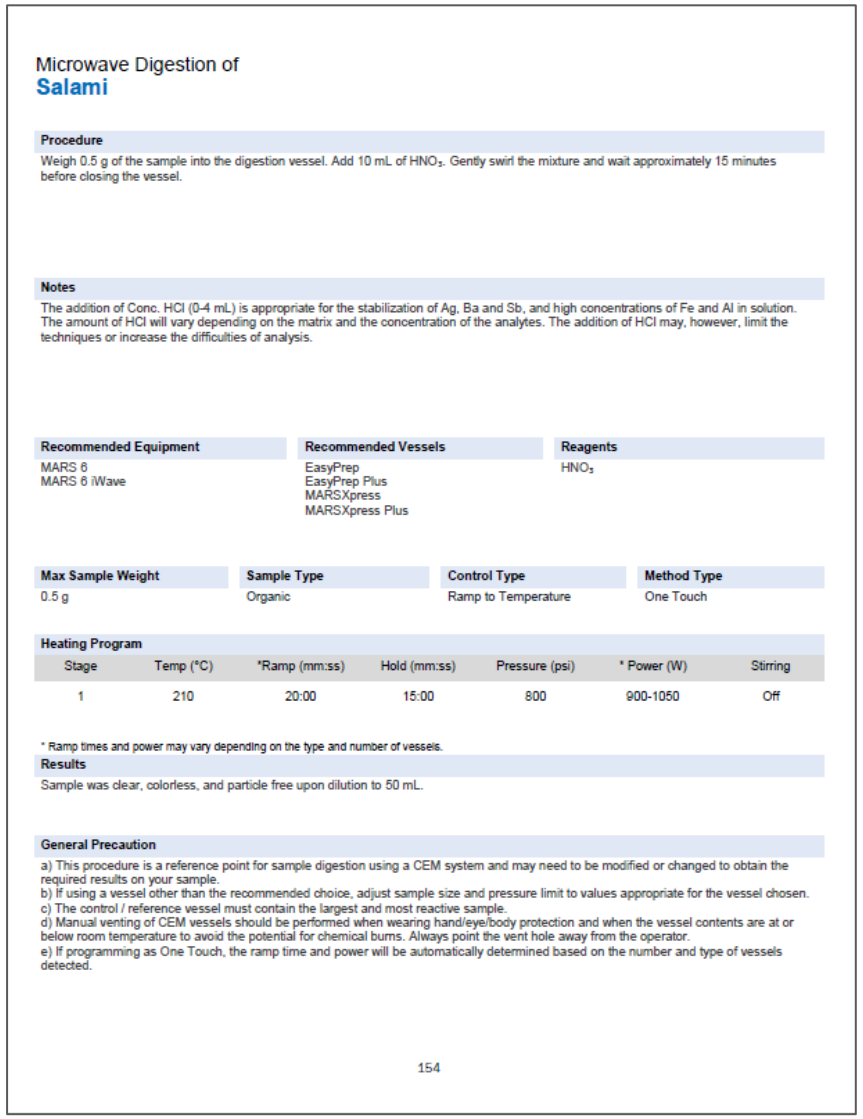
Organic Digestions

- 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.

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- 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

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
- 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

CEM

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

Lithium Battery Materials Sample Preparation

Materials of Interest

- Lithium Sources
  - Spodumene
  - Lepidolite
  - Petalite
  - Li_2CO_3
  - LiOH
- Recycled Material
  - Spent Li-Battery
- Cathode Materials
  - LCO
  - NMC
  - LFP
  - NCA
- Anode Material
  - Graphite

Sample Prep Protocol

- Sample sizes of 0.25 – 0.5 g
- Lepidolite Sample was in rock form and had to be ground
  - SPEX Shattterbox 8530
- All other samples were digested as received
- As these are inorganics the use of the proper acid mix is critical
- All samples digested in triplicate including method blanks
- Calibration
  - Two custom (1000 mg/L) multi-element standards from Inorganic Ventures
- Validation
  - Three NIST SRMS used - lithium ore 182 (petalite), lithium ore 183 (lepidolite), 2711a (Montana Soil II)
  - Lithium Carbonate Spikes at various levels

The System

MARS 6 iWave – EasyPrep

- Digest up to 12 samples per batch
- Preprogrammed methods w/ recipe for digestion
  - Sample size
  - Acid type
  - Acid volume
- Onboard instructional videos

Acid Mixtures and Digestion Temperatures

Sample	Acid Mixture	Temperature Required
Spodumene	(1:1) HCl:H2O + 5mL HF	210°C
Montana Soil II (SRM 2711a)	(1:1) HCl:H2O + 5mL HF	210°C
Lepidolite (SRM 183)	(1:1) HCl:H2O + 5mL HF	210°C
Petalite (SRM 182)	(1:1) HCl:H2O + 5mL HF	210°C
Lithium Hydroxide	(1:1) HNO3:H2O	180°C
Lithium Carbonate	(1:1) HNO3:H2O	180°C
Lithium Iron Phosphate (LFP)	(3:1) HCl:HNO3	220°C
Lithium Nickel Manganese Cobalt Oxide (NMC)	(9:1) HNO3:HCl	210°C
Lithium Nickel Cobalt Aluminum Oxide (NCA)	(1:1) HCl:H2O	230°C
Lithium Cobalt Oxide (LCO)	(9:1) HNO3:HCl	210°C
Graphite	(3:1) HCl:HNO3	220°C
Spent Li-Battery (recycled)	(3:1) HCl:HNO3	220°C

Digestion Procedure for NMC 811

CEM MARS 6™ Method Note

Microwave Digestion of Lithium Nickel Manganese Cobalt Oxide (NMC)

Procedure

Weigh 0.25 g of the sample into the digestion vessel. Add 9 mL of HNO_3 and 1 mL of HCl. Gently swirl the mixture 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 HCl

Max Sample Weight	Sample Type	Control Type	Method Type
0.25 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	15:00	15:00	800	400-1800	Off

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

Results

Sample was clear, faint green in color, and particle free upon dilution to 50 mL with deionized water. Depending upon which version of NMC is digested, the color of the solution could vary.

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.

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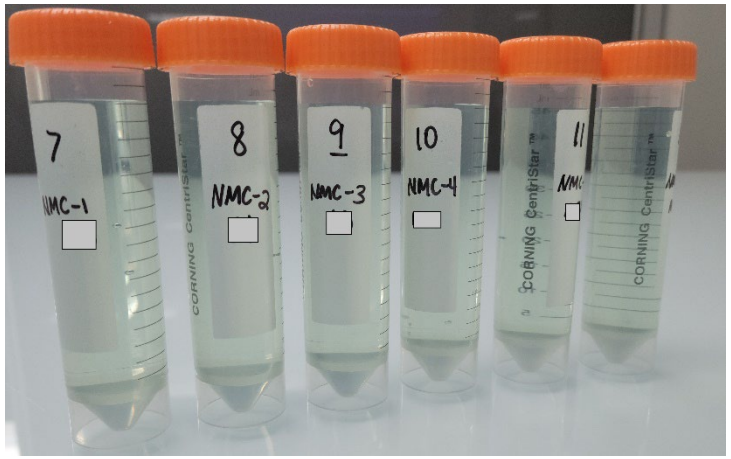
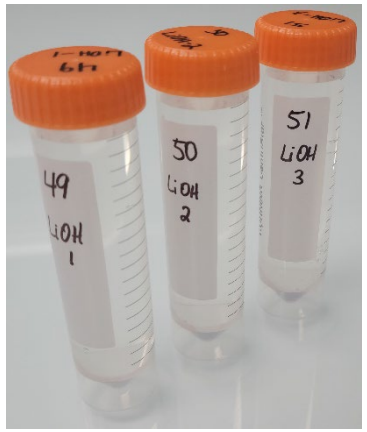
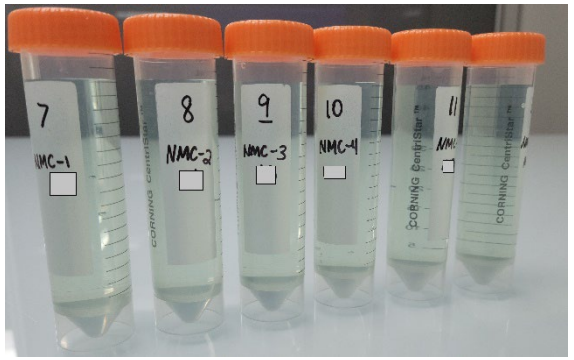
- Simple acid matrix (9:1) HNO3:HCl
- Others have used various combinations of HNO3:HCl for digestion
- Depending on dosage ratios of Ni, Mn, Co – the color of the digest may vary

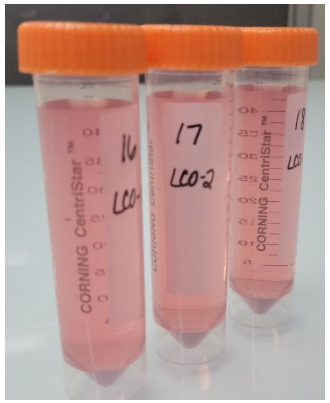


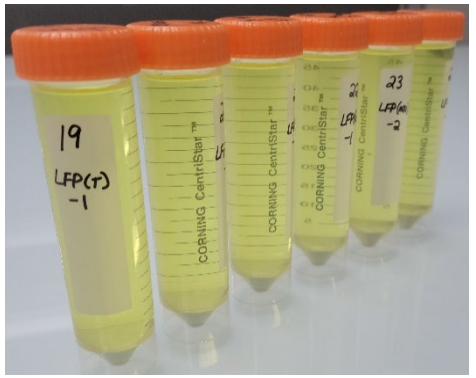
Digested Samples

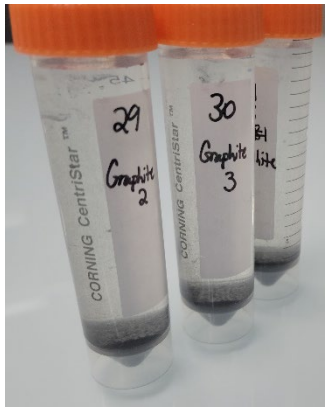
- Lithium Sources will provide clear, colorless solutions
- Cathode materials will often provide clear, nicely colored solutions
  - It can tell us something about our ratio in NMC for example
- Anode materials will often provide clear, colorless solutions
  - Leached materials will always have material remaining undigested











Lithium Sources and SRM Results by ICP-OES

Montana Soil II Recovery – NIST SRM 2711a												
	Al	Ca	Co	Fe	K	Mn	Na	P	Si	Ti	V	Zn
% Recovery	93.32	92.89	101.4	94.84	101.7	95.84	107.7	101.1	96.60	98.91	97.75	96.81

Lepidolite – NIST SRM 182	
Li Recovery	
% Rec.	99.70

Lepidolite – NIST SRM 183	
Li Recovery	
% Rec.	96.40

Cathode Material Results by ICP-OES

NMC 811 (ppm)

Al	Ca	Fe	K	Na	P	Si	Ti	V	Zn
16.71	1.930	2.180	199.6	13.48	14.06	1168	7.836	3.763	23.37

NMC 811 (%)

Co	Li	Mn	Ni
7.046	7.560	3.388	55.98

LFP (ppm)

Al	Ca	Co	K	Mn	Na	Si	Ti	V	Zn
53.90	5.280	4.167	213.8	80.27	124.2	51.15	1600	11.42	12.67

LFP (%)

Fe	Li	P
23.85	4.780	14.36

Anode Material Results by ICP-OES

Graphite (ppm)												
Al	Ca	Co	Fe	K	Li	Mn	Na	P	Si	Ti	V	Zn
1.780	2.423	0.4700	94.44	36.65	38.96	0.5600	<LOD	2.860	29.30	13.26	6.280	0.0333

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
- Microwave digestion provides a good solution for preparing the varied sample types for lithium battery production and recycling
- For more information visit cem.com/microwave-digestion

Thank You

Questions?