MILESTONE
H E L P I N G
C H E M I S T S

SUPERIOR SAMPLE PREPARATION FOR
ELEMENTAL ANALYSIS OF Li-ION
BATTERY MATERIALS

Trace metals sample prep via Single Reaction Chamber (SRC) technology leads to superior analytical results.

| INTRODUCTION

In recent years, efforts to combat climate change have intensified, leading to new research and innovations that are paving the way for the eventual transition away from combustion engines to cleaner electric vehicles.
A central challenge of this transition is in addressing the current technological limitations within lithium-ion batteries. Before a broad shift from combustion, gasoline-powered vehicles can occur, battery performance, efficiency, and lifespan must dramatically improve. The chemical analysis of battery components is a necessary step in this process. More specifically, qualitative and quantitative elemental analyses of the anode, cathode, and electrolyte materials present in batteries are required.
These types of analyses are performed using ICP-based analyzers, which require solid samples to be decomposed and dissolved in an acid solution through a digestion process before the digested solutions are then injected into the analyzer.

The materials present in batteries are primarily of inorganic origin, which are very often stable and resistant materials that make acid dissolution complicated.
For each sample matrix there is a specific acid mixture required (depending on the composition of the material) and that mixture must be used concurrently with high temperature and pressure conditions to achieve complete digestion of the materials before analysis.
Closed-vessel microwave digestion is a proven technique, capable of achieving rapid sample digestions. More importantly, microwave digestion enables superior analytical accuracy when compared to other techniques through its higher temperature and pressure capabilities that ensure complete digestions, along with built-in safeguards that prevent analyte losses and contamination inherent to open-vessel techniques.
Milestone's innovative ultraWAVE with Single Reaction Chamber (SRC) technology is a revolutionary new approach

to closed-vessel microwave digestion that simplifies the sample preparation step. When compared to traditional rotor-based systems, SRC technology clearly provides faster, more efficient, and higher quality digestions for every Li-ion battery sample matrix.

In the following test, we demonstrate the system's performance after digesting three common lithium battery-related sample matrices: Li-ores, Anodes, and Cathodes.

| EXPERIMENTAL

INSTRUMENT

ultraWAVE meets the requirements of battery development and testing laboratories, thanks to its unique benefits, such as:

- Superior digestion quality
- High productivity
- Ease of use
- Enhanced safety and flexibility

Figure 1: Milestone's ultraWAVE system

Developed by Milestone, the ultraWAVE with Single Reaction Chamber (SRC) technology utilizes high-performance stainless steel, enabling higher pressures and temperatures, and is compatible with all types of acid. Disposable vessels eliminate the need to assemble, disassemble, or clean between runs. Just as important, dissimilar samples can be processed simultaneously using any mixture of disposable glass, quartz, or TFM vials, thus saving time and money. ultraWAVE is simply the fastest, easiest, and most efficient digestion system available today.

REAGENTS

a. HNO_3, nitric acid, 65%, ACS reagent (Sigma-Aldrich)
b. HCl, hydrochloric acid, 37%, ACS reagent (Sigma-Aldrich)
c. HF, hydrofluoric acid, 48%, ACS reagent (Sigma-Aldrich)
d. H_3PO_4, ortho-phosphoric acid, 85%, ACS reagent (Sigma-Aldrich)
e. H_2SO_4, sulfuric acid, 96-98%, ACS reagent (Sigma-Aldrich)
f. $HClO_4$, perchloric acid, 70%, ACS reagent, technical grade (Sigma-Aldrich)
g. Vanadium (V) standard solution, 1000 mg/L V in nitric acid (TraceCERT, Sigma-Aldrich)
h. Periodic table mix 1 for ICP, 10 mg/L (TraceCERT, Sigma-Aldrich): Al, As, Ba, Be, Bi, B, Ca, Cd, Cs, Cr, Co, Cu, Ga, In, Fe, Pb, Li, Mg, Mn, Ni, P, K, Rb, Se, Si, Ag, Na, Sr, S, Te, Tl, V, and Zn in 10% V/V nitric acid (contains HF traces)
i. Periodic table mix 2 for ICP, 10 mg/L (TraceCERT, Sigma-Aldrich): Au, Ge, Hf, Ir, Mo, Nb, Pd, Pt, Re, Rh, Ru, Sb, Sn, Ta, Ti, W, and Zr in 5% V/V hydrochloric acid and 1% V/V hydrofluoric acid (contains HNO_3 traces)
j. Yttrium standard for ICP, 10000 mg/L (TraceCERT, Sigma-Aldrich)

ANALYTICAL PROCEDURE

ultraWAVE — SRC Technology			
SAMPLE		SAMPLE AMOUNT	ACID MIXTURE
Lithium Ore	Spodumene	100 mg	1.5 mL of H_3PO_4 + 1.5 mL of H_2SO_4 + 2 mL of HF (dil. 1:3)
Anode	Graphite	200 mg	3 mL of H_2SO_4 + 2 mL of $HClO_4$ + 500 µL of Vanadium std solution (1000 mg/L)*
Cathode	LMO-Lithium Manganese Oxide	500 mg	1 mL of HNO_3 + 3 mL of HCl

Vanadium works as a catalyst to efficiently break the C-C bonds of graphite.
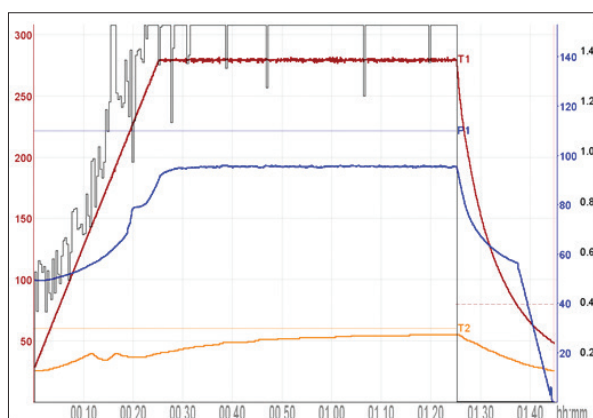*Table 1 - Sample amounts and acid mixtures used for the microwave digestion runs*

Figure 2: Samples were digested using this microwave program at 280 °C

QUANTIFICATION

For the Li-ore sample, we determined the concentrations of the elements present in major quantities: Al, Li, and Si. For the Anode and Cathode samples, three replicates out of six were spiked with 250 µL of periodic table mix 1 (solution h) and mix 2 (solution i) ICP standards respectively, immediately after sample weighing and prior to reagent addition. These samples were used for the recovery studies performed to validate the method. After microwave digestion, the sample solutions were spiked with Yttrium internal standard solution*, diluted to 50 mL with DI water, and subsequently analyzed by ICP-OES. An additional dilution was required for the LMO samples to reduce their acid concentration.

10 µg/mL of Yttrium standard (e) was added to calibration standards, blanks, and digested/diluted sample solutions as an internal standard to correct for matrix effects.

The instrument setup and operating conditions are reported in the following table:

Parameter	Setting
RF applied power (kW)	1.3
Plasma gas flow rate (L/min)	15
Auxiliary gas flow rate (L/min)	1.5
Nebulizer gas flow rate (L/min)	0.75
Replicate read time (s)	5
Stabilization delay (s)	30
Sample uptake delay (s)	30
Pump rate (rpm)	15
Rinse time (s)	15
Replicates	3
Emission lines (nm)	See Tables 3, 4, and 5

Table 2 - ICP-OES settings and operating conditions.

RESULTS AND DISCUSSION

The performance of the Milestone ultraWAVE was evaluated by the determination of major elements in a Li-ore sample and a recovery study on battery anode and cathode materials.

Following use of the ultraWAVE system to perform the digestion of all three samples types we obtained transparent solutions with no visible solid particles, indicating complete digestion of the samples.

As shown in Figure 2, the system automatically adjusted its microwave power to achieve the programmed profile up to the 280 °C temperature required for complete digestion.

The complete digestion and reproducible determination of major elements in the Li-ore samples demonstrate the ability of the system to handle use of perchloric acid, which is problematic for other types of digestion systems. The full recovery of the added elements to the anode and cathode samples and the good reproducibility of the measurements demonstrates the robustness of the digestion method as there are no loss of volatiles elements or cross contamination between the samples.

The concentrations and recoveries below were obtained via ICP-OES analysis:

Element and Wavelength (nm)	Determined Concentration (%)	RSD % (n=6)
Al 396.152	12.9	1.67
Li 670.783	2.95	0.92
Si 251.611	27.9	1.12

Table 3 - Concentrations of major elements in the Spodumene sample.

Element and wavelength (nm)	Determined concentration (µg/L)	RSD % (n=3)	Spiked sample concentration (µg/L)	RSD % (n=3)	Spike recovery (%)
Ag 328.068	15.5	7.4	61.0	7.57	91
Al 396.152	48.9	6.29	96.7	4.58	96
As 193.696	109	7.20	165	2.26	114
Ba 455.403	<MDL	-	54.9	2.69	110
Be 313.107	<MDL	-	47.7	2.70	95
Bi 223.061	<MDL	-	46.3	5.11	93
Cd 214.439	<MDL	-	47.7	1.94	95
Co 238.892	58.7	4.78	107	0.88	96
Cr 267.716	48.6	8.1	102	1.44	107
Cu 324.754	24.9		78.9	2.94	108
K 766.491	58.0	7.2	106	8.30	95
Li 670.783	32.2	4.8	89.5	0.72	115
Mg 279.553	50.1	2.29	96.3	2.00	92
Mn 257.610	<MDL	2.89	49.6	3.85	99
Mo 202.032	54.1	-	106	0.76	103
Ni 231.604	<MDL	1.71	54.6	3.53	109
P 213.618	71.1	-	123	8.94	103
Pb 220.353	<MDL	4.50	47.4	5.80	95
Rb 421.552		-	51.1	2.96	102
Ti 336.122	75.3	-	125	1.44	99
Zn 213.857	<MDL	2.23	45.9	5.62	92

Table 4 - Data of the recovery of Graphite sample.

Element and wavelength (nm)	Determined concentration (µg/L)	RSD % (n=3)	Spiked sample concentration (µg/L)	RSD % (n=3)	Spike recovery (%)
As 188.890	161	0.62	259	2.49	122
Ba 455.403	4.31	3.29	79.6	2.79	94
Be 313.042	<MDL	-	77.8	2.71	97
Bi 223.061	176	0.66	263	1.87	110
Cd 214.439	<MDL	-	78.6	3.60	98
Cu 324.754	<MDL	-	83.8	5.05	105
Fe 234.350	166	1.20	261	0.59	118
Ir 212.681	<MDL	-	77.1	3.38	96
Mo 202.032	<MDL	-	90.9	2.26	114
Pb 182.143	<MDL	-	80.2	7.78	100
Rb 421.552	14.7	2.39	89.2	2.60	93
Sb 217.582	152	3.24	243	4.18	113
Sn 189.925	<MDL	-	84.7	5.86	106
Sr 407.771	14.3	2.83	90.3	2.92	95
Te 214.282	75.7	2.67	163	1.06	109
Ti 334.941	103	3.64	197	1.93	117
V 292.401	<MDL	-	73.9	3.57	92
Zn 206.200	12.9	1.62	87.5	2.03	93

Table 5- Data of the recovery of LMO sample (The digested solutions were further diluted by 1:2 V/V with water to lower their acid concentration prior to ICP-OES analysis. The final spiked concentration was 80 µg/L)

CONCLUSION

The superior performance of ultraWAVE makes it possible to completely mineralize any type of component present in Li-ion batteries, including materials such as ores and graphite that can be very difficult to digest.
SRC technology makes it possible to mineralize all samples simultaneously in a single run, which can dramatically boost productivity for high-volume labs.

ABOUT MILESTONE

Milestone has been innovating microwave sample preparation for over 30 years and offers an array of solutions that are perfectly tailored for modern testing labs within the battery industry. With over 25,000 instruments installed worldwide, we are the acknowledged industry leader in microwave technology and offer the most technologically advanced instrumentation for research and quality control. For more information, please visit www.milestonesrl.com.