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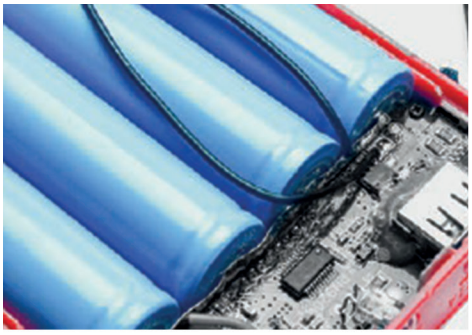



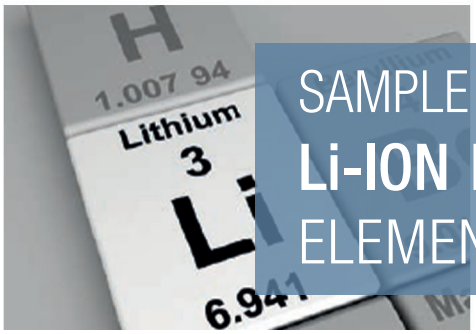

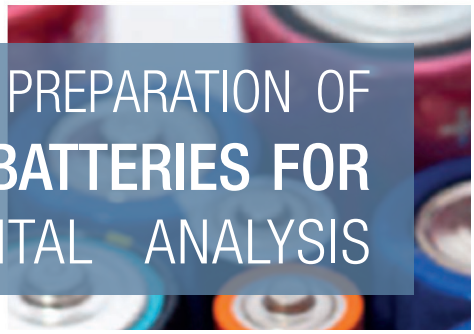

SAMPLE PREPARATION OF **Li-ION BATTERIES FOR** ELEMENTAL ANALYSIS

High throughput, elemental analysis of Li-ion battery samples using Milestone's ETHOS UP with SK-15 easyTEMP (eT) rotor.

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 ETHOS UP microwave digestion system incorporates all of the benefits of closed-vessel

microwave digestion while making sample preparation fast, easy, and effective.
In the following test, we demonstrate the system's performance for mineralizing two commonly-employed types of cathodes within the battery industry.

EXPERIMENTAL

INSTRUMENT

ETHOS UP is the most advanced rotor-based microwave sample preparation system available today, meeting the requirements for a wide variety of modern analytical labs.

Figure 1: Milestone's ETHOS UP

The ETHOS UP used in this study was equipped with an SK-15 eT rotor, controlled by Milestone's easyTEMP contactless temperature sensor. The superior temperature measurement of easyTEMP allows different samples of similar reactivities to be processed concurrently, reducing lab labor while increasing overall throughput.

SK-15 eT HIGH PRESSURE ROTOR

The SK-15 eT suits the analytical needs for determining trace elements in challenging samples, thanks to its capability to digest large sample amounts and its ability to attain higher temperature and pressure conditions.
The 15-position, high-pressure rotor is safely controlled via the easyTEMP sensor that consistently monitors and controls digestion temperature within each vessel, ensuring complete digestion of even the most difficult and reactive samples.

Figure 2: SK-15 easyTEMP (eT) High Pressure Rotor

REAGENTS

a. HNO_3, nitric acid, 65%, ACS reagent (Sigma-Aldrich)
b. HCl, hydrochloric acid, 37%, ACS reagent (Sigma-Aldrich)
c. 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)
d. 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)
e. Yttrium standard for ICP, 10000 mg/L (TraceCERT, Sigma-Aldrich)

ANALYTICAL PROCEDURE

ETHOS UP with SK-15 eT rotor	
SAMPLE	SAMPLE AMOUNT*
NCA—Lithium Nickel Cobalt Aluminum Oxide	0.5 g
NMC—Lithium Nickel Manganese Cobalt Oxide	0.5 g

** Acid Mixture: 2 mL of HNO_3 (65%), 6 mL HCl (37%).*
Table 1 - Sample list and amount digested.

Approximately 0.5 g of each sample was placed into individual SK-15 eT vessels (as reported in table 1). The acid mixture (trace metal grade) was then added to each vessel (according to the data reported in Table 1).
Three replicates out of six were spiked with 250 µL of the periodic table mix 1 (solution c) and mix 2 (solution d) 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.
The vessels were sealed and loaded into the rotor, the rotor was placed in the microwave cavity, and microwave method (reported in Table 2) was run.

Step	Time	T2	Power
1	00:25:00	230 °C	1800 W
2	00:15:00	230 °C	1800 W

Table 2: SK-15 eT microwave program.

After microwave digestion, the sample solutions were spiked with Yttrium internal standard solution*, diluted with DI water, and subsequently analyzed by ICP-OES.
**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 4 and 5

Table 3 - ICP-OES settings and operating conditions.

RESULTS AND DISCUSSION

The performance of Milestone's ETHOS UP, powered by the SK-15 eT rotor, was evaluated through a recovery study on spiked samples.
After the digestion run, we obtained transparent solutions that contained no visible solid particles, indicating complete digestion of the samples.

The recoveries below were obtained via ICP-OES analysis:

Element and wavelength (nm)	Determined concentration (µg/L)	RSD % (n=3)	Spiked sample concentration (µg/L)	RSD % (n=3)	Spike recovery (%)
Ag 328.068	<MDL	-	81.5	8.11	102
As 193.696	<MDL	-	81.8	2.15	102
Ba 455.403	<MDL	-	75.03	2.39	94
Be 313.107	<MDL	-	75.8	3.72	95
Cd 214.439	<MDL	-	71.7	2.67	90
Cr 267.716	<MDL	-	73.8	3.88	92
Cu 324.754	<MDL	-	74.3	7.41	93
Fe 238.204	65.9	1.93	138	1.82	91
Mn 257.610	<MDL	-	77.0	3.48	96
Mo 202.032	<MDL	-	72.5	3.77	91
Na 588.995	13.5	15.2	95.7	3.9	103
Nb 309.417	71.9	0.29	143	3.51	89
Pb 220.353	<MDL	-	91.9	4.44	115
Se 196.026	15.5	3.77	89.5	6.55	93
Sn 189.925	<MDL	-	75.9	5.26	95
Sr 407.771	12.6	0.56	86.2	3.18	92
Ti 336.122	<MDL	-	71.7	2.39	90
V 292.401	25.3	1.96	97.1	2.68	90
Zn 213.857	11.4	265	86.3	1.54	94

Table 4– Data of the recovery of NCA 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)

Element and wavelength (nm)	Determined concentration (µg/L)	RSD % (n=3)	Spiked sample concentration (µg/L)	RSD % (n=3)	Spike recovery (%)
Ag 338.289	145	1.44	191	1.60	93
As 188.980	121	3.35	178	2.03	115
Ba 455.403	<MDL	-	49.9	1.48	100
Be 234.861	<MDL	-	45.3	2.11	91
Cd 214.439	40.9	8.43	98.4	2.81	115
Cu 324.754	<MDL	-	44.8	0.93	90
K 766.491	106	2.59	156	0.64	100
Mo 202.032	<MDL	-	44.9	5.35	90
Pb 220.353	32.5	3.41	80.1	2.88	95
Ru 267.876	50.8	6.21	97.6	0.58	94
Sn 189.925	<MDL	-	47.1	2.10	94
Sr 407.771	5.72	2.14	50.5	2.29	90
Ti 336.122	53.6	4.73	98.8	1.94	90
V 292.401	<MDL	-	52.8	2.08	106

Table 5– Data of the recovery of NMC 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 data shown in this industry report demonstrates full recovery of the elements of spiked solutions, validating the methods of sample preparation and analysis. The low RSD's indicate that the methods are reproducible.
The ETHOS UP with SK-15 eT rotor was successfully applied in digesting several cathode samples, ensuring superior digestion quality and reliable results.
This configuration provides a complete solution for digestion of a wide variety of Li-ion battery samples.
In addition, microwave digestion using the Milestone ETHOS UP with easyTEMP control, provides the highest level of reproducibility and great ease of use, ensuring high quality digestion run after run.

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.

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