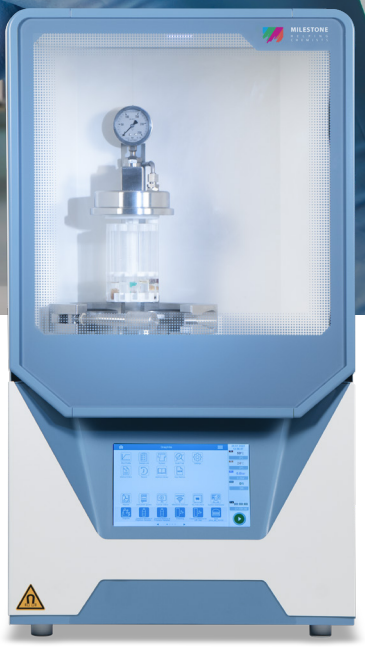
THE BENEFITS OF **SRC TECHNOLOGY** APPLIED ON SEVERAL **INDUSTRIES**



Milestone's new ultraWAVE 3 is the latest generation of SRC technology. It provides all the benefits of its revolutionary predecessor, while taking sample prep productivity and performance to the next level. Several aspects of the system, such as no batching, less operating time, and faster digestions, reduce turnaround time and increase lab efficiency for elemental analysis.

- INCREASED THROUGHPUT
- HIGHER-QUALITY RESULTS
- SIMPLIFIED WORKFLOW
- LOWER OPERATIONAL COSTS

ultraWAVE 3

Single Reaction Chamber
Microwave Digestion System

USING **ultraWAVE 3** FOR TRACE METAL ANALYSIS

DIGESTION OF
MIXED-BATCH FOOD
SAMPLES

DIGESTION OF
LITHIUM ION BATTERIES
MATERIALS

SIMULTANEOUS DIGESTION OF
POLYMER
SAMPLES

SAMPLE PREP OF
PHARMACEUTICAL
SAMPLES

MILESTONE
HELPING CHEMISTS

SIMULTANEOUS DIGESTION OF MIXED-BATCH FOOD SAMPLES FOR TRACE METAL ANALYSIS

Mixed-batch digestion of large sample amounts for high productivity and improved detection limits

I INTRODUCTION

Growing awareness and concern regarding food safety is reflected in the tightening of regulations governing toxic elements and compounds in food. Many toxic elements such as As, Hg, Cd, Pb etc. are routinely monitored, while minerals that are beneficial/essential to human health such as Se, Na, Mg, K, Ca, etc., are also measured.

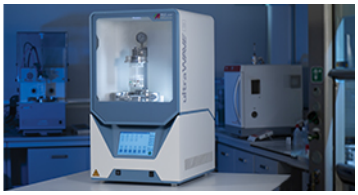
Traditional sample preparation techniques for food include hot block and closed-vessel microwave digestion.

Hot block digestions are time consuming, suffer from airborne contamination, poor digestion quality, and poor recovery of volatile compounds.

Closed-vessel microwave digestion has proven to be an effective technique with fast, complete digestions, a clean environment, and superior recovery of volatile compounds.

Milestone's Single Reaction Chamber (SRC) microwave digestion, is a revolutionary new approach, incorporating all of the benefits of closed vessel microwave digestion with new levels of convenience and effectiveness. The Milestone ultraWAVE 3 is a bench-top instrument that operates at very high pressures and temperatures, capable of processing large, dissimilar and difficult samples quickly, easily—all without batching. The data shown in this technical note demonstrates that the digestion of samples in the ultraWAVE results in uniformly high analytical data quality, making it the ideal solution for trace metals detection in any food matrix.

This industry report describes how a variety of samples from the food industry were digested simultaneously using the Milestone's ultraWAVE 3, and this can be replicated in previous ultraWAVE generation, without sample-to-sample cross contamination.



| EXPERIMENTAL

INSTRUMENTATION

The ultraWAVE 3 is designed with a 1 Liter reactor, capable of operating at very high temperature and pressure (300 °C and 199 bar respectively). This capability ensures complete digestion of even the largest sample sizes (up to 0.5 g of polymers) as well as highly reactive and difficult-to-digest samples.

Figure 1 – Milestone's ultraWAVE 3

For the first time, a microwave digestion system ensures equal temperature and pressure conditions in all positions, even when different samples and/or chemistries are used. This results in superior digestion capabilities, higher productivity and better workflow for the lab.

The ultraWAVE 3 base load and positive pressure load prior to heating generates an equilibrium of temperature and pressure in each position, thus avoiding sample/ elemental loss and cross contamination.

Samples can be weighed directly into disposable glass vials, eliminating the cleaning step. The easy handling of the vials and racks greatly reduces the operator time and associated labor costs.

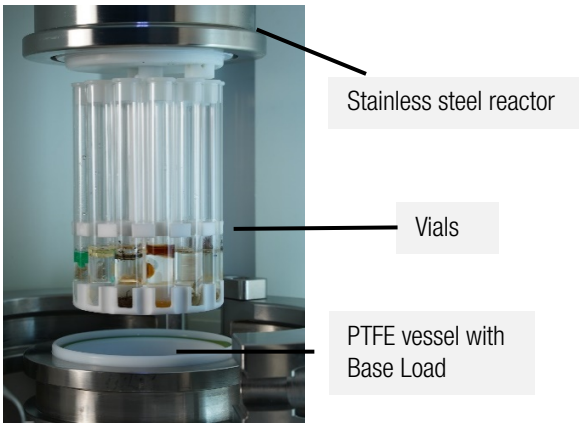


Figure 2 – Schematic of the ultraWAVE 3 Single Reaction Chamber (SRC)

SAMPLES

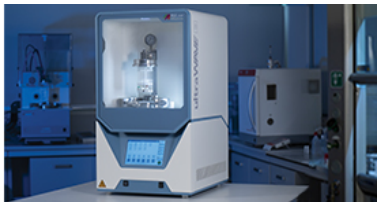
In this industry report, a recovery study was performed on certified reference materials and pharmaceutical samples spiked with a multielement standard (impurities according to ICH Q3D) to demonstrate the efficacy of the ultraWAVE in the preparation of mixed samples from 0.5 g to 2 g in a single digestion program.

Reference Material Code	Name of Sample
NIST 1567b	Wheat flour
NIST 1568b	Rice Flour
NIST 1515	Apple Leaves
NIST 1573a	Tomato Leaves

Table 1: Samples used for the study

PROCEDURE AND METHOD

Sample weights up to 1.0 g for each of the flour CRMs (NIST 1567b, NIST 1568b) and up to 0.5 g for each of the other sample types (NIST 1515, NIST 1573a) were accurately weighed into PTFE vials (quartz and disposable glass vials are also available). Five mL of HNO_3 67% and 0.5 mL of HCl 37% (electronics (EL) grade acids, Kanto Chemicals) were added to the PTFE vials. A base load of 120 mL DI H_2O and 5 mL HNO_3 67% was added into the 1 Liter PTFE vessel. The analysis was performed with a Triple Quadrupole ICP-MS.



Step	Time (hh:mm:ss)	Power (W)	Temp T1 (°C)	Temp T2 (°C)	Pressure (bar)
1	00:10:00	800	110	70	90
2	00:10:00	1200	180	70	90
3	00:10:00	1500	220	70	120
4	00:10:00	1500	220	70	120

Table 2: ultraWAVE digestion heating program for the simultaneous digestion of four CRM food samples.

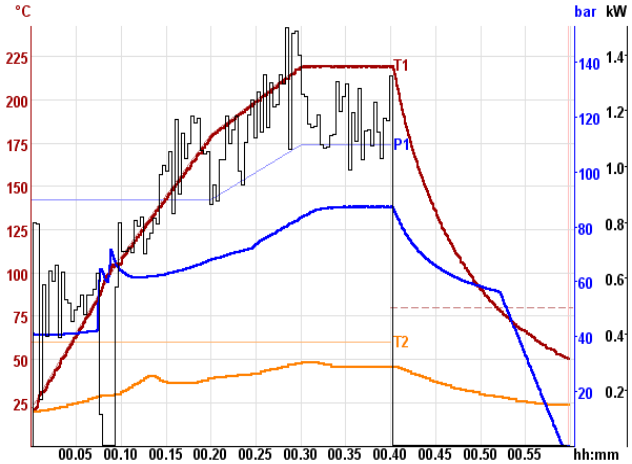


Figure 2: Internal temperature (red), external temperature (orange), pressure (blue) and power (black) graphs.

Parameter	Setting	
Cell mode	He mode	O_2 mode
Svan type	Single Quad	MS/MS
Plasma conditions	UHM-4	
RF power (W)	1600	
Sampling depth (mm)	10	
Carrier gas flow rate (L/min)	0.77	
Dilution gas flow rate (L/min	0.15	
Extract 1 (V)	0	
Extract 2 (V)	-250	
Omega bias (V)	-140	
Omega lens (V)	8.8	
Cell gas flow rate (mL/min)	5.5	0.3 (20% of full scale)
KED (V)	5	-7

Table 3: Triple Quadrupole ICP-MS operating conditions

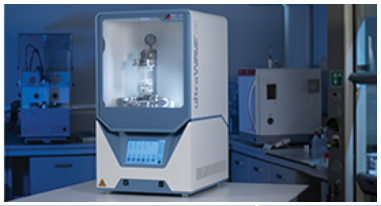
RESULTS AND DISCUSSION

The ultraWAVE 3 system performed simultaneous digestion of four different reference materials with different sample amounts. The total time from weighing to analysis was less than one hour.

As shown in Figure 2, the system automatically adjusts the microwave power to follow the temperature profile.

Digestion of reactive samples such as oil, butter and other high fat content samples require precise, accurate and direct temperature control, which is especially important to control exothermic reactions and to ensure complete digestion.

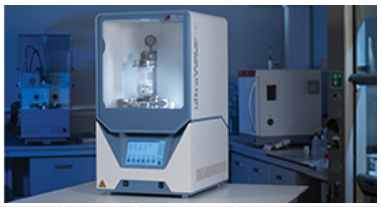
The data shows excellent recoveries for all elements including volatiles, which is reflected in Tables 4 to 7 below.



Element	Measured Solution Concentration (µg/L)	RSD (%)	Calculated Sample Concentration (mg/kg)			Certified Concentration (mg/kg)			Recovery (%)
23 Na	65.2	2.3	6.50	±	0.15	6.71	±	0.21	97
24 Mg	3842	1.6	383	±	6	398	±	12	96
27 Al	39	2.8	3.9	±	0.1	4.4	±	1.2	88
31 -> 47 P	12936	2.0	1291	±	26	1333	±	36	97
32 -> 48 S	15496	2.2	1546	±	34	1645	±	25	94
39 K	12700	2.3	1267	±	29	1325	±	20	96
44 Ca	1871	1.8	186.7	±	3.4	191.4	±	3.3	98
51 V	0.10	8.1	0.010	±	0.001	0.01*			100
55 Mn	86	1.7	8.54	±	0.14	9.00	±	0.78	95
56 Fe	142	1.6	14.20	±	0.22	14.11	±	0.33	101
63 Cu	19	1.6	1.94	±	0.03	2.03	±	0.14	96
66 Zn	112	1.9	11.17	±	0.21	11.61	±	0.26	96
75 As	0.047	16.5	0.0046	±	0.001	0.0048	±	0.0003	97
75-> 91 As	0.049	19.4	0.0049	±	0.001	0.0048	±	0.0003	101
78 Se	11.5	4.2	1.15	±	0.05	1.14	±	0.10	101
78-> 94 Se	11.8	1.9	1.17	±	0.02	1.14	±	0.10	103
85 Rb	6.54	1.8	0.652	±	0.012	0.671	±	0.012	97
95 Mo	4.60	2.1	0.459	±	0.009	0.464	±	0.034	99
111 Cd	0.239	5.7	0.0238	±	0.0014	0.0254	±	0.0009	94
118 Sn	0.0355	12.8	0.0035	±	0.0005	0.003*			118
202 Hg	0.0066	11.3	0.0007	±	0.0001	0.0005*			131
208 Pb	0.0937	4.4	0.0094	±	0.0004	0.0104	±	0.0024	90

*Table 4: Results for NIST 1567b, Wheat flour, n=24 - *Reference value*

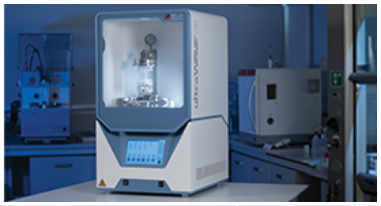
Element	Measured Solution Concentration (µg/L)	RSD (%)	Calculated Sample Concentration (mg/kg)			Certified Concentration (mg/kg)			Recovery (%)
23 Na	65.6	3.2	6.54	±	0.28	6.74	±	0.19	97
24 Mg	5454	1.5	543	±	8	559	±	10	97
27 Al	40.3	3.3	4.01	±	0.13	4.21	±	0.34	95
31 ->47 P	15162	2.8	1510	±	43	1530	±	40	99
32 ->48 S	11369	2.5	1133	±	28	1200	±	10	94
39 K	12371	2.0	1233	±	24	1282	±	11	96
44 Ca	1158	2.1	115.3	±	2.5	118.4	±	3.1	97
51 V	182.3	1.0	18.2	±	0.2	19.2	±	1.8	95
55 Mn	75.4	1.0	7.51	±	0.08	7.42	±	0.44	101
56 Fe	0.173	1.7	0.0173	±	0.0003	0.0177	±	0.0005*	98
63 Cu	22.7	1.0	2.26	±	0.02	2.35	±	0.16	96
66 Zn	191.7	1.4	19.10	±	0.26	19.42	±	0.26	98
75 As	2.97	1.4	0.296	±	0.004	0.285	±	0.014	104
75 -> 91 As	3.01	1.7	0.300	±	0.005	0.285	±	0.014	105



78 Se	3.4	8.9	0.341	±	0.030	0.365	±	0.029	93
78 ->94 Se	3.5	3.8	0.352	±	0.013	0.365	±	0.029	96
85 Rb	61.1	1.1	6.088	±	0.069	6.198	±	0.026	98
95 Mo	13.96	1.2	1.391	±	0.017	1.451	±	0.048	96
111 Cd	0.201	4.9	0.0201	±	0.0010	0.0224	±	0.0013	90
118 Sn	0.060	7.4	0.0060	±	0.0004	0.005	±	0.001*	121
202 Hg	0.0529	2.1	0.0053	±	0.0001	0.0059	±	0.0004	89
208 Pb	0.068	3.0	0.0068	±	0.0002	0.008	±	0.003*	85

*Table 5: Results for NIST 1568b Rice Flour, n = 24 - *Reference value*

Element	Measured Solution Concentration (µg/L)	RSD (%)	Calculated Sample Concentration (mg/kg)			Certified Concentration (mg/kg)			Recovery (%)
11 B	141	2.9	28	±	0.8	27	±	2	104
23 Na	196	1.6	39.1	±	0.6	24.4	±	1.2	160*1
24 Mg	14083	1.3	2812	±	36	2710	±	80	104
27 Al	1458	1.6	291	±	5	286	±	9	102
31 -> 47 P	8088	2.2	1615	±	35	1590*			102
32 ->48 S	9211	1.4	1839	±	26	1800*			102
39 K	80429	2.2	16057	±	361	16100	±	200	100
44 Ca	74060	1.2	14786	±	172	15260	±	1500	97
51 V	1.20	2.8	0.24	±	0.01	0.26	±	0.03	92
52 Cr	1.3	1.4	0.25	±	0.00	0.3*			85
55 Mn	265	1.0	53	±	1	54	±	3	98
56 Fe	379	0.8	76	±	1	80*			95
59 Co	0.44	1.5	0.088	±	0.001	0.09*			98
60 Ni	4.4	1.7	0.88	±	0.02	0.91	±	0.12	97
63 Cu	28.2	1.0	5.62	±	0.06	5.64	±	0.24	100
66 Zn	60.3	0.9	12.0	±	0.1	12.5	±	0.3	96
75 ->91 As	0.2	3.7	0.036	±	0.001	0.038	±	0.007	94
78 -> 94 Se	0.271	13.8	0.054	±	0.008	0.050	±	0.009	108
85 Rb	46.3	0.9	9.2	±	0.1	9*			103
88 Sr	123.0	1.0	25	±	0	25	±	2	98
95 Mo	0.44	5.3	0.088	±	0.005	0.094	±	0.013	94
111 Cd	0.06	7.0	0.013	±	0.001	0.014*			91
121 Sb	0.06	4.6	0.011	±	0.001	0.013*			85
138 Ba	245	1.9	49	±	1	49	±	2	100
202 Hg	0.21	2.0	0.041	±	0.001	0.044	±	0.004	93
208 Pb	2.3	1.3	0.452	±	0.006	0.470	±	0.024	96



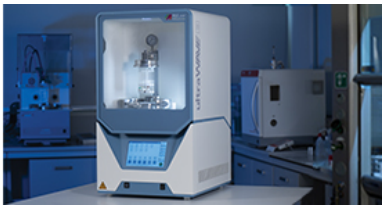
232 Th	0.14	2.2	0.028	±	0.001	0.03*	93
238 U	0.034	3.7	0.0068	±	0.0003	0.006*	113

*Table 6: Results for NIST 1515 Apple leaves, n=24 - *Reference value.*

*[1] *The measured Na result was high compared to the reference value; the same result was obtained from a repeated analysis of the same solution, so a spike recovery test was performed for confirmation. The spike recovery result was good (recovery: 99%), suggesting that the original sample had suffered Na contamination.*

Element	Measured Solution Concentration (µg/L)	RSD (%)	Calculated Sample Concentration (mg/kg)			Certified Concentration (mg/kg)			Recovery (%)
11 B	167	1.9	33.3	±	0.6	33.3	±	0.7	100
23 Na	613	2.5	122	±	3	136	±	4	90
24 Mg	57311	2.0	11412	±	225	12000*			95
27 Al	2573	2.4	512	±	12	598	±	12	86
31 ->47 P	10928	2.7	2176	±	59	2160	±	40	101
32 -< 48 S	48387	1.4	9635	±	131	9600*			100
39 K	134250	2.2	26732	±	591	27000	±	500	99
44 Ca	243939	1.4	48574	±	671	50500	±	900	96
51 V	4.0	2.2	0.792	±	0.017	0.835	±	0.010	95
52 Cr	9.3	1.6	1.85	±	0.03	1.99	±	0.06	93
55 Mn	1236.5	1.5	246	±	4	246	±	8	100
56 Fe	1843.3	1.7	367	±	6	368	±	7	100
59 Co	2.8	1.4	0.55	±	0.01	0.57	±	0.02	96
60 Ni	7.9	1.9	1.56	±	0.03	1.59	±	0.07	98
63 Cu	23.7	1.5	4.71	±	0.07	4.70	±	0.14	100
66 Zn	149.4	1.5	29.8	±	0.5	30.9	±	0.7	96
75 As	0.7	2.3	0.141	±	0.003	0.112	±	0.004	126
75 ->91 As	0.6	1.7	0.112	±	0.002	0.112	±	0.004	100
78 -> 94 Se	0.31	11.2	0.061	±	0.007	0.054	±	0.003	113
85 Rb	69.7	1.2	13.88	±	0.16	14.89	±	0.27	93
88 Sr	421.0	1.3	84	±	1	85*			99
95 Mo	2.1	2.8	0.42	±	0.01	0.46*			91
107 Ag	0.09	9.1	0.018	±	0.002	0.017*			104
111 Cd	7.4	1.4	1.47	±	0.02	1.52	±	0.04	97
121 Sb	0.28	3.4	0.055	±	0.002	0.063	±	0.006	88
138 Ba	302.8	2.1	60.3	±	1.3	63*			96
202 Hg	0.15	2.4	0.030	±	0.001	0.034	±	0.004	88
232 Th	0.52	2.1	0.104	±	0.002	0.12*			87
238 U	0.14	2.3	0.029	±	0.001	0.035*			81

*Table 7: Results for NIST 1573a Tomato Leaves, n = 24 - *Reference value.*



| CONCLUSION

The data illustrated in this industry report demonstrates the ultraWAVE 3 ability to provide full recovery of all elements, while avoiding cross contamination even when different samples and sample weights are digested in the same run. The ultraWAVE 3 ability to simultaneously digest different sample types, easy sample handling and superior throughput surpass the capabilities of hot blocks and traditional rotor-based microwave digestion systems. Its superior capabilities in terms of processing mixed samples, large sample amounts and ease of use provide unmatched productivity. The superior digestion quality achieved at high temperature and pressure maximizes the performance of the ICP-MS by reducing interferences, blanks and overall maintenance.

MILESTONE
HELPING CHEMISTS

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, thorough qualitative and quantitative elemental analyses of the anode, cathode, and electrolyte materials present in batteries are required.

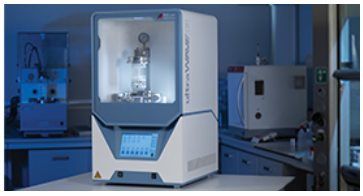
These types of analyses are performed using ICP-based analyzers, which require solid samples to be decomposed and dissolved in an acid solution through a digestion process before the digested solutions are then injected into the analyzer.

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 3 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.
This industry report describes how three common lithium battery related sample matrices (Li-ores, Anodes and Cathodes) were digested simultaneously using the Milestone's ultraWAVE 3, and this can be replicated in previous ultraWAVE generation, without sample-to-sample cross contamination.

EXPERIMENTAL

INSTRUMENT

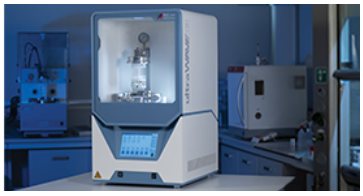
- Milestone's ultraWAVE 3
- 20-positions rack with 15 mL quartz, glass and TFM vials
- Analytical balance
- ICP-MS

Figure 1 – Milestone's ultraWAVE 3

Developed and patented by Milestone, the ultraWAVE 3 represents another significant step forward for SRC technology and embrace Milestone 20+ years of experience. The stainless-steel reactor with a high-purity PTFE-TFM liner and cover, enables to achieve, higher pressures and temperatures regardless the sample type and acid mixture. The digestion process is continuosly controlled by easyTEMP, an advance contactless sensor that measure the temperature directly of the reaction chamber. The simplified rack construction eliminates the time need to assemble and disassemble the vessels. Just as important, dissimilar samples can be processed simultaneously using disposable glass, quartz or PTFE-TFM vials, thus saving time and money. The ultraWAVE 3 addressed all the sample preparation challenges related to performance, time, workflow, and cost of ownership.

REAGENTS

a) a. HNO3, nitric acid, 65%, ACS reagent (Sigma-Aldrich)
b) b. HCl, hydrochloric acid, 37%, ACS reagent
c) (Sigma-Aldrich)
d) c. HF, hydrofluoric acid, 48%, ACS reagent
e) (Sigma-Aldrich)
f) d. H3PO4, ortho-phosphoric acid, 85%, ACS reagent
g) (Sigma-Aldrich)
h) e. H2SO4, sulfuric acid, 96-98%, ACS reagent
i) (Sigma-Aldrich)
j) f. HClO4, perchloric acid, 70%, ACS reagent, technical
k) grade (Sigma-Aldrich)
l) g. Vanadium (V) standard solution, 1000 mg/L V in
m) nitric acid (TraceCERT, Sigma-Aldrich)
n) h. Periodic table mix 1 for ICP, 10 mg/L (TraceCERT,
o) Sigma-Aldrich): Al, As, Ba, Be, Bi, B, Ca, Cd, Cs, Cr,
p) Co, Cu, Ga, In, Fe, Pb, Li, Mg, Mn, Ni, P, K, Rb, Se,
q) Si, Ag, Na, Sr, S, Te, Tl, V, and Zn in 10% V/V nitric
r) acid (contains HF traces)



s) i. Periodic table mix 2 for ICP, 10 mg/L (TraceCERT,
t) Sigma-Aldrich): Au, Ge, Hf, Ir, Mo, Nb, Pd, Pt, Re,
u) Rh, Ru, Sb, Sn, Ta, Ti, W, and Zr in 5% V/V
v) hydrochloric acid and 1% V/V hydrofluoric acid
w) (contains HNO3 traces)
x) j. Yttrium standard for ICP, 10000 mg/L (TraceCERT,
y) Sigma-Aldrich)

SAMPLES

Spodumene (Lithium ore), Graphite (Anode) and LMO-Lithium Manganese Oxide (Cathode), were digested.

SAMPLE PREPARATION

An amount of 0.1 g of Spodumene were weighed inside a 15 mL vial and 1.5 mL of H_3PO_4 + 1.5 mL of H_2SO_4+ 2 mL of HF (dil. 1:3) were added.

An amount of 0.2 g of Graphite and 0.5 g of LMO-Lithium Manganese Oxide were weighed inside a 15 mL vial and 3 mL of H_2SO_4 + 2 mL of $HClO_4$ + 500 μ L of Vanadium std solution (1000 mg/L)* were added.

An amount of 0.5 g of LMO-Lithium Manganese Oxide were weighed inside a 15 mL vial and 1 mL of HNO_3 + 3 mL of HCl were added.

**Vanadium works as a catalyst to efficiently break the C-C bonds of graphite.*

The 20-positions rack was positioned inside the SRC TFM liner inside the reaction chamber, which was previously filled with 120 mL of H_2O and 5 mL of HNO_3. The SRC system was pressurized up to 40 bar with Nitrogen gas to close the glass vials.

The following microwave heating program was applied:

Step	Time (min)	Power (W)	T1 (°C)	T2 (°C)	P (bar)
1	25	1500	280	60	110
2	60	1500	280	60	110

Table 1 - Microwave Program for the sponges

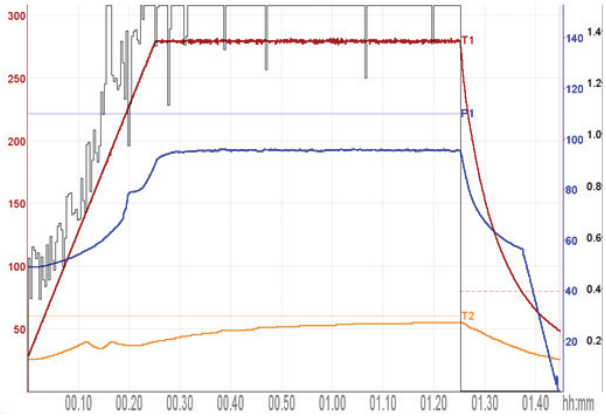


Figure 2 – Samples were digested using the microwave program at 280°C

QUANTIFICATION

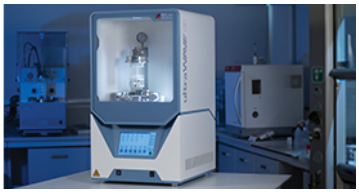
For the Li-ore sample, we determined the concentrations of the elements present in major quantities: Al, Li, and Si.

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 3 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 3 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.

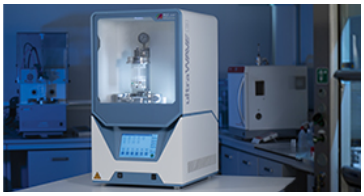
The full recovery of the added elements to the anode and cathode samples and the good reproducibility of the measurements demonstrates the robustness of the digestion method as there are no loss of volatiles elements or cross contamination between the samples.

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 – Concentration 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

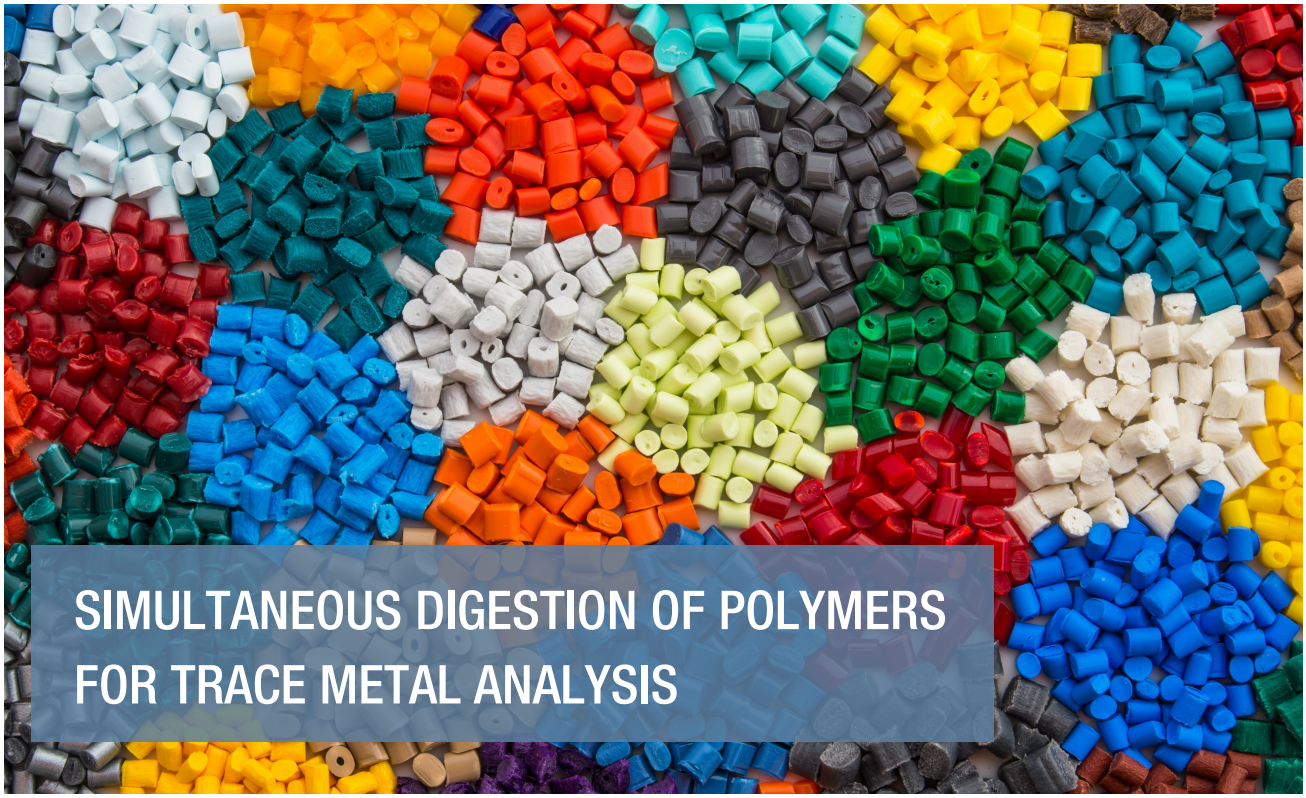
CONCLUSIONS

The superior performance of ultraWAVE 3 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

At Milestone we help chemists by providing the most innovative technology for metals analysis, direct mercury analysis and the application of microwave technology to extraction, ashing and synthesis. Since 1988 Milestone has helped chemists in their work to enhance food, pharmaceutical and consumer product safety, and to improve our world by controlling pollutants in the environment.



SIMULTANEOUS DIGESTION OF POLYMERS FOR TRACE METAL ANALYSIS

Utilizing Single Reaction Chamber (SRC) Technology for trace metal analysis in polymer samples.

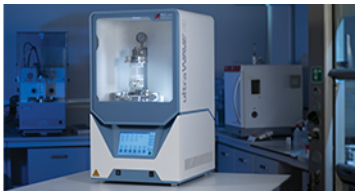
I INTRODUCTION

With stricter industry regulations now in place, demand for trace metals analysis at lower detection levels has reached an all-time high, placing increased emphasis on sample preparation methodologies. Closed-vessel microwave digestion has proven to be an effective technique, offering fast, complete digestions, a clean environment, and effective recovery of volatile compounds.

Polymers, for their part, represent a broad class of compounds with a tremendous range of physical properties. While some of these compounds are relatively easy to prepare for trace metals analysis, most polymeric and plastic materials are very stable matrices and require extremely high temperatures and pressures to achieve complete digestion, which can be difficult to achieve even with conventional closed-vessel microwave systems. Since polymers are principally organic, they generate a lot of pressure during the organic decomposition of digestion processes.

Milestone's Single Reaction Chamber (SRC) microwave digestion, is a revolutionary new approach, incorporating all of the benefits of closed vessel microwave digestion with new levels of convenience and effectiveness. The Milestone ultraWAVE 3 is a bench-top instrument that operates at very high pressures and temperatures, capable of processing large, dissimilar and difficult samples quickly, easily—all without batching. The data shown in this technical note demonstrates that the digestion of samples in the ultraWAVE results in uniformly high analytical data quality, making it the ideal solution for trace metals detection in specialty polymer samples.

This industry report describes how a variety of samples from the polymer industry were digested simultaneously using the Milestone's ultraWAVE 3, and this can be replicated in previous ultraWAVE generation, without sample-to-sample cross contamination.



| EXPERIMENTAL

INSTRUMENTATION

The ultraWAVE 3 is designed with a 1 Liter reactor, capable of operating at very high temperature and pressure (300 °C and 199 bar respectively). This capability ensures complete digestion of even the largest sample sizes (up to 0.5 g of polymers) as well as highly reactive and difficult-to-digest samples.

Figure 1 – Milestone's ultraWAVE 3

For the first time, a microwave digestion system ensures equal temperature and pressure conditions in all positions, even when different samples and/or chemistries are used. This results in superior digestion capabilities, higher productivity and better workflow for the lab.

The ultraWAVE 3 base load and positive pressure load prior to heating generates an equilibrium of temperature and pressure in each position, thus avoiding sample/ elemental loss and cross contamination.

Samples can be weighed directly into disposable glass vials, eliminating the cleaning step. The easy handling of the vials and racks greatly reduces the operator time and associated labor costs.

Figure 2 – Schematic of the ultraWAVE 3 Single Reaction Chamber (SRC)

SAMPLES

In this industry report, a recovery study was performed working with two different Certified Reference Materials and one polymer sample, spiked with a standard solution at known concentration of metals.

Sample ID	Sample Type	Sample matrix
ERM-EC680	Certified Reference Material	Polyethylene (Low level)
ERM-EC680k	Certified Reference Material	Polyethylene
ABS	Spiked	Acrylnitrile-Butadiene-Styrene-Copolymer

Table 1: Samples used for the study

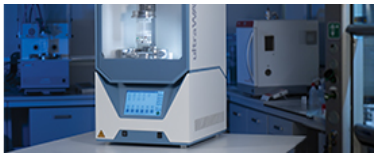
PROCEDURE AND METHOD

0.2 g of each sample were accurately weighed into disposable glass vials. Quartz vials are also available. PTFE vials are usually not recommended for polymer digestions.

Three replicates of each CRM and six replicates of ABS sample were prepared to evaluate the repeatability of the digestion step.

Prior to acid addition, three ABS samples out of six were spiked with 800 µL of a 10 mg/L Multi-element Standard solution. Considering a final volume of 50 mL, it resulted in a spiked concentration of 160 µg/L.

3 mL of HNO_3 67% and 0.5 mL of HCl 37% (ACS reagent grade) were added to the samples. Two



blanks with the same amount of acids were included. A base load of 120 mL DI H_2O and 5 mL HNO_3 67% was added into the 1 Liter PTFE vessel. The analysis was performed with an Optical Emission Spectometer ICP (ICP-OES).

Step	Time (hh:mm:ss)	Power (W)	Temp T1 (°C)	Temp T2 (°C)	Pressure (bar)
1	00:10:00	800	130	60	60
2	00:10:00	1200	180	60	80
3	00:10:00	1500	250	60	110
4	00:10:00	1500	250	60	110

Table 2: ultraWAVE digestion heating program for the simultaneous digestion of polymer samples.

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 (n°)	3

Table 3: ICP-OES operating conditions

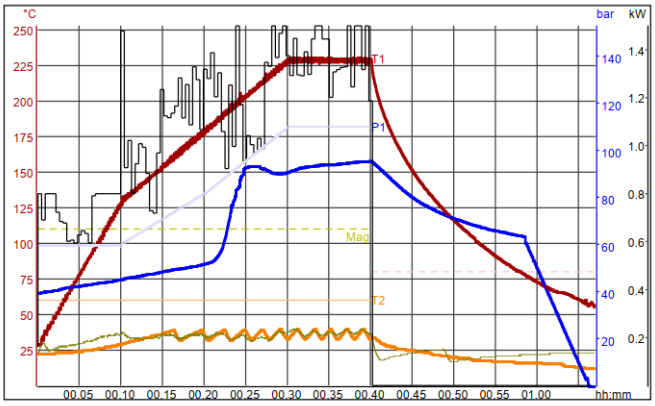


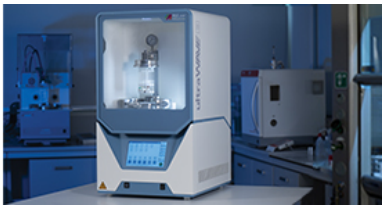
Figure 2: Internal temperature (red), external temperature (orange), pressure (blue) and power (black) graphs.

RESULTS AND DISCUSSION

The analytical results are shown in Tables 4, 5 and 6 with good recoveries of all analytes and RSDs below 10%. This demonstrates the robustness and reproducibility of microwave digestion using the ultraWAVE 3 with SRC technology.

Element	*Measured Concentration (mg/kg)*	*RSD% (n=3)*	*Certified Concentration (mg/kg)*			*Recovery (%)*
As 188.980	*29.2*	*8.4*	*30.9*	*± 0.7*		*95*
Cd 214.439	*136.2*	*1.9*	*140.8*	*± 2.5*		*97*
Cr 267.716	*110.2*	*1.7*	*114.6*	*± 2.6*		*96*
Pb 220.353	*101.5*	*1.7*	*107.6*	*± 2.8*		*94*

Table 4: Results for ERM-EC680, Polyethylene (Low level)



Element	Measured Concentration (mg/kg)	RSD% (n=3)	Certified Concentration (mg/kg)		Recovery (%)
As 188.980	3.65	8.9	4.1	± 0.5	90
Cd 214.439	20.1	0.9	19.6	± 1.4	103
Cr 267.716	7.62	7.8	20.2	± 1.1	38 [a]
Pb 220.353	13.1	3.8	13.6	± 0.5	97
Zn 213.857	140	1.7	137	± 20	102

[a] Relatively low recovery is due to the presence of a significant fraction of Chromium in the form of Cr_2O_3.
Refer to EC680k Certificate for detailed information.

Table 5: Results for ERM-EC680k, Polyethylene

Element	Measured Concentration (µg/L)		RSD% (n=3)	Spike Recovery (%)
	ABS	ABS + Spike		
Ag 328.068	<20	150	2.31	94
Al 396.152	<20	169	3.60	106
As 188.980	<20	167	3.74	104
Cd 214.439	<20	152	1.74	95
Co 238.892	<20	155	1.97	97
Cr 267.716	<20	164	5.49	103
Cu 327.395	<20	164	1.54	102
Fe 238.204	<20	179	1.41	112
Li 670.783	<20	148	3.36	93
Mn 257.610	<20	153	1.31	96
Pb 220.353	<20	160	0.36	100
Zn 213.857	<20	161	2.72	101

Table 6: Results for ABS, Acrylnitrile-Butadiene-Styrene-Copolymer

| CONCLUSION

The data illustrated in this industry report demonstrates the ultraWAVE 3 ability to provide full recovery of all elements, while avoiding cross contamination even when different samples are digested in the same run. The ultraWAVE 3 ability to simultaneously digest different sample types, easy sample handling and superior throughput surpass the capabilities of hot blocks and traditional rotor-based microwave digestion systems. Its superior capabilities in terms of processing mixed samples, large sample amounts and ease of use provide unmatched productivity. The superior digestion quality achieved at high temperature and pressure maximizes the performance of the ICP-MS by reducing interferences, blanks and overall maintenance.

MILESTONE
HELPING CHEMISTS

PREPARATION OF PHARMACEUTICAL SAMPLES IN ACCORDANCE WITH USP <232>/<233>

Utilizing Single Reaction Chamber (SRC) Technology for trace metals analysis for pharmaceutical samples.

INTRODUCTION

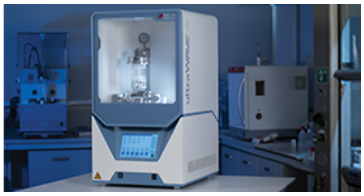
With stricter industry regulations now in place, demand for trace metals analysis at lower detection levels has reached an all-time high. ICP, once the standard for pharmaceutical metals analysis, is rapidly being replaced by ICP-MS, placing increased emphasis on sample preparation methodologies. Closed-vessel microwave digestion has proven to be an effective technique, offering fast, complete digestions, a clean environment, and effective recovery of volatile compounds. The single drawback has been the inability to run digestion on several matrix types simultaneously. Milestone's Single Reaction Chamber (SRC) microwave digestion is a revolutionary new approach, incorporating all of the benefits of closed vessel microwave digestion with new levels of convenience and effectiveness.

The Milestone ultraWAVE 3 is a benchtop instrument that operates at very high pressures and temperatures, capable of processing large, dissimilar and difficult samples quickly, easily—all without batching. The data shown in this technical note demonstrates that the digestion of samples in the ultraWAVE 3 results in uniformly high analytical data quality, making it the ideal solution for trace metals detection in pharmaceutical samples.

This industry report describes how a variety of samples from the pharmaceutical industry were digested simultaneously using the Milestone's ultraWAVE 3, and this can be replicated in previous ultraWAVE generation, without sample-to-sample cross contamination.

EXPERIMENTAL

Following the optimization of digestion methodology (vial type, digestion matrix and temperature program), dietary supplements were digested and analyzed for the "big four" toxic elements. Good QC data demonstrates the suitability of SRC microwave digestion for this application. New USP chapters <232> and <233> for the measurement of inorganic



contaminants in pharmaceutical samples have been implemented. While samples that are soluble in aqueous and organic solvents may be analyzed directly, a large portion of samples will require digestion, and in fact, digestion may be preferred for ICP-MS analysis even if the sample is soluble in organic solvent. Closed-vessel digestion is stipulated by USP and it is expected that microwave digestion will be the predominant digestion technique used: its high pressure and temperature capability offering greater digestion power than hot plate open vessel digestion for example.

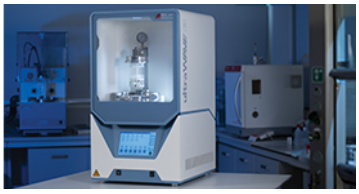
SRC microwave digestion is a relatively new type of closed vessel digestion that differs significantly from traditional closed vessel digestion. A commercially available benchtop SRC digestion system can digest up to 15 samples simultaneously, at high temperature and pressure. This high temperature and pressure capability enables the complete digestion of virtually every pharmaceutical sample type, producing digest solutions with a very low total organic carbon (TOC) content which is beneficial for ICP-MS analysis. Two sample types, St. John's Wort and fish oil, typical of finished product pharmaceuticals, were digested using an SRC digestion system and analyzed for the four toxic USP elements using collision cell ICP-MS to evaluate the effectiveness of SRC digestion for this application. Since all samples are digested together in a single chamber with SRC, duplicates and spike recoveries were performed to confirm the retention of volatile elements and the absence of cross contamination.

INSTRUMENT

- Milestone's ultraWAVE 3
- 20-positions rack with 15 mL glass vials
- Analytical balance
- ICP-MS

Figure 1 – Milestone's ultraWAVE 3

Developed and patented by Milestone, the ultraWAVE 3 represents another significant step forward for SRC technology and embrace Milestone 20+ years of experience. The stainless-steel reactor with a high-purity PTFE-TFM liner and cover, enables to achieve, higher pressures and temperatures regardless the sample type and acid mixture. The digestion process is continuosly controlled by easyTEMP, an advance contactless sensor that measure the temperature directly of the reaction chamber. The simplified rack construction eliminates the time need to assemble and disassemble the vessels. Just as important, dissimilar samples can be processed simultaneously using disposable glass, quartz or PTFE-TFM vials, thus saving time and money. The ultraWAVE 3 addressed all the sample preparation challenges related to performance, time, workflow, and cost of ownership.



PROCEDURE AND METHOD OPTIMIZATION

Sample vials used in SRC instrumentation are typically available in quartz, TFM (a high temperature polymer) and borosilicate glass. The benefit of glass is very low cost which makes them disposable, eliminating vial cleaning procedures. The drawback of glass is elevated backgrounds (ppb level) for some elements - namely B, Na, Mg, Al, K and Ca.

However, since these elements are not stipulated in USP <232>, glass vials can be used. Fig. 3 shows the digestion blanks obtained from glass, quartz and TFM digestion vials for USP elements. In this data, Ru, Os and the Pt group elements were not measured. However, it can be assumed that the vial contribution for these elements is extremely low.

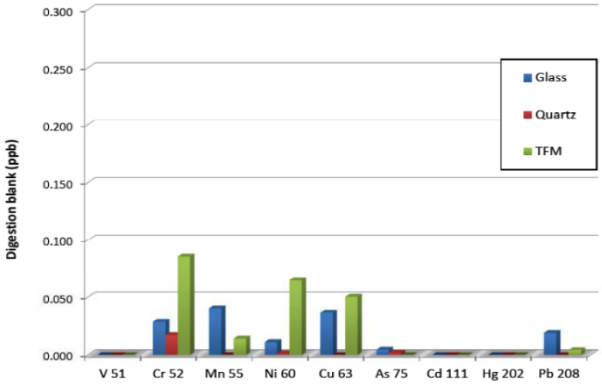


Figure 2 - Digestion blanks obtained from 2 different vial materials selected USP elements

Because the SRC system is capable of very high pressure, higher weights of high organic content sample can be digested, including whole gel caps, which is a benefit for pharmaceutical sample analysis. Also, the higher-pressure capability allows a higher temperature to be achieved, which gives a more complete digestion. Even with high organic content samples such as oils, virtually all the organic carbon is decomposed to CO2 giving the sample digest and very low TOC content. This is a benefit for ICP-MS analysis, as the presence of carbon in the sample enhances on the sensitivity of poorly ionized elements, thus enhancing repeatability and reliability.

SAMPLES

Two set of samples were prepared for analysis by two different instruments: ICP-OES and ICP-MS. The first set of samples analyzed by ICP-OES, includes fish oil capsules, magnesium stearate and a dietary supplement (Table 1). St. John's Wort has been analyzed by ICP-MS (Table 2) together with a laboratory fortified blank.

SAMPLE PREPARATION

Digest matrix depends on the sample type and weight. An amount of 0.5 g of each pharmaceutical sample were weighed inside a 15 mL glass vial and 4 mL of 65% HNO_3 + 1 mL of 37% HCl were added together with a 50 ppb of a multielement solution.
For fish oil gel caps, an entire gel cap (1 g) was digested with 9 mL HNO_3 + 1 mL HCl.

The vial size used was 15 mL, allowing 15 samples to be digested simultaneously. Since all samples are digested together under the same pressure and temperature control, different sample weights and acid chemistries can be digested simultaneously. The only requirement is that the digestion temperature selected must be sufficient to digest the most difficult sample in the batch.

The rack with the 20 glass vials was positioned inside the SRC TFM liner inside the reaction chamber, which was previously filled with 120 mL of H_2O and 5 mL of HNO_3. The SRC system was pressurized up to 40 bar with Nitrogen gas to close the glass vials. The following microwave heating program was applied:

Step	Time (min)	Power (W)	T1 (°C)	T2 (°C)	P (bar)
1	20	1500	240	60	90
2	20	1500	240	60	90

Table 1 - Microwave Program

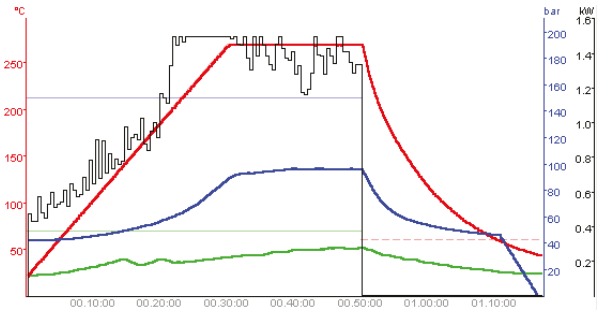
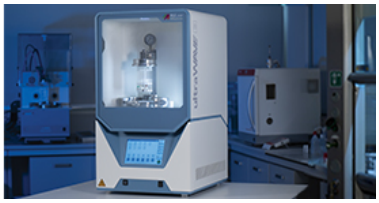


Figure 3 –Microwave program from simultaneous digestion of multiple pharmaceutical samples.



ICP-OES AND ICP-MS RESULTS

Two set of samples were prepared for analysis by two different instruments: ICP-OES and ICP-MS. The first set of samples analyzed by ICP-OES, includes fish oil capsules, magnesium stearate and a dietary supplement (Table 1). St. John's Wort has been analyzed by ICP-MS (Table 2) together with a laboratory fortified blank.

Element	Blank	Spike	Fish Oil		Magnesium Stearate		Dietary Supplement	
	ppb	ppb	ppb	recovery	ppb	recovery	ppb	recovery
As	<	50	56.35	112.7 %	52.75	105.5 %	56.20	112.4 %
Cd	<	50	50.55	101.1 %	44.20	88.4 %	45.70	91.0 %
Pb	<	50	50.40	100.8 %	46.20	92.4 %	49.30	98.6 %
Hg	<	50	49.36	98.7 %	47.70	95.4 %	50.11	100.2 %

Table 1: ICP-OES analysis of the "Big Four" USP analytes on fish oils, magnesium stearate and dietary supplement following digestion in the ultraWAVE 3. Samples were spiked with 50 ppb of a multielement solution prior digestion.

St. John's Wort (µg/g)			Laboratory fortified blank (µg/g)			
Element	Detection limit	Sample result	Sample result	Spike conc	Spike result	Spike % recovery
As	0.008	0.184	ND	5.6	5.39	96
Cd	0.003	0.109	ND	1.9	1.86	98
Pb	0.03	0.24	ND	3.8	3.58	94
Hg	0.1	ND	ND	5.6	6.06	106

Table 2: ICP-MS analysis of the "Big Four" USP analytes in St. John's Wort & fish oil gelcaps following digestion in the ultraWAVE 3. The table shows the recovery study on St. John's Wort and on a laboratory fortified blank.

CONCLUSIONS

Milestone's Single Reaction Chamber technology offers multiple benefits for sample preparation for trace metals analysis over conventional microwave digestion systems. Due to its higher sample capacity, use of disposable vials and faster cooling down time, sample processing throughput is 2x – 3x higher than conventional closed vessel digestion systems. The superior digestion quality achieved at higher temperatures (and pressure) makes analysis by ICP-OES and ICP-MS more accurate.

The data shown in this technical note demonstrates that the digestion of samples in a SRC, in vials with loose-fitting caps ensures complete recovery and full digestion. Furthermore, the ability to digest different sample types together and larger sample weights with minimum acid volume (1-4 mL per sample) makes it the optimal technique to perform pharmaceutical sample prep for trace metals analysis.

WATCH VIDEOS

The ultraWAVE 3, at its third generation, encompasses Milestones 20 years of experience on Single Reaction Chamber (SRC) technology. This latest model incorporates several features to enhance the lab workflow and productivity without compromising the quality of the digestion process and the following analysis. The ultraWAVE 3 boosts to the next level: Productivity, Performance, Safety and Usability whilst reducing the cost of ownership.

Learn about how the ultraWAVE 3 with Single Reaction Chamber (SRC) technology provides significantly greater digestion capabilities for even the most difficult sample types over traditional digestion systems. High-performance stainless steel construction allows for higher pressures and temperatures, while disposable vessels eliminate the need to assemble, disassemble or clean between processing. Just as important, dissimilar samples can be processed simultaneously, saving time and money.