



WWW.INNOVATEK.COM.CO

Cra 21 No. 41 – 26

PBX (57) 338 0711

Bogotá, Colombia

contacto@innovatek.com.co

Spectroscopy®

Revolutionizing Sample Preparation with Single-Reaction Chamber Microwave Digestion

AUGUST 2018



Any Sample Any Time: The Benefits of Single Reaction Chamber (SRC) Microwave Digestion for Trace Element Analysis



Microwave Digestion for Specialty Polymers

Technical Application Note



Utilizing Single Reaction Chamber (SRC) Technology for Trace Metals Analysis in Accordance with USP <232>/<233>

Application Note



Mixed-Batch Food Sample Microwave Digestion:

Technical Application Note



New Approaches in Sample Preparation and Precise Multielement Analysis of Crude Oils and Refined Petroleum Products Using Single-Reaction-Chamber (SRC) Microwave Digestion and Triple-Quadrupole ICP-MS

John F. Casey, Yongjun Gao, Weihang Yang, and Robert Thomas



Simultaneous Mixed-batch Sample Preparation for Metals Testing of Medical Cannabis

Sponsored by

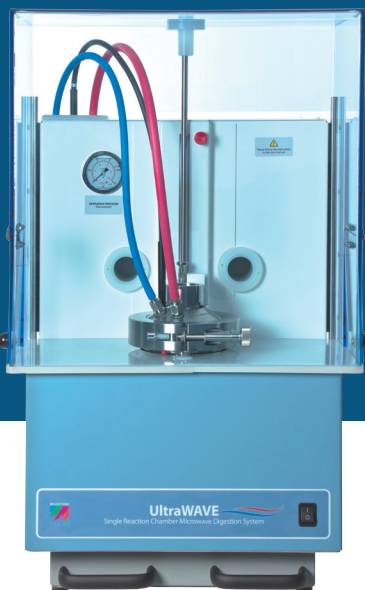


MILESTONE
HELPING
CHEMISTS

50%
reduction in
cycle time

2X
the
throughput

50%
lower
labor costs



Numbers Don't Lie

Improved workflow

Maximum throughput

No batching required

Lower operating costs

With over a thousand units installed globally, Milestone's Single Reaction Chamber (SRC) technology has revolutionized how industrial and research laboratories around the world prep samples for analysis.

Our UltraWAVE transcends traditional closed and open vessel digestion, offering faster digestions, maximum throughput and lower cost of ownership.

High-performance stainless steel construction allows for higher pressures and temperatures and any combination of acids to be used, 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 resources. The bottom line? The Milestone UltraWAVE is the superior solution to handle all your sample prep challenges.

[See what the UltraWAVE can do for your lab.](#)

Visit us at www.milestonesci.com to schedule an onsite demonstration.

powered by **milestone**
connect 



Ethos UP



UltraWAVE



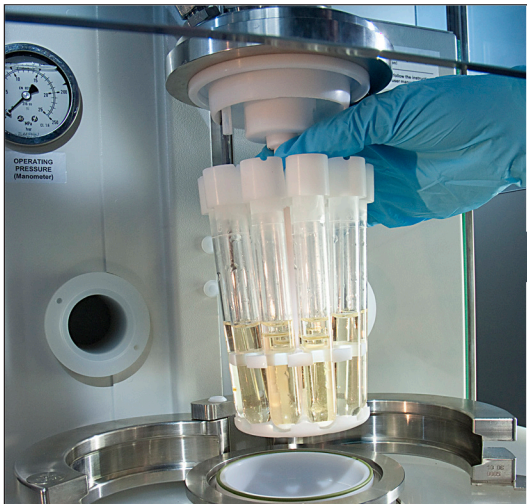
UltraCLAVE

Microwave Digestion

Extraction | Mercury | Ashing | Determination | Synthesis | Clean Chemistry

milestonesci.com | 866.995.5100





SPONSORED CONTENT

Any Sample Any Time: The Benefits of Single Reaction Chamber (SRC) Microwave Digestion for Trace Element Analysis

You've decided to invest in a microwave digestion system for your trace element requirements. So, how do you go about selecting the optimum technology for your samples? What types of mineral acids will be best suited for your elements of interest, and what temperature and pressure will be required for the digestion process of your sample matrices? It's only when you have a good understanding of these issues that you can begin to look more closely at the pros and cons of the various commercially available microwave technologies.

Table 1 shows a comparison of three different microwave technologies. On the left is a sequential system, which allows for single sample digestion, one at a time and offers limited temperature and pressure capability. Productivity is considered to be low because it is digesting one sample at a time. The middle column shows traditional rotor-based system, offering good temperature

and pressure capability, decent sample throughput with medium productivity. Last, the right-hand column shows SRC technology, which offers high temperature and pressure capability as well as maximum productivity.

Rotor-Based Technology

Before we focus on SRC technology, let's take a closer look at some of the recognized limitations of traditional rotor-based systems. The main drawback is that they require batching of similar matrices and chemistries because control of the power is based on the reaction of one vessel at a time. Regardless of how temperature is being measured, it's still measuring the power level based on one sample at a time. By batching similar samples, under-digestion of some samples can be minimized due to the pressure and temperature required by others. In fact, the vessels in rotor-based systems are typically made from Teflon, which limits the temperature and pressure. The multiple



Table 1: Comparison of the three major commercially available microwave digestion technologies.

Specification	Sequential	Rotor Based	Single Reaction Chamber (SRC)
Working temperature	200 °C	230 °C	300 °C
Maximum pressure capability	~30 bar	100 bar	200 bar
Number of samples per run	One vial per run	15 vessels per run	15 vials per run
Typical digestion time (including cooling time)	10–15 minutes for each vials	1½ hours for 15 vessels	Less than 1 hour for 15 vials
Productivity	Low	Medium	High

components of vessels require additional handling before and after digestion, which could impact productivity. Depending on detection limit requirements, the vessel liners may also require extra cleaning between runs.

SRC Technology Principles of Operation

Let's take a more detailed look at the principles of SRC technology and how it differs from the rotor-based system (1). Instead of a rotor with discrete sample vessel, the samples are put into vials with loose-fitting caps, which sit in a rack that is lowered into a larger vessel containing a base load of acidified water. This base-load absorbs the microwave energy and transfers it to the vial, which allows every vial to react independently within the base load and ensures that all samples achieve maximum temperature with pressures contained up to 200 bar. No batching of samples is necessary and any combination of sample type and acid chemistry can be run simultaneously in the same chamber. A schematic of the SRC is shown on the

left side of **Figure 1**, while an actual photograph of sample vials being lowered into the chamber is shown on the right.

As previously mentioned, loose-fitting caps are used to seal the vials. This is possible because they are pre-pressurized with 40 bar of nitrogen before the start of the microwave program, which acts as a gas cap and keeps all the vials independently closed. As the pressure builds, equilibrium is achieved inside and outside the vial. As a result, a variety of vial types including disposable glass, quartz, and Teflon, or any combination of these materials, can be used.

Benefit of Nitrogen Pressurized Caps

To exemplify that 40 bar of nitrogen is sufficient to seal the vials, an experiment was carried out in which vials containing 110 ppm of mercury, were placed right next to blank solutions in a 15-rack sample holder. In other words, every alternate sample vial in the rack was either 110 ppm or 0 ppm mercury. It is well recognized that mercury is highly volatile, particularly when heated and would contaminate any

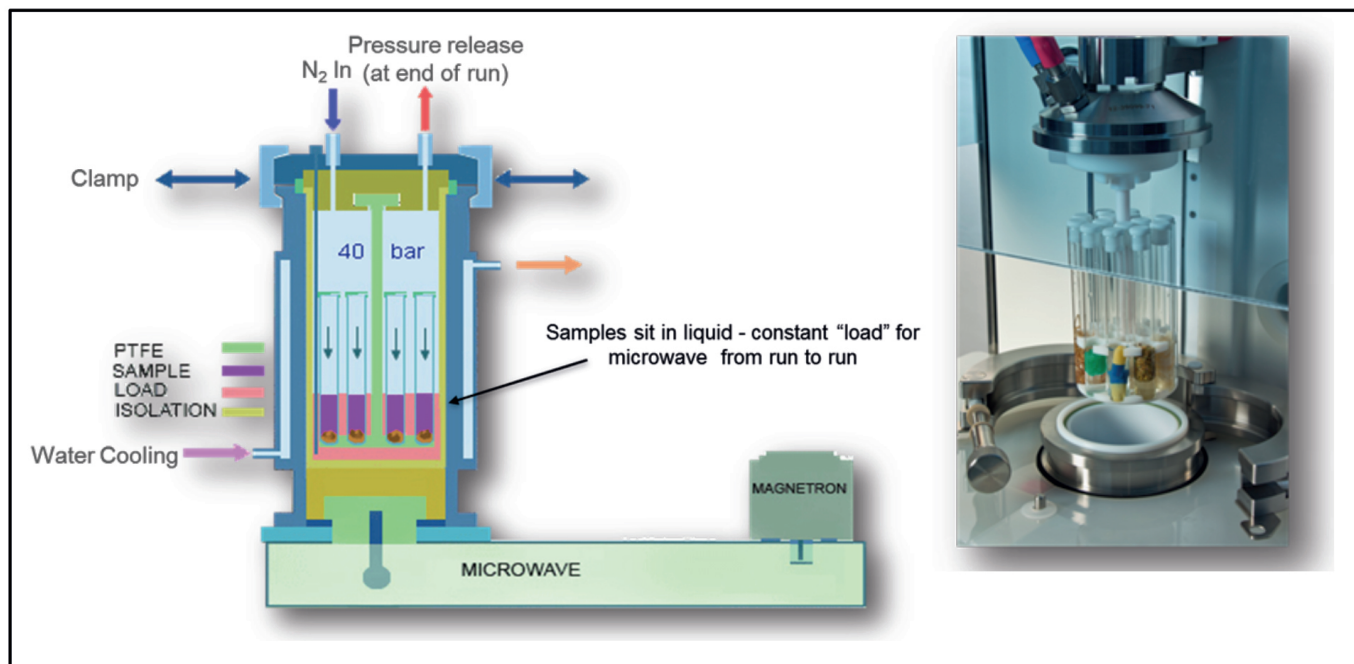
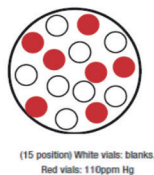


Figure 1: Single Reaction Chamber microwave digestion technology.



(15 position) White vials: blanks.
Red vials: 110ppm Hg

	Hg (ppt)
Blk position 01	0.020
Blk position 03	0.032
Blk position 05	0.001
Blk position 07	0.002
Blk position 09	-0.003
Blk position 11	-0.007
Blk position 13	-0.007
Blk position 15	-0.006

SCIENTIFIC SOLUTIONS - An Independent Consultant Serving the Needs of the Trace Element Analysis Community



Figure 2: Study of sealing capability of nitrogen gas shows no sign of contamination from mercury.

surrounding vessels if not capped tightly. However, it can be seen in **Figure 2** that the measurement of every alternate blank sample by inductively coupled plasma mass spectrometry (ICP-MS) is actually at the limit of detection for the technique, which is a clear indication that SRC technology using pressurized nitrogen gas as a sealant eliminates the potential of cross-contamination in the sample chamber.

Benefits of High Temperature and Pressure

Let's evaluate the high temperature and pressure capabilities of SRC technology to digest a wide array of organic-based matrices that would typically be found in the pharmaceutical, dietary supplements, food, agriculture, petroleum, petrochemical, plastics, or polymer industries. Although the technology works extremely well with inorganic-based samples such as metallurgical, geological, environmental, and consumer products, its ability to utilize extremely high temperature and pressure to digest organic-based samples sets it apart from other traditional microwave technology. So, for that reason, this white paper will focus on the capability of the SRC approach for digesting organic-based samples (2).

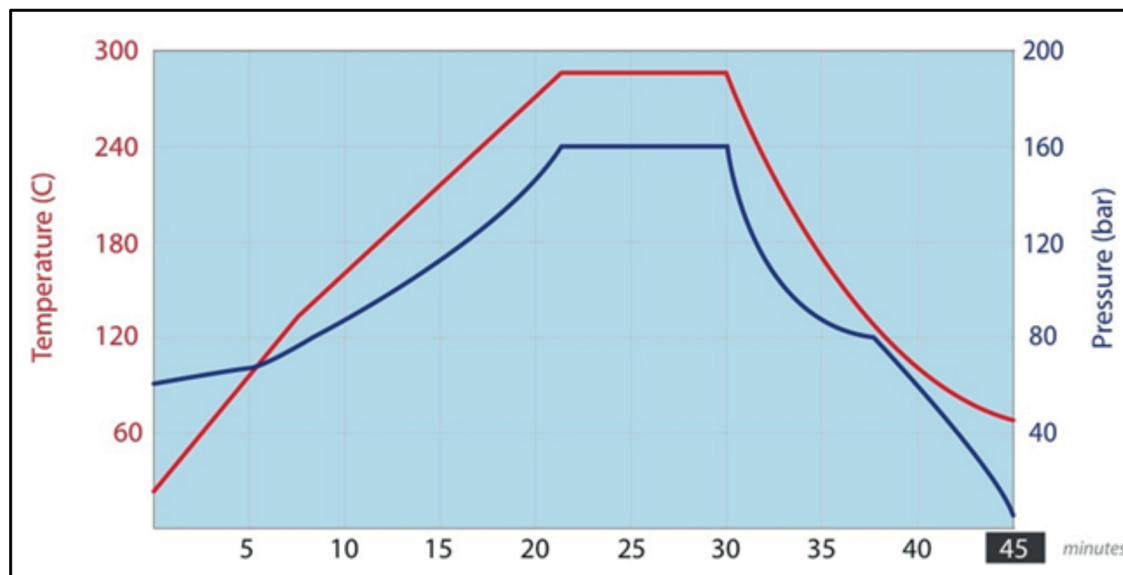


Figure 3: High temperature and pressure is achieved with the SRC approach. The blue line is chamber pressure, and the red line is temperature.

With the majority of organic matrices, the most efficient mineral acid digestion media is typically a strong oxidizing agent such as HNO_3 , which tends to generate large amounts of CO_2 and various nitrogen oxides (NO_x). Therefore, the microwave technology will not only need to accommodate the high temp required to digest all the different sample types, but also be able to handle the subsequent increase in pressure produced by the generation of these gases.

Thus, a successful sample preparation for organic samples depends on selecting the correct acid chemistries and obtaining a suitable temperature to properly extract the elements of interest and create a homogenous and representative solution. The high temperature capability of SRC technology is exemplified by **Figure 3**, which is a plot of chamber pressure (in blue)

and temperature (in red). It can be seen that the sample has reached a pressure of 160 bar and a temperature of 280 °C, in 20 minutes, maintained at that level for 10 minutes and then cooled back down again in 15 minutes. The complete digestion process in this example took about 45 minutes in total, which is fairly typical for most samples using this technology.

One of the main advantages of SRC technology is that the digestion process for widely different samples can all be combined together in one simultaneous run, which has a significant impact on digestion efficiency and productivity. Since the base load of the chamber is monitored, the sample type inside each vial is almost irrelevant to the dissolution process. It's also important to emphasize that the quality of the data generated by the plasma spectrochemi-

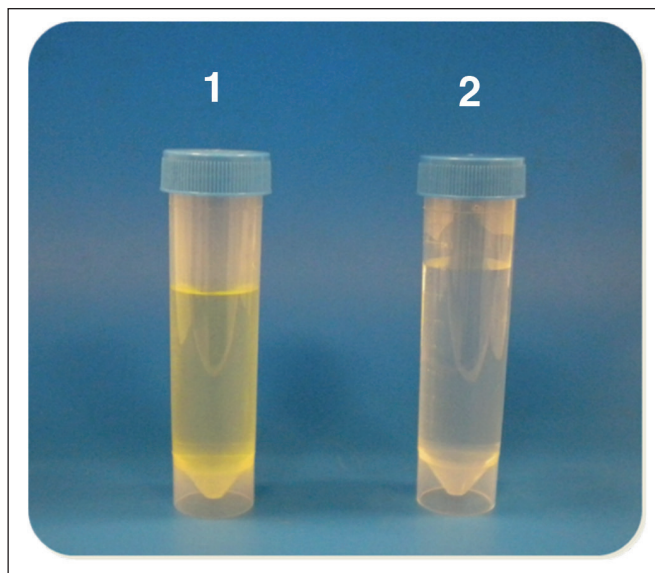


Figure 4: Digestion of an API (0.3 g of sample with 10 mL HNO₃) at different temperatures and pressure (1) 180 °C/32 bar and (2) 210 °C/45 bar in a rotor-based system.

cal technique for trace element analysis is only as good as the sample solution being analyzed, which is directly affected the efficiency and completeness of the sample dissolution procedure.

Typical Applications

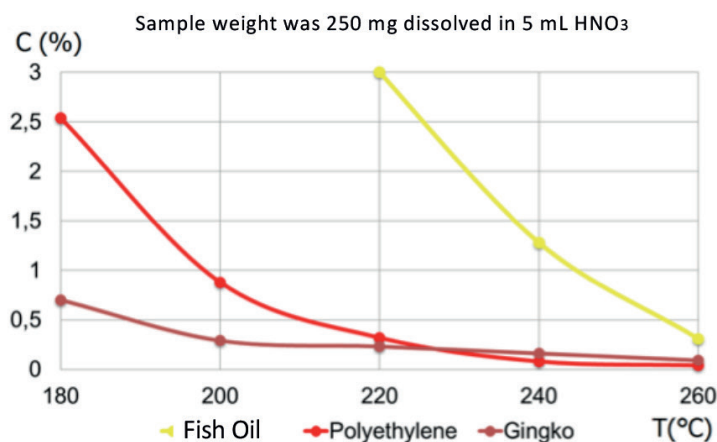
Now, let's look at a typical SRC sample preparation procedure for some common organic matrices. The measurement of elemental impurities in pharmaceutical samples is receiving much attention because of the recent implementation of regulations described in the new *United States Pharmacopeia* (USP) (3) and *International Conference on Harmonization* (ICH) (4) directives, which sets permitted daily exposure (PDE) levels and suggests analytical procedures for the determination 24 trace elements in pharmaceutical raw

materials, drug products and dietary supplements.

Digestion of Pharmaceutical and Related Materials

Using SRC technology, sample size for pharmaceutical matrices is typically about 0.5 g, but can be modified due to detection needs and sample homogeneity. As mentioned, the best acid to use is 5–10 mL of nitric acid. Alternatively, a 4:1 nitric acid–hydrochloric acid mix will work for many sample types encountered in USP work. If nitric acid is being used on its own, about 0.5 mL of hydrochloric acid will often help to stabilize some elements, particularly mercury (Hg) and the platinum group elements. However, it should be emphasized that if an ICP-MS system is being used, the ⁴⁰Ar³⁵Cl polyatomic species will interfere with monoisotopic arsenic (As) at 75 atomic mass units (amu). This can be alleviated using a collision/reaction cell (CRC), but it is important to be aware of this, so that the optimum instrumental conditions can be used. It should also be noted, that hydrofluoric acid is sometimes needed to completely digest silicate material and several other elements including titanium and tungsten.

To exemplify why temperature and pressure is so critical for these types of samples, a study was carried out to digest an active pharmaceutical ingredient (API) under two different temperature and pressure conditions. The sample weight (0.3 g), acid (HNO₃), volume (10 mL), vessel (quartz), and digestion time (20 min) were all exactly the same; the only differ-



SCIENTIFIC SOLUTIONS : An Independent Consultant Serving the Needs of the Trace Element Analysis Community



Figure 5: Residual carbon content versus digestion temperature using SRC technology.

ence was that one sample was digested at a temperature of 180 °C and pressure of 32 bar, while the other one was digested at 210 °C and 45 bar.

The results of the experiment are shown in **Figure 4**. The API sample on the left (labeled #1) is still dark yellow in color due to the higher residual carbon content (RCC). The oxidative digestion process was incomplete because of the lower temperature (180 °C). Whereas, the sample on the right (labeled #2), which achieved a higher temperature of 210 °C, clearly resulted in a more complete digestion.

The conclusion from this study is that if the sample is dark yellow in color, chances are that it still contains undigested organic material. This is important to know because high residual carbon content will potentially be problematic for the measurement of some elemental impurities by both ICP-optical emission spectrometry (OES) and ICP-MS systems. In fact, a recent study

published by Muller and coworkers at the Federal University of Santa Maria in Brazil showed an order of magnitude lower RCC levels were achieved in three API samples using SRC technology compared with a traditional rotor-based microwave approach (5).

To help us quantify this, **Figure 5** shows a plot of residual carbon content against digestion temperature for three organic samples: fish oil, polyethylene, and ginkgo biloba (herbal supplement). It can be seen that the RCC has been reduced to below 0.1% for polyethylene and ginkgo and less than 0.2% for fish oil at 260 °C.

As mentioned previously a low carbon content in the final solution is more desirable to reduce the impact of carbon-based polyatomic spectral interferences when using ICP-MS as demonstrated by **Table 2**, which shows carbon-based polyatomic spectral interferences cited in the literature (6) on the left that can



Table 2: Common carbon-based polyatomic interferences in ICP-MS.

Interference	Analyte Mass
^{12}C	^{11}B
$^{12}\text{C}^{12}\text{C}$	^{24}Mg
$^{40}\text{Ar}^{12}\text{C}$	^{52}Cr
$^{38}\text{Ar}^{13}\text{C}$	^{51}V
$^{12}\text{C}^{14}\text{N}$	^{26}Mg
$^{12}\text{C}^{16}\text{O}$	^{28}Si
$^{12}\text{C}^{16}\text{OH}$	^{29}Si
$^{12}\text{C}^{16}\text{O}^{16}\text{O}$	^{44}Ca
$^{12}\text{C}^{16}\text{O}^{16}\text{O}^{16}\text{O}$	^{60}Ni
$^{35}\text{Cl}^{12}\text{C}$	^{47}Ti
$^{37}\text{Cl}^{12}\text{C}$	^{49}Ti

potentially interfere with the elemental masses shown in the right-hand column.

It's also important to point out that high residual carbon content not only impacts the severity of polyatomic interferences, but it can also potentially clog the interface cones. This is seen in **Figure 6**, which is an ICP-MS sampler cone that has been blocked by carbon deposits building up on the tip after extended use of aspirating organic-based samples.

Food and Agricultural Matrices

Let's now turn our attention to food samples. A food manufacturer or a contract lab that specializes in the analysis of foodstuffs typically utilizes many different



Figure 6: An ICP-MS sampler cone that has been blocked by carbon deposits building up on the tip after extended use of aspirating organic-based samples.

analytical techniques to fully characterize food materials for a full suite of macronutrients, micronutrients, and elemental impurities. Whereas historically, flame and furnace atomic absorption together were used to cover the wide range of elements in foodstuffs, often multiple sample preparation steps were needed to determine the full suite of elements. Today, however, plasma spectrochemistry is widely used for this type of analysis. Because modern instrumentation can cover such a wide elemental and concentration range, ICP-MS and ICP-OES techniques are now being used to measure sub-ppb levels for contaminant elements such as lead and arsenic, while at the same time measuring high ppm levels of elements like Ca and K. For this reason, it is important that the sample preparation procedure allows the complete multielement suite to be measured in the same analytical method.

The digestion of infant formula is particularly challenging because it has up to 3% protein, 14% carbohydrate, and 6% fat content. The majority of elemental nutrients and minerals in infant formula are not particularly low and are easily covered by ICP-OES analysis. However, some

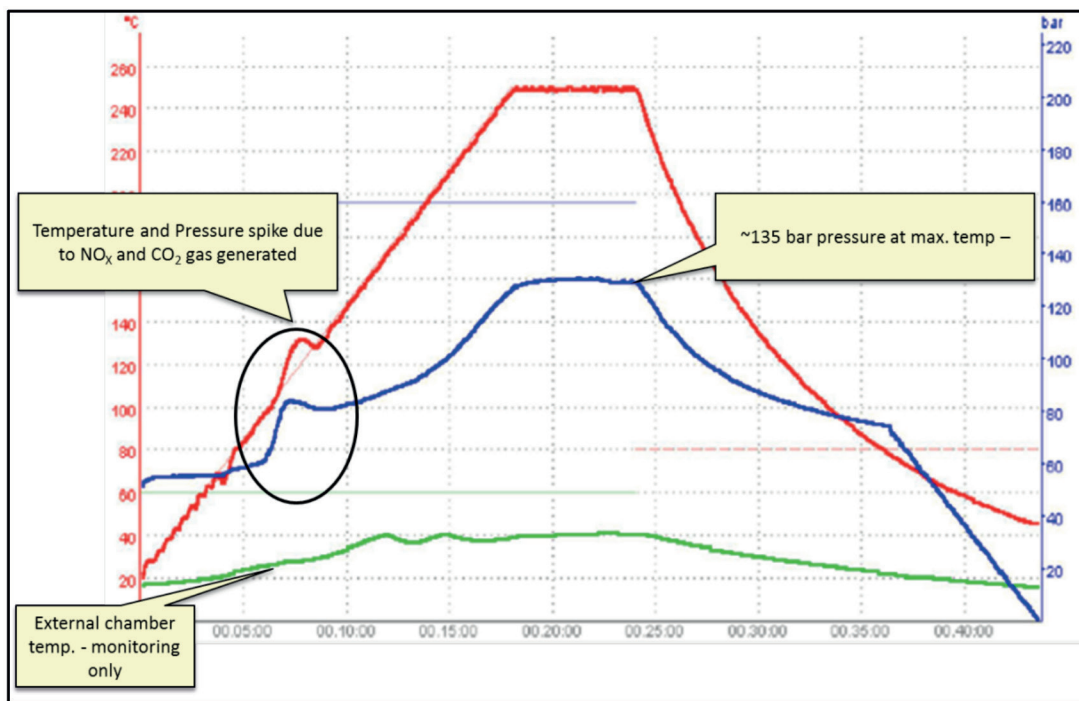


Figure 7: The benefit of high pressure and temperature on the digestion of 2 g of infant formula.

elements such as Fe and Zn are often present at trace levels and therefore close to the detection limit for the technique. So, the ability to digest higher sample weights and make different sample dilutions means that ICP-OES can be used for the full suite of analytes. An additional benefit of increased sample weights is that it allows a more homogeneous and representative sample to be taken.

So, let's examine the pressure/temperature plot of infant formula. Similar to pharmaceutical samples, the high organic content of infant formula will produce CO_2 and NO_x during digestion, which rapidly increases pressure in the sample vessel. The large chamber size and high-pressure capability of SRC technology allows up to 2 g of infant formula to be

digested with 10 mL of HNO_3 and 5 mL of H_2O in a 40-mL vial.

Temperature and pressure will spike due to CO_2 and NO_x gases generated as organic material starts to digest, as can be seen in **Figure 7**. The benefit with SRC is that every sample has direct monitoring of temperature and pressure, so at 135 bar pressure a maximum temperature of 250 °C is achieved. These data, which were published by Nobrego and coworkers at the Federal University of Sao Carlos in Brazil, showed that the residual carbon content at this temperature was less than 0.1% (7). With 2 g of infant formula, this would be very difficult with a closed-vessel, rotor-based system. In fact, the maximum sample weight with a high-pressure closed-digestion system is approximately 0.5 g.

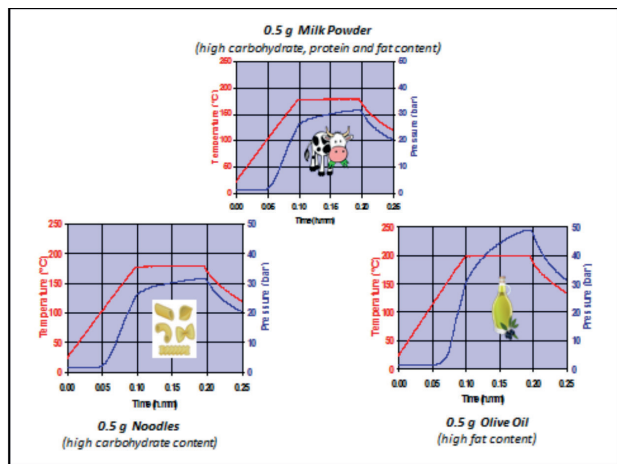


Figure 8: Pressure/temperature plots, based on differing carbohydrate, protein, and fat content of three food matrices.

Various food samples require different temperatures and generate varying pressures during digestion, based on their composition, as seen by these three pressure/temperature plots of foods with differing carbohydrate, protein, and fat content shown in **Figure 8**. As exemplified by the plots, the resulting pressures can vary from about 30 bar all the way up to 60 bar. For this reason, digestion of these types of samples requires microwave technology, which is flexible and can accommodate variable heating conditions. Even though a high pressure rotor-based system will do an adequate job for these kinds of samples, the capability of SRC technology, which can achieve temperatures up to 300 °C, is better suited because of its ability to digest mixed batches of samples simultaneously in a single run.

Polymer, Plastics and Petrochemical Samples

Polymers, plastics, resins, oils, and petrochemicals represent a broad class of

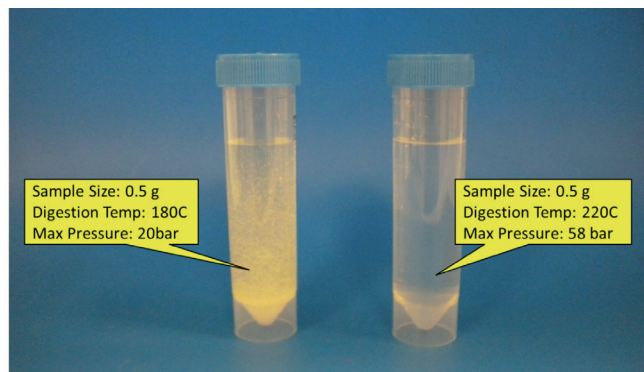


Figure 9: A comparison of microwave digestion of high density polyethylene (HDPE) at two different temperatures: 180 °C/20 bar and 220 °C/58 bar.

compounds with a tremendous range of physical properties. While some of these compounds are relatively easy to prepare for trace metals analysis, most of these materials are very stable matrices and require extremely high temperatures and pressures to achieve complete digestion, which can be difficult with conventional closed-vessel microwave systems.

Since these types of samples are principally organic in nature, they generate high pressure during the digestion processes. Laboratories in these industries typically complement microwave technology with traditional dissolution tools like hot plates and Parr bombs to digest these highly stable matrices. These techniques have their own set of challenges associated with handling large volumes of acids, contamination, lengthy digestions cycles, and exposure of the operator to acid fumes.

Although multiple samples can be digested in closed-vessel microwaves simultaneously, samples of similar matrices need to be batched to ensure complete control over the digestion process. This limits the productivity of a lab testing wide varieties of sample matrices. SRC tech-

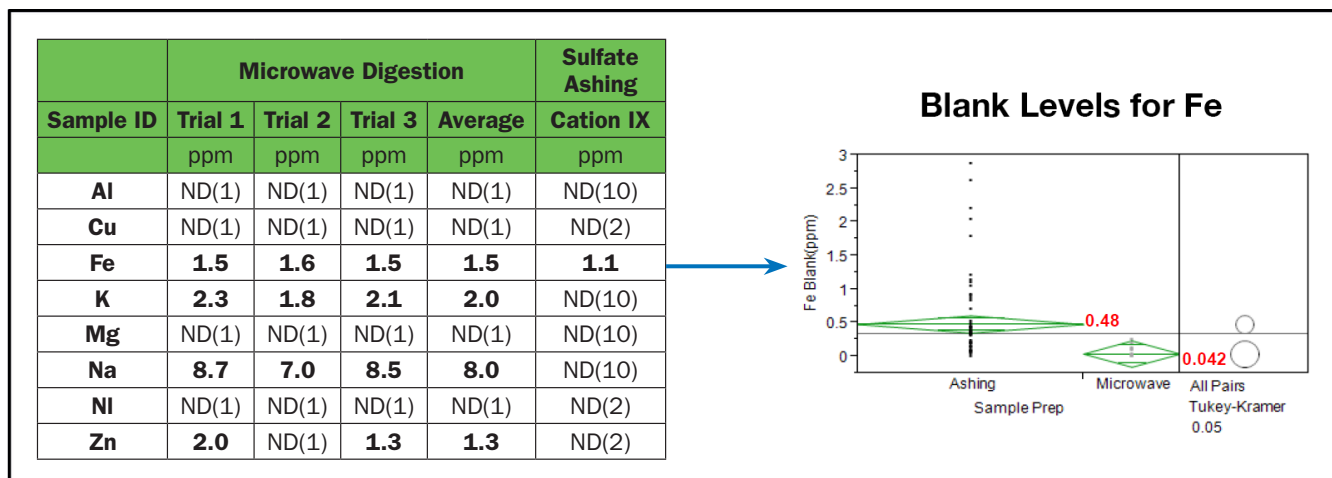


Table 3: Blank levels are 12x lower using SRC technology compared to the sulfated ash method (9).

nology, therefore, offers a multitude of advantages, as previously described. The benefits of SRC technology for the digestion of plastic materials can be observed in **Figure 9**, which shows a comparison of microwave digestion of high-density polyethylene (HDPE) at two different temperatures and pressures. The sample size was 0.5 g dissolved in 10 mL of conc HNO₃. It can clearly be seen that the sample on the left, which achieved a temperature of 180 °C and pressure of

20 bar, still has small particles of undissolved HDPE floating in it. Meanwhile, the sample on the right achieved a temperature of 220 °C and 58 bar pressure and has been completely dissolved.

A further example of the benefits of SRC technology for polymer materials is demonstrated by comparing SRC technology with the sulfated ash method for dissolving organic-type samples. The sulfated ash test utilizes a procedure to measure the amount of residual substance not



SPONSOR'S CONTENT



Performance Characteristics of the Milestone UltraWAVE



volatilized from a sample when it is ignited in the presence of sulfuric acid. The test is usually used for determining the content of inorganic impurities in an organic substance. Unfortunately, it takes an extremely long time (up to five hours) and is prone to high levels of contamination. With this method, about 1 g of the substance is accurately weighed into a suitable platinum crucible and moistened with concentrated sulfuric acid. It is then heated gently to remove the excess acid and ignited at about 800 °C until all the carbon particles have disappeared. The residue is then moistened again with sulfuric acid and reignited. This process is repeated multiple times until a constant weight of residue is achieved. The final step is to redissolve the residue in a suitable acid, dilute with deionized water and analyze by ICP-OES or ICP-MS techniques. The entire process can easily take up to five hours to complete (8).

Table 3 shows comparative data generated by researchers at Dow Chemicals between an SRC digestion and the sulfated ash method for analysis of a polymeric cation exchange membrane by ICP-OES. It can be seen that the sulfated ash method cannot detect the majority of the elements as indicated by “Not Detected” (ND) because of high blanks resulting from severe contamination. Using SRC technology, the numbers in parentheses show that the LOD was on average 2–10x lower than the sulfated ash method, as a result of the much cleaner microwave digestion process. And if we look specifically at Fe, which was the only element

detected by the sulfated ash method, the blank levels were approximately 12x lower using SRC technology (0.042 ppm compared to 0.48 ppm) (9).

Summary

SRC microwave technology has found a place in a wide variety of market segments, including contract, production and research laboratories in the pharmaceutical, food, agriculture, fossil fuel, petrochemical, polymer, metallurgical, geological, environmental, and consumer products industries, mainly because it overcomes many of the limitations of conventional microwave sample preparation system (10–16).

With SRC technology, there is no requirement to batch samples with a similar matrix; so as a result, all sample types can be digested at the same time. Additionally, the high temperature and pressure capabilities of the technology allow even the most difficult organic matrices to be digested in the minimum amount of time. And with the nitrogen-pressurized capping system, samples of widely different analyte concentration can be positioned next to each other in the chamber without concerns of cross-contamination. It’s also worth pointing out that there is no minimum volume of acid that must be used with the SRC, which is extremely useful particularly when looking to lower detection capability or to analyzing very small sample sizes.

By offering enhanced performance, with high sample throughput, no requirement for vessel assembly and the ability to rap-



idly cool down, an improved workflow can be achieved without having to batch the samples. And by using disposable glass vials and fewer vial components, it will reduce labor costs and lower the costs of consumables compared to the vessels used in traditional microwave approaches. Therefore, the real-world benefits of SRC microwave digestion in preparing samples for trace element analysis are truly “*Any Sample at Any Time*” (17).

Further Reading

1. UltraWAVE: The game changer in microwave sample preparation; <https://milestonesci.com/ultrawave-microwave-acid-digestion-system>
2. UltraWAVE Industrial Applications; <https://milestonesci.com/ultrawave-microwave-acid-digestion-system>
3. Elemental Impurities in Pharmaceuticals: Updates: USP Website; <http://www.usp.org/chemical-medicines/elemental-impurities-updates>
4. International Conference on Harmonization of Technical Requirements for Registration of Pharmaceuticals for Human Use; <http://www.ich.org/products/guidelines/quality/article/quality-guidelines.html>.
5. Study and determination of elemental impurities by ICP-MS in active pharmaceutical ingredients using single reaction chamber digestion in compliance with USP requirements; A.L.H.Muller, J.S.S.Oliveira, P.A.Mello, E.Muller, E.M.M.Flores; *Talanta*, 136, 161–169, (2015).
6. A Table of Polyatomic Interferences in ICP-MS, T.W. May and R.H. Wiedmeyer, *Atomic Spectroscopy*, 19 (5), 150-155, (1998).
7. Microwave-assisted digestion of organic samples: how simple can it become?, J.A. Nobrega, C. Pirolla, L.L. Fialho, G. Rota, C.E.K.M.A. de Campos Jordao and F. Pollo, *Talanta*, 98, 30, 272-276, (2012).
8. Sulfated Ash Test Method: Limitations of Reliability and Reproducibility; SAE International Standards Website, <https://www.sae.org/publications/technical-papers/content/952548/>
9. Single Reaction Chamber microwave digestion for better trace metals analysis, H. Zhang, J. Bonadies, M. Zoellner, J. Orłowski; The Dow Chemical Company, Analytical Technology Center, Midland, MI, Poster Presentation; Need a link for this...couldn't find it on the Milestone website.
10. The Application of Single-Reaction-Chamber Microwave Digestion to the Preparation of Pharmaceutical Samples in Accordance with USP <232> and <233>, S. Hussain, T. Michel, *Spectroscopy Magazine Special Issue*, 27, 10, (2012), <http://www.spectroscopyonline.com/application-single-reaction-chamber-microwave-digestion-preparation-pharmaceutical-samples-accordanc?id=&sk=&date=&%0A%09%09%09&pageID=3>
11. New Approaches in Sample Preparation and Precise Multielement Analysis of Crude Oils and Refined Petroleum Products Using Single-Reaction-Chamber Microwave Digestion and Triple-Quadrupole ICP-MS; J. Casey, Y. Gao, R. Thomas, W. Yang, *Spectroscopy*, 31, 10, 11–22, (2017), <http://www.spectroscopyonline.com/new-approaches-sample-preparation-and-precise-multielement-analysis-crude-oils-and-refined-petroleum>
12. Simultaneous Single Reaction Chamber Microwave Digestion of Mixed-Consumer Products; N. Pedjie *Spectroscopy Application Notebook*, Sept 01, (2014), <http://www.spectroscopyonline.com/simultaneous-single-reaction-chamber-microwave-digestion-mixed-consumer-products>
13. Optimizing the Sample Preparation of Metals: Single-Reaction-Chamber Microwave Digestions for Contract Analytical Laboratories, *Spectroscopy Magazine Special Issue*, 28, 11, (2013), <http://www.spectroscopyonline.com/optimizing-sample-preparation-metals-single-reaction-chamber-microwave-digestions-contract-analytica?id=&sk=&date=&pageID=3>



SRC Microwave Digestion Overview	Sample Prep: Specialty Polymers	Sample Prep: Pharma	Sample Prep: Food	Sample Prep: Crude Oil	Sample Prep: Cannabis
----------------------------------	---------------------------------	---------------------	-------------------	------------------------	-----------------------

14. Single Reaction Chamber Microwave Digestion for Specialty Chemicals; S. Phatak, Spectroscopy Application Notebook, Feb 01, (2013), <http://www.spectroscopyonline.com/single-reaction-chamber-microwave-digestion-specialty-chemicals>
15. Simplifying Mixed-Food Microwave Sample Preparation for ICP-MS Analysis, Spectroscopy Magazine Website, May 28, 2018, http://www.spectroscopyonline.com/search/apachesolr_search/single%20reaction%20chamber?page=1&keys=single%20reaction%20chamber
16. Determination of elemental impurities in poly vinyl chloride by ICP-OES; L. S.F. Pereira, M. F.Pedrotti, T. M.Miceli, J. S.F.Pereira, E. M.M.Flores, Talanta, 152, 371–377, (2016)
17. Any Sample, Any Time: the Benefits of Single Reaction Chamber Microwave Digestion for Trace Element Analysis, On demand webinar, Spectroscopy Magazine, <http://www.spectroscopyonline.com/any-sample-any-time-benefits-single-reaction-chamber-microwave-digestion-trace-element-analysis>

This article is based on a Spectroscopy web-cast that can be [viewed on demand here](#).

No Limits: How SRC Technology is Changing the Game for Metals Prep

A revolutionary advance in benchtop microwave digestion, the UltraWAVE features patented Single Reaction Chamber (SRC) technology.

Benefits

Convenient

- No assembly or disassembly of vessels is required
- Uses simple and inexpensive disposable vials
- Eliminates method development, using the same method for almost every sample type

Efficient

- Offers high sample throughput, 2x traditional microwave systems
- Disposable vessels eliminate the need for cleaning between sample runs
- Digests any combination of samples simultaneously, no batching required

Productive

- Stainless steel chamber construction can heat to extremely high temperatures and withstand pressures greater than 2.5x that of any other closed-vessel microwave digestion system
- Digests even the most difficult sample types
- Maximizes sample size to address homogeneity and/or detection needs

Cost-Effective

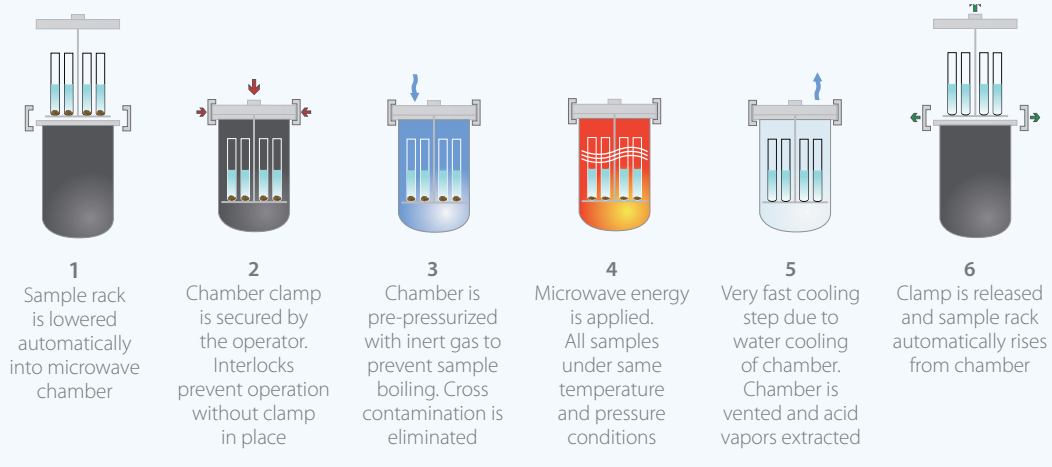
- Lowest cost per sample
- Lower labor costs
- Significantly reduced consumables costs

What It Is

The superior alternative to traditional closed and open vessel digestion, the UltraWAVE offers industrial and research labs greater digestion capability, at least double the sample throughput, improved workflow and significantly lower operating costs—all with a single, easy-to-use instrument.



How It Works



About Milestone

With over 50 patents and more than 18,000 instruments installed in laboratories around the world, Milestone has been widely recognized as the global leader in metals prep technology for the past 26 years. Committed to providing safe, reliable and flexible platforms to enhance your lab's productivity, customers worldwide look to Milestone for their metals digestion, organic extractions, mercury analysis and clean chemistry processing needs.

Learn more or request an onsite demonstration:
info@milestonesci.com or 1-866-995-5100





SPONSORED CONTENT

Microwave Digestion for Specialty Polymers

Utilizing Single Reaction Chamber (SRC) Technology for Trace Metals Analysis of Polymer Samples

Technical Application Note

Images under license from Shutterstock.com

Summary

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 metals analysis of polymers, 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 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 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 polymers.

SRC technology enables a chemist to digest up to 15 different polymer samples simultaneously at temperatures up to 300°C and pressures up to 199 bar, simplifying the workflow, while maintaining superior quality digestions.

Polymers 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. Today's chemist usually complements microwave technology with traditional tools like hot plates and Parr bombs to digest these highly stable matrices which in turn have their own set of limitations—large acid requirements, contamination, acid handling challenges, lengthy digestions cycles and exposure of chemists to acid fumes. Finally, although multiple samples can be digested in closed-vessel microwaves simultaneously, samples of similar matrices need to be batched to ensure complete control over the system. This limits the productivity of a lab testing wide varieties of sample matrices.

Milestone's UltraWAVE SRC benchtop digestion system can digest up to 15

different samples simultaneously at temperatures and pressures as high as 300°C and 199 bar. This high temperature and pressure capability enables a complete digestion of almost any specialty chemical that needs to be analyzed for trace metals. Samples can be directly weighed into disposable glass, autosampler type vials with the appropriate acid mixtures—no minimum acid quantity is required. Quartz and TFM vials can also be used depending on the user's application. This minimizes acid handling and transferring steps, reduces errors due to contamination and the chemist's exposure to acids. It also completely eliminates the need to clean, assemble and disassemble vessels used in conventional microwave systems.

Method Optimization

The reaction chamber was pre-pressurized to 40 bar to prevent the acids from boiling which subsequently prevented cross-contamination and loss of volatiles. A 15 position rack was used with disposable glass vials during digestion, which were covered by loose fitting caps. This ensures pressure equilibrium on either sides of



SPONSOR'S CONTENT



Single Reaction Chamber Microwave Digestion of Highly Organic Matrices

David Gunn, Milestone, Inc.



the vial while preventing the condensation from the top of the chamber from dripping into the sample. Two polymer excipient samples, Polyplasdnone XL-10 and Plasdnone K90, were digested in one single run using 1 g in 5 mL conc HNO₃. The heating profile used in the microwave is listed below:

Table 1. Microwave program used for digestion of Polyplasdnone and Plasdnone

Time (min)	Power (watts)	Temp (°C)	Pressure (bar)
20	1500	260°C	150
15	1500	260°C	150

The actual microwave digestion profile shows a resultant pressure over ~90 bar (~1350 psi) was generated during the digestion cycle. As previously noted, many microwave vessel designs will not be usable for these digestion conditions. The digested samples were diluted to 30 mL with DI water and analyzed for the certified elements. The certified values for these elements and the recovery achieved after the digestion is mentioned in **Table 2**.

Certified Reference Materials

Two certified polymer reference materials (ERM681- low density polyethylene and CRM8112A - ABS Resin) were also digested in the UltraWAVE in the 15 position rack using 0.2 g in 4 mL of conc HNO₃.

Table 2. Recovery of various trace metal elements from Polyplasdnone and Plasdnone K 90 (% Recovery)

Catalyst Element	Polyplasdnone XL-10 (% Recovery)	Weight
Chromium	82.8	78.4
Copper	93.0	91.2
Manganese	91.4	76.2
Molybdenum	76.2	76.2
Nickel	89.0	78.6
Palladium	88.4	92.0
Platinum	92.0	74.0
Vanadium	91.6	77.8
Rhodium	89.8	84.6
Ruthenium	78.0	78.8
Iridium	92.4	76.8

Table 3. Microwave program used for digestion of CRMs -ERM681 and CRM8112A.

Time (mins)	Power (watts)	Temp (°C)	Pressure limit (bar)
15	1500	225°C	150
15	1500	225°C	150



SPONSOR'S CONTENT

Single Reaction Chamber Microwave Digestion for Better Trace-metals Analysis

Haoyi Zhang, Joseph Bonadies, Michael Zoellner, James Orlowski

The Dow Chemical Company, Analytical Technology Center, Midland, Michigan, USA

Introduction

Demand for trace metals analysis is growing strongly and will continue to grow due to new regulations, needs of electronic materials, energy materials (e.g. solar, battery) and other new chemical materials. The trend is to be able to get to lower levels of detection. The current sample preparation techniques have challenges due to the wide variety of sample types and levels of metals found, that makes it necessary to investigate new and better sample preparation techniques with contamination control. The purpose of this study was to identify a clean sample preparation technology with improved productivity, reliability and capability for trace-level metal analysis in chemical industry.

Single Reaction Chamber Microwave Technology

- 1L stainless steel reaction vessel
- Higher pressure (160 bar)
- Higher temperature (300 °C)
- Samples digested simultaneously
- Direct T & P control

Analytical Blanks

Digestion blanks from UltraWAVE digestion

Pd Blanks by Sulfate Ashing for Ion Exchange Resins

Sulfate Ashing V.S. UltraWAVE (Fe Blank, ppm)

Difficult analytes (Pd, Cu, Sn etc) in complex matrices

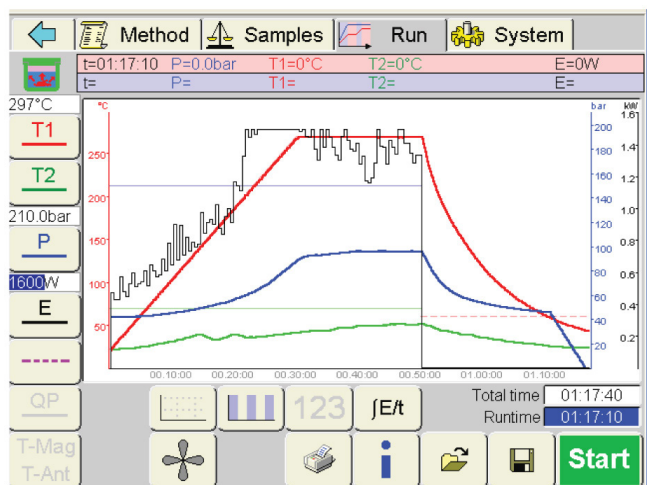
Pd-Phosphine Catalysts Analysis

Stochastic monomer samples have challenges for normal sample digestion. UltraWAVE provides reliable results with quicker turn-around.

High-throughput analysis of Pd & Pt in 1-methoxy-octadecane samples, monitoring catalyst degradation.

Ultra-trace Copper in Polyethylene Pellets

Tin analysis in Polyethylene Pellets



The UltraWAVE's touch screen controller. The red line is the internal digestion temperature, while the blue line indicates the real-time pressure that is being monitored of the entire stainless steel chamber. The black line indicates the microwave power being emitted during the entire digestion cycle.

Table 4. CRM Recovery Results Post Digestion.

Element	CRM 8112A Cert (ppm)	CRM 8112 found (ppm)	% recovery
Pb(220)	94.98	86.6	91.2
Cd	9.383	9.166	97.7
Hg	94.1	84.77	90.1

Element	ERM681 Cert (ppm)	ERM681 found (ppm)	% recovery
Pb(22)	98.0	90.31	92.2
Cd	13.7.0	124.6	90.9
Hg	23.7	22.93	96.8
Pb(283)	98.0	95.09	97.0

The microwave program used for digestion of these samples is listed in **Table 3**.

Conclusion

The data in **Table 4** shows excellent detection limits and recoveries. No loss of volatile elements (e.g., Hg) and no cross contamination was observed. Due to higher sample capacity, use of disposable vials and faster cool down time, the UltraWAVE sample throughput is 2–3x times higher as compared to traditional closed-vessel microwave digestions. No other system is capable of handling the reported high pressures that are generated during the digestion of these challenging sample polymers. Its lower consumables costs, simple operation, and superior digestion quality makes Milestone's UltraWAVE a perfect choice for specialty polymers' sample prep for trace metals analysis.

Acknowledgement

We would like to thank Wayne Xu of International Specialty Products for sharing data of Plasdane/Polyplasdane.

SPONSOR'S CONTENT



THINK BLANK

Clean Chemistry Tools for Atomic Spectroscopy



Utilizing Single Reaction Chamber (SRC) Technology for Trace Metals Analysis in Accordance with USP <232>/<233>

Technical Application Note

SRC microwave digestion offers significant benefits over traditional microwave digestion for pharmaceutical samples: higher sample throughput, reduced labor and consumables costs, simplified workflow and superior digestion quality.

Summary

New USP chapters <232> and <233> for the measurement of inorganic contaminants in pharmaceutical samples have been implemented. While samples can be dissolved in aqueous or organic solvents, the large majority will require digestion, and closed vessel microwave digestion is stipulated by USP. SRC microwave digestion is a new type of closed vessel digestion that was developed by Milestone and offers many advantages over closed vessel digestion—particularly for pharmaceutical sample types.

Instrumentation

The Milestone UltraWAVE can digest up to 15 samples simultaneously, at up to 300° C and 199 bar pressure. Its high temperature and pressure capability en-

St. John's Wort

Parts Per Million (ug/g)

Step	Arsenic	Cadium	Lead	Mercury
Sample Result	0.184	0.109	0.24	ND
Duplicate Result	0.195	0.115	0.19	ND
Detection Limit	0.008	0.003	0.03	0.1

Fish Oil Gelcaps

Parts Per Million (ug/g)

Step	Arsenic	Cadium	Lead	Mercury
Sample Result	0.007	ND	0.018	0.035
Duplicate Result	0.006	ND	0.022	0.024
Detection Limit	0.002	0.0007	0.007	0.008

Quality Control Summary (Fish Oil Gelcaps)

Parts Per Million (ug/g)

Step	Arsenic	Cadium	Lead	Mercury
Spike Conc	15.3	5.09	10.2	15.3
Spike Result	15.6	5.15	9.96	14.2

The data above shows excellent DLs and recovery – even for the volatile element mercury – no loss of volatiles or cross-contamination with the UltraWAVE.

ables the complete digestion of virtually every sample type. Samples are weighed into vials are placed in the chamber: and any combination of sample types can be



digested together—greatly simplifying the sample prep workflow. Raw materials, excipients, API, and final product can all be digested together in the same run. And the UltraWAVE uses disposable glass vials, eliminating vessel assembly/disassembly and vessel cleaning which significantly reduces labor and consumables costs. Most pharmaceutical sample types have high organic content, including oils and fats, which are difficult to digest and generate CO₂, which increases pressure in the reaction vessel. The high pressure capability of the UltraWAVE enables it to digest entire fish oil gelcaps—not possible with traditional closed-vessel microwave.

The UltraWAVE can digest samples in as little as 3 mL acid which minimizes reagent blank levels—important since ICP-MS will be used predominantly for USP <232>/<233> when implemented. The SRC is pre-pressurized with N₂ prior to the start of the run—this prevents sample boiling, eliminating cross-contamination and loss of volatiles.

Due to its higher sample capacity, use of disposable vials, and faster cool down time, UltraWAVE sample throughput is 2x–3x higher than closed vessel digestion. Its lower consumables costs, simple operation, and superior digestion quality also make the Milestone UltraWAVE the perfect choice for pharmaceutical sample prep.

SPONSOR'S CONTENT



GETTING READY FOR USP 232, 233 AND 2232

Microwave-Assisted Sample Preparation
and Determination of Elemental Impurities
in Pharmaceutical Products



SPONSORED CONTENT

Mixed-Batch Food Sample Microwave Digestion

Utilizing Single Reaction Chamber (SRC) Technology for Trace Metals Analysis for food samples.

Technical Application Note

Summary

With stricter food 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 food 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 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 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 food.

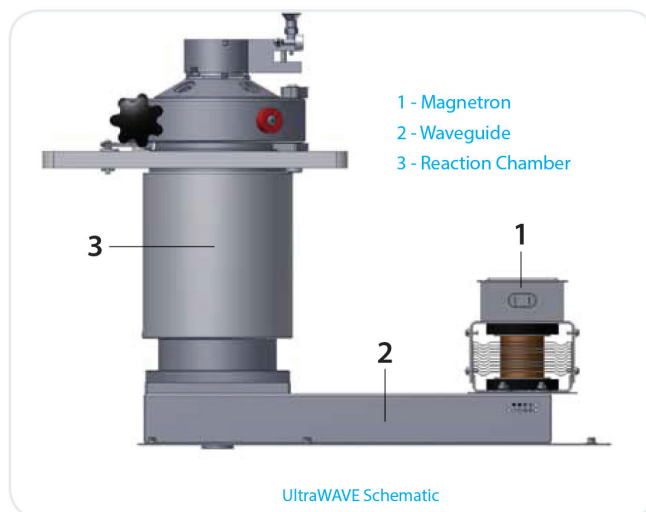
Demand for trace metals analysis in the food industry is growing due to stricter food regulations such as the recent Food Safety Modernization Act.

ICP has been the standard for metals analysis for food, but as demand for lower levels of detection grows, the industry is experiencing a significant transition to ICP-MS thus placing increased emphasis on the method of sample preparation. Traditional sample preparation techniques for food include hot block digestion, closed-vessel microwave digestion, and ashing—each posing different challenges. Hot block digestions suffer from long digestions, airborne contamination, poor digestion quality, and poor recovery of volatile compounds. Closed-vessel microwave digestion has proven an effective technique with fast, complete digestions, clean environment, and recovery of volatile compounds. One challenge with closed-vessel microwave digestion for sample prep is the inability to run digestion on several matrix types simultaneously.



Milestone's SRC microwave digestion, a completely new approach, incorporates all of the benefits of closed vessel microwave digestion while making sample preparation fast, easy, effective, and the highest quality. SRC operates at very high temperature and pressure (300°C and 199 bar respectively), thus complete digestion of even the largest sample size (up to 3-5 g) and most difficult samples can be achieved. The sample can be weighed directly into a disposable glass vial, eliminating the need for acid cleaning and vessel assembly. With SRC there is no need to batch sample types because mixed sample and mixed acid chemistries can be successfully processed in the same run. This technical note

Milestone's SRC microwave digestion incorporates all of the benefits of closed vessel microwave digestion while making sample preparation fast, easy, effective, and the highest quality.



describes how a variety of sample food matrices were digested simultaneously with complete recovery of the trace metals without sample-to-sample cross-contamination, including volatile analytes such as Hg.

SPONSOR'S CONTENT: CASE STUDY



Unilever counts on Milestone's UltraWAVE to reach very low detection limits



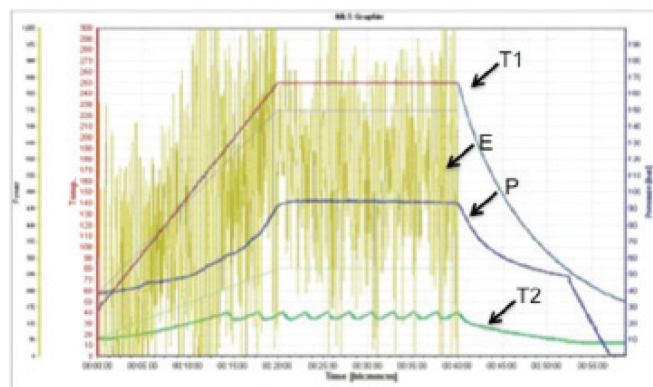


Figure 1. UltraWAVE microwave program.

Instrumentation

The SRC features a large 1-liter pressurized stainless steel reaction chamber, which also serves as the microwave cavity. This enables the intensity and distribution of the delivered microwave energy to be optimized to the shape of the reaction vessel, ensuring even heating without the need to rotate samples during the digestion program.

Samples are placed inside the SRC together and digested simultaneously. Because the samples are placed inside a pressurized vessel, individual pressure vessels are not needed. Samples are weighed into auto sampler-type vials with

the appropriate digestion acid and loaded into a rack. Loose fitting vial caps prevent condensation from the roof of the chamber dripping into the samples (the caps must be loose fitting to ensure pressure equalization within the chamber).

The rack is loaded into the chamber, which is then sealed and pre-pressurized with nitrogen to 40 bar prior to microwave heating. Pre-pressurization prevents splashing or boiling of the sample solutions, which prevents cross contamination or loss of volatiles. Because the pressure in the chamber increases with sample temperature, boiling never occurs. SRC can operate at very high temperature and pressure—up to 300°C and 199 bar, which enables the complete digestion of virtually every sample-type. Samples with high organic content generate pressure in the microwave vessel due to the generation of NO_x and CO₂: in traditional microwave digestion, high-pressure vessels (typically 100 bar) must be used. The higher pressure capability of a SRC allows higher sample weights to be digested—up to 1 gm organic in a 15 position rack.

SPONSOR'S CONTENT



Single Reaction Chamber Microwave Digestion of Food Samples for Trace Metals Analysis

Tim Michel, Milestone Inc.

Single reaction chamber (SRC) microwave digestion offers significant benefits over traditional methods of microwave digestion for foods analysis: higher sample throughput, reduced labor costs, use of disposable digestion vials, and higher performance.



With SRC, because all the samples are digested together under the same conditions, different sample types can be run simultaneously—there is no need to “batch” digestion runs into identical sample types as with traditional microwave digestion. For example, polymers, oils, food and pharmaceutical products can all be digested together in the same run. The SRC also requires less digestion acid (typically 2–4 mL), which lowers the reagent blank. On completion of the program, the chamber is vented and the rack removed. Samples are diluted to volume in the vials, ready for aliquoting and measurement. The SRC microwave system used in this work was a benchtop UltraWAVE instrument (Milestone Inc. Shelton, CT).

Digestion Method Optimization

Figure 1 illustrates the UltraWAVE microwave program for the digestion of eight different food sample SRMs, 500 mg each: ramp to 240°C and hold for 15 min. The line marked T1 shows the actual digestion temperature achieved (T1 line). The applied microwave power (E) is automatically controlled by the system so the actual digestion temperature precisely follows the programmed temperature profile. The outer temperature of the reaction chamber is also monitored (T2). At the end of the run, pressure was released automatically resulting in a total run time of 50 min. Note that pressure reached more than 100 bar, which is not possible in conventional closed-vessel digestion. This is due to the high organic content

Table 1. Food Samples

Vessel	Standard Reference Material	Weight (g)
1	Blank	-
2	Blank + Spike	-
3	Apple Leaves NIST 1515	0.5328
4	Apple Leaves NIST 1515 (dup)	0.5045
5	Peach Leaves NIST 1547	0.5384
6	Peach Leaves NIST 1547 + Spike	0.5198
7	Tomato Leaves NIST 1573a	0.5223
8	Tomato Leaves NIST 1573a (dup)	0.5025
9	Spinach Leaves NIST 1570a	0.5020
10	Pine Needles NIST 1575a	0.5375

of the sample generating CO₂ during the digestion giving a sample digestate with very low TOC.

This is a benefit for ICP-MS analysis: the presence of carbon in the sample enhances on the sensitivity of poorly ionized elements. By removing the organic carbon, the analysis of poorly ionized elements becomes more predictable and reliable.

The samples were digested in disposable glass vials in a 15-position rack in UltraWAVE; 2 mls H₂O and 2 ml conc HNO₃ was added to each vial prior to the digestion. 0.25 mls of 1.0 ppm (Se, As, Cd, Pb)/0.1 ppm Hg spike standard was also added to a blank (vial#2) and peach leaves (vial#6) (see **Table 1**).





Table 2. ICP-MS Trace Element Recovery Data

	Blank (ppb)	Blank + spike	NIST 1515	NIST 1515 dup	NIST 1547	NIST 1547 + spike	NIST 1573a	NIST 1573a dup	NIST 1570a	NIST 1575a
Se (H ₂ mode)	0.005	103.24	108.34	107.13	95.29	98.58	108.08	102.58	91.838	97.722
As (O ₂ mode)	0.001	105.94	98.520	88.418	108.78	103.66	98.479	112.27	93.268	100.86
Se (O ₂ mode)	0.003	102.3	99.159	87.877	95.481	98.78	102.08	119.30	90.520	102.17
Cd (He mode)	0.000	103.06	110.04	112.40	101.81	100.26	104.10	101.29	101.06	106.491
Hg (He mode)	<0.005	105.4	105.22	104.72	104.76	107.2	100.65	94.598	92.502	95.735
Pb (He mode)	0.089	106.78	96.42	97.074	98.543	98.62	N/A	N/A	N/A	89.839

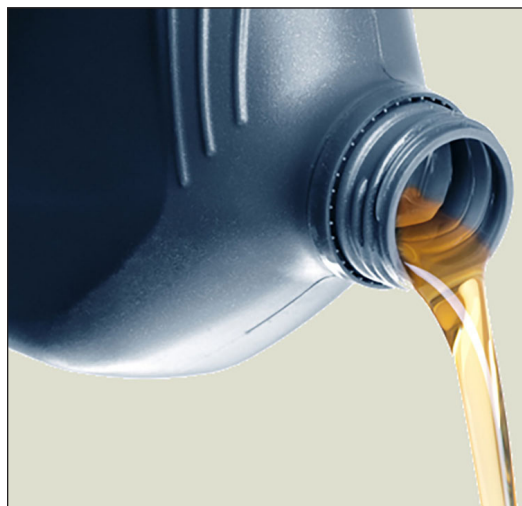
Sample Results

All the standard reference materials (SRMs) were digested as described above. The sample digested completely, forming a clear digestate, which was made up to 50 ml with DI water. The samples were analyzed for toxic elements like Lead (Pb), Cadmium (Cd), Mercury (Hg), Arsenic (As) and Selenium (Se) on an Agilent 8800 ICP-MS (Agilent Technologies, Santa Clara, CA) (see **Table 2**).

Duplicate analysis is generally good for all SRMs and excellent recovery was obtained for the spiked samples and for the spiked reagent blanks. Excellent recoveries for Hg demonstrate the effectiveness of pre-pressurization of the SRC prior to the digestion sequence. Volatile elements such as Hg are not lost, and no cross-contamination of samples occur due to sample splashing or boiling. This is illustrated with low blank concentrations obtained from the same digestion run.

Conclusion

Milestone’s SRC microwave digestion (UltraWAVE) offers multiple benefits for sample preparation for trace metals analysis over conventional benchtop microwave digestion systems. Due to its higher sample capacity, use of disposable vials and faster cool down time, sample processing throughput is 2x – 3x higher than conventional closed vessel digestion. The better digestion quality achieved at higher temperatures (and pressure) and low TOC content of the digestates makes analysis by ICP-MS more accurate. The data showed in this technical note demonstrates that the digestion of samples in a single chamber, in loosely capped vials, does not negatively impact analytical data quality, while the ability to digest different sample types together and larger sample weights with minimum acid volume (1-4 ml per sample) makes it very suitable technique to perform sample prep for trace metals analysis.



New Approaches in Sample Preparation and Precise Multielement Analysis of Crude Oils and Refined Petroleum Products Using Single-Reaction-Chamber (SRC) Microwave Digestion and Triple-Quadrupole ICP-MS

John F. Casey, Yongjun Gao, Weihang Yang, and Robert Thomas

Comprehensive multielement determinations in crude oil and refined petroleum products have been a difficult task, historically resulting in myriad developed sample preparation and instrumental analytical methods (1). These methods are somewhat limited and many do not include all elements that are important to the petroleum industry. Most methods previously developed tend to have limited numbers of targeted elements, which are often determined based on specific method detection limits (MDL), method quantification limits (MQL), or a specific single element need. The quality and comprehensive nature of a suite of elements measured can therefore be dependent on a number of factors:

- suitability of sample preparation techniques and resultant element recovery for specific analytes;
- sample matrix, the weight of the sample prepared, and the necessary dilution factors;
- sensitivity of the analytical instruments to be used;

- nature and availability of certain non-standard instrument sample introduction systems;
- the ability to mitigate complex spectral interferences, especially for routine analysis of many low-abundance elements;
- quality of standards available;
- purity of the reagent and blanks, impacting the accuracy and precision; and
- repeatability of the method for particular analytes.

As a result of these limitations, the elemental suite is typically limited and also different from one method to the next.

Source of Elemental Constituents in Crude Oil and Petroleum Products

Along with their dominant organic major elemental constituents (for example, C, H, O, and N), crude oil and refined petroleum products are highly variable in minor to ultratrace elemental abundances. Trace and minor elements are generally complexed in the heavier organic molecules or inorganic salts and typically constitute less than 1% by weight of the sample.



In general, organic matrices pose major obstacles for a routine method of comprehensive multielement analysis when trying to adopt a single sample preparation technique. A single analytical instrument would require an exceptionally wide dynamic range necessary to cover broad inorganic elemental concentrations that can range from 5% to 6% (50–60 mg/g), such as sulfur, down to minor elements at ~1000–2000 $\mu\text{g/g}$, such as vanadium, and to ultratrace element concentrations of $<1 \mu\text{g/g}$, such as the rare earth elements. For this reason, a single crude oil multielement analysis method is elusive without multiple, often complex and time consuming sample preparation or elemental group separation steps. In fact, most elements detectable in crude oils are low in abundance (nanograms per gram or less) and many are plagued by interferences when using traditional single-quadrupole-based inductively coupled plasma–mass spectrometry (ICP-MS) instrumentation. Thus, comprehensive analyses of trace elements in organic matrices by either inductively coupled plasma–optical emission spectrometry (ICP-OES) or ICP-MS

have proven to be a challenging problem. Whereas ICP-MS technology has the added sensitivity and multielement capabilities desired for low abundances, there are many hurdles to overcome using a single sample preparation technique.

In this study, we describe a sample preparation method that uses a microwave digestion system with a SRC (UltraWAVE, Milestone Inc.). This method is capable of producing an organic-free sample solution ($<0.1\%$ total carbon) used for analysis of up to 55–57 elements with the appropriate ICP technique (2,3). In this approach, we use in tandem an ICP-OES system (Model 725, Agilent Technologies) for quantitation and screening of higher abundance elements and an ICP-MS system with a triple-quadrupole mass spectrometer (Model 8800, Agilent Technologies) specifically to allow interference-free analysis of low-abundance elements. The single digestion procedure with these two instrumental techniques accommodates the wide range of elemental concentrations necessary for characterizing crude and refined oils in a more comprehensive and routine manner.



SPONSOR'S CONTENT

The UltraWAVE Opens the Doors to New Research Frontiers in Analytical Geochemistry.



Oil Sample Preparation Methods

ICP-MS is now the standard technique for low-abundance elemental analysis because of its high sensitivity for measurements at parts per billion (nanograms per gram) or lower levels. Sample preparation generally contributes the most to the inaccuracy, poor precision, or lack of reproducibility through either incomplete dissolution, contamination, or analyte loss during the dissolution or because of solubility issues. Safe, clean, and full-recovery sample preparation of combustible crude oils for multielement analysis is difficult because of the high organic matrix, element volatility, solution solubility, possible contaminants with various methods, and, to a certain extent, sample sizes that may have to be constrained by certain closed system preparation vessels because of safety or sample loss issues. Four approaches to sample preparation for elemental analysis have generally been used for crude oils and their refined petroleum products (1,4–6):

- Strong acid “wet” digestions by open vessel, closed high pressure–temperature bomb or closed high pres-

sure–temperature microwave-assisted mineralization

- Mineralization by high-pressure combustion in a chamber or ashing followed by strong acid digestions
- Direct sample introduction by dilution with organic solvents
- Direct sample introduction of an emulsion or microemulsion

The latter two have tended to be judged as safer, more expedient, and simpler for the analyst. A drawback for solvent dilution is that it tends to result in high dilution factors (100–1000-fold for heavier oils) and can result in heavy organic loads for the instruments used. They have proven successful in some limited analyte applications, but also have been considered a safer decomposition than high pressure and temperature used in mineralization procedures with bombs or closed-vessel rotor-based microwave systems. They remain somewhat limited in analysis of the large range of elements that can be detected by some methods in crude oils or fuel oils. In all of these methods, clean facilities, ultrapure or doubly distilled reagents including ultrapure water, clean,

SPONSOR'S CONTENT

MILESTONE



Application Note

SRC Microwave Digestion



Petrochemical

Heavy Crude Oil Samples



and low contaminant sample vessels, and well-developed cleaning protocols are critical for high precision and accuracy as well as better detection capability.

The “Dilute-and-Shoot” Approach

As stated above, commonly used methods of direct sample introduction known as the dilute-and-shoot methods involve dilution and stabilization of the hydrocarbon sample with an organic solvent, such as toluene, xylene, or kerosene, that is aspirated directly into an argon plasma for routine quantification by ICP-OES, with more recent attempts to adapt the technique for ICP-MS (1,6). In these solvent methods, the instruments have to be standardized with organic solutions with trace-element compounds that are also soluble in organic solvents. There are, however, a few natural crude or fuel oil standards (for example, National Institute of Standards and Technology [NIST] standard reference materials [SRMs]) and generally they are certified for a small number of elements (such as V, Co, Ni, Hg, or S) with additional noncertified reference or information values reported for some elements within some standards. In addition, there are multiple analytical methods used because of the difficulties in certification or the referencing process. For example, for the NIST 1634c residual fuel oil examined here, seven different analytical methods were used for three certified elements, two noncertified referenced elements, and three noncertified information values (seven methods, eight elements to achieve reported values).

Such a suite of instruments and analytical techniques would be impractical for routine multielement analysis and extremely time consuming. Synthetic organometallic standards can be purchased with more elements certified, but often they are expensive and tend to have limited stability and shelf life. They are useful in high-throughput laboratories where long shelf stability is typically not required, but may cause analysis repeatability issues in some laboratories. Another drawback of these direct ICP-OES introduction methods is the lower sensitivity of the ICP-OES compared to the more sensitive ICP-MS. This and the high method dilution factors will limit the number of elements that can be successfully quantified. This limitation has led to method developments that analyze a greater numbers of elements with dilute-and-shoot organic solutions (1) or microemulsions (5) that have been adapted directly to ICP-MS. These direct introduction techniques are not as simple for ICP-MS because of deleterious effects on plasma stability, complex ionization effects, deposition or clogging of carbon on the sampler or skimmer cones, carbon-based interferences caused by the solvent, much longer wash out times, and crude oil solubility issues. Some of these effects can be mitigated by desolvation or ultrasonic nebulization techniques (1). Preparation by emulsification with water offers some of the same problems in terms of larger dilution factors and multiple short-term solution analyte stability issues, but it does remove the necessity of organic standards.



Combustion Methods

Our investigations of open- and closed-vessel “combustion” of standard multielement certified oils, followed by strong acid digestions as a method of preparation, showed that both contamination and some very severe elemental losses occur, demonstrating that the combustion method is probably unsuitable for the broad multielement analyses of the large element suites that we are attempting. Although, in part, the dilute-and-shoot solvent, emulsification, and combustion methods as a group have been successfully applied for select groups of targeted elements, they have not resulted routinely in extensive element suites measured using ICP methods for more complete fingerprinting of elemental abundances in crude oil or refined products. Nor have they consistently proven to be high precision or highly repeatable in intra- and inter-laboratory studies (1). They are important, however, for some targeted applications and analytical needs.

Acid Digestion Techniques

For strong acid-based digestions that attempt to destroy the organic matrix, closed-vessel digestion procedures are typically advantageous to minimize the analyte loss, but sample sizes have generally been limited to 0.1–0.25 g to avoid damage to the digestion apparatus at high pressures or sample loss and this can limit detection. Alternatively, open-vessel digestion procedures offer the ability to dissolve much larger samples under relatively mild conditions, but are subject

to sample loss and contamination. In a recent study by Yasnygina and colleagues (7), the analysis of 39 elements by ICP-MS was attempted using a technique of heating a large sample of 3.5 g of crude oil in strong acid and peroxide in quartz tubes, followed by ashing at 300 °C for 8 h in a low-pressure muffle furnace. Their analytical results based on four replicates of natural oils showed percent relative standard deviations (%RSDs) for 14 elements were better than 10%, but the remaining 25 showed poorer precisions ranging from 10% to 50%. Open vessels can be used, however, after acid digestions to eliminate residual concentrated acids and volatile matrix constituents by evaporation in ultra-clean high-efficiency particulate arrestance (HEPA) filtered hood environments. The microwave-assisted strong acid digestion method described here (2,3) combines the use of larger sample sizes and microwave closed system techniques, with an approach using a recently developed SRC microwave system that results not only in good recoveries, but more efficient throughput, larger samples sizes, and enhanced safety.

Microwave-Assisted Strong Acid Wet Digestion Techniques

In general, it is well-accepted that decompositions (mineralization) are more robust and accurate than dilute and shoot methods, but they have been considered more time consuming and to date have not produced more comprehensive data sets with a single methodology. More common rotor-based closed microwave systems



have been utilized in the past to prepare crude or fuel oil samples, including SRMs. Wondimu and Goessler (8), for example, conducted these digestions on NIST fuel oil 1634c, but their digestions were limited in sample size because testing showed vessel venting and sample loss if sample sizes were greater than ~0.25 g. However, this 0.25-g weight is well below the 1.0-g sample size recommended by NIST based on their sample homogeneity tests. The investigators were still able to successfully measure 17 out of 24 elements on NIST residual fuel oil 1634c with <5% RSD and good recovery using their digests with ICP-MS. Ducyk and colleagues (9) likewise were able to quantify nine elements in crude oil, and up to 15 in trace element-enriched asphaltene fractions of the crude oil by rotor-based microwave digestion and ultrasonic nebulization coupled with ICP-MS. Periera and colleagues (10) compared microwave-assisted digestion for up to 12 elements with a novel microwave-induced combustion method to achieve multielement analysis of up to 17 elements that were above MDL using both ICP-OES and ICP-MS for trace element-enriched heavy oils, although more elements were attempted. These methods were among several that showed the promise of microwave assisted digestions at least for smaller samples but wider suites of elements were still not possible because of the higher MDL and MQL.

At the University of Houston we have carried out exhaustive testing of various sample preparation techniques including

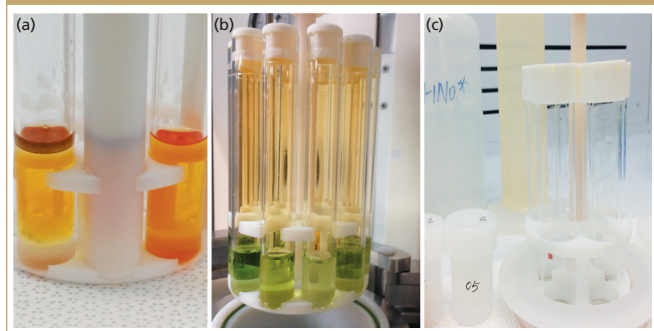
- high pressure combustion followed by acid digestion;

- high pressure–temperature acid digestions;
- microwave assisted high pressure–temperature acid digestions; and
- the use of strong acids and reagent mixtures for digestion, using various other vessel types.

These approaches have all been explored in an attempt to develop methodologies that can produce a more comprehensive elemental suite with a single method. These methods have been previously summarized in an American Chemical Society (ACS) webinar (2), conference proceedings (3), and more-detailed procedural outlines and fully compiled data sets on multiple NIST standards and crude samples will appear in two upcoming papers by Casey and colleagues (under review) and Yang and colleagues (under review) (20,21). We found that combustion methods resulted in low recovery of many of the analyte target elements. We also concluded that whereas mineralization approaches in closed-system high pressure–temperature bombs with PTFE vessels are acceptable for analysis, they are more time consuming and lacked the adequate sample size characteristics necessary for desired sample throughput, sample homogeneity, and the required MDL and MQL. The mineralization procedures in the microwave SRC high pressure–temperature system using high-purity quartz glass vessels and ultrapure strong acids and reagents alternatively offers clear advantages for both mineralization and more complete analysis of extensive suites of up to 57 elements. Exact procedures, methodologies, and more extensive data



Figure 1: Single-reaction-chamber microwave digestion of crude oil, showing the various dissolution stages.



will be presented in the future papers listed above, but we provide a general overview of the methodology in this study.

SRC Microwave Digestion

Let's take a closer look at the methodology we have developed in our laboratory with a microwave digestion system using mixtures of concentrated acids such as HNO_3 , HCl , and 30% H_2O_2 in high-purity quartz tubes. With an approximately 1.0-g crude oil or petroleum-based sample, the hydrocarbons are completely oxidized to CO_2 and H_2O and leave a clear aqueous solution with very small residual carbon content of $<0.1\%$. This approach is exemplified in **Figure 1a**, which shows weighed samples of crude oil (mostly floating) loaded into high-purity quartz glass vials with doubly distilled strong acid-ultrapure peroxide mixture in a multisample numbered rack and readied for digestion.

Figure 1b shows a completed high-pressure and temperature digestion just after the rack is raised from a previously sealed acid-resistant PTFE-lined stainless steel reaction chamber, which is prepressurized with inert gas before the digestion and then automati-

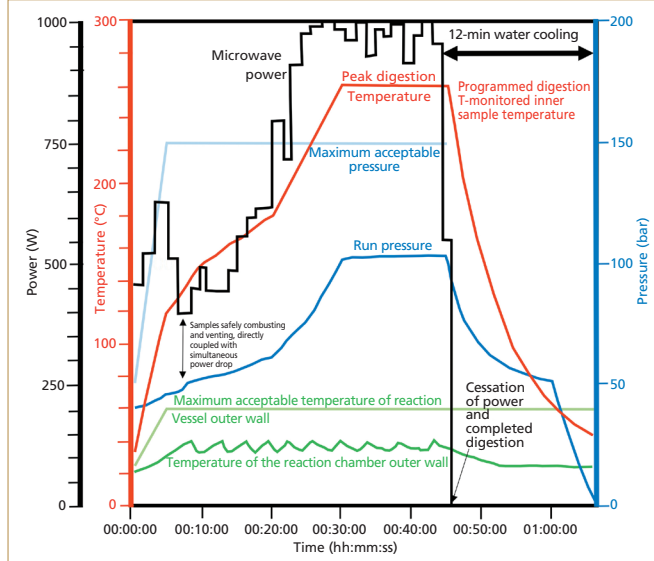
cally ventilated upon completion and before extraction; the close-up image shows the undegassed digested sample (green solution containing oxides of nitrogen and carbon dioxide) in quartz vials with white laterally vented PTFE caps. Finally, **Figure 1c** shows subsequent degassed clear digest solutions in quartz glass PTFE-capped tubes, which are then placed in capsules ready for heating and dry-down procedures.

Digest solutions are then evaporated to near-dryness to remove strong acids and diluted with 2% HNO_3 using a low dilution factor (8–10x). These solutions, which are basically free of carbon based spectral interferences are then introduced into the ICP-OES or ICP-MS system and analyzed using longer shelf life, commercially available aqueous calibration standards.

Compared to bomb mineralization or traditional closed-system rotor-based microwave systems, the advantage of the microwave-assisted strong acid wet digestion technique using the SRC include:

- The multisample digestions are completed within 1 h compared to >24 h for bomb digestions.
- Multiple samples of different oils can be run at the same time under the same pressure–temperature conditions within a SRC.
- Pressure and temperature of the chamber wall and interior fluid chamber and microwave power is precisely controlled.
- High temperatures of $260\text{ }^\circ\text{C}$ under controlled pressure can be achieved during glass vessel digestion for all samples.
- Sample sizes can be larger (for example, 0.6–1.2 g per vessel depending on rack sizes used), compared to 0.1 g for bombs or

Figure 2: Plot of power, temperature, and pressure against time using a single-reaction-chamber microwave digestion system (refer to text for details).



0.25 g for typical rotor-based microwaves or closed-vessel bombs that are more limited to prevent venting and sample loss.

- Digestion vessel sizes can be varied (with multiple racks and vessel sizes possible within the single reaction cell) and can be used to influence ultimate measured sample sizes, dilution factors, and effectively will allow more control over all MDLs and MOLs.

This final point is particularly important when analyzing and quantifying very light oils, condensates, or naphtha, which collectively might have very low abundances of trace and ultratrace elements. The analysis of larger sample sizes is achieved by using larger vessels or combining sample digests from multiple vessels. They also ensure the likelihood of sample homogeneity.

Because the microwave energy is

applied to all samples under the same temperature and pressure conditions, the system can sense highly exothermic reactions, pressure increases, and potential venting surges in real time in the single reaction vessel. It can then control power, which means it has the ability to abort potentially dangerous runs instantly if the outer chamber wall exceeds preset temperature limits or chamber pressure limits are exceeded. This leads to very safe digestions of combustible crude or fuel oils. The microwave system allows rapid digestion for increased throughput, allows minimal quantities of reagent use for clean chemistry, results in improved accuracy and precision because of minimal risk of contamination, minimizes sample loss of volatile elements, and leads to the destruction of organics because temperatures can exceed the boiling temperatures of reagents under pressure. Finally, the ability to use low-cost aqueous solution standards is important and cost effective, because the digestions can produce clear solutions for both crude and refined oils. This precise control over power, temperature, and pressure using this approach is seen in **Figure 2**, which shows a plot of the following metrics against time:

- programmed digestion temperature (red)
- maximum pressure (light blue)
- actual pressure (dark blue)
- maximum temperature of the reaction vessel outer wall (light green)
- actual temperature of the chamber outer wall (dark green)
- microwave power (black)



ICP-OES and Triple-Quadrupole ICP-MS in Tandem for Routine Analysis

Crude oils and derivatives have elemental concentrations that range from 10–60 mg/g (1–6 wt %) to 1 pg/g, which means no single sample preparation methodology can be used with a single instrument that would have the dynamic range to analyze a comprehensive suite of elements detectable in crude oils without multiple preconcentration or added preparation steps, which would be very time consuming. However, by using the single prepared sample with two plasma spectrochemical techniques with different dynamic ranges (ICP-OES and ICP-MS), as used in our studies in tandem, the single sample preparation step outlined above can be used without the necessity of other time-consuming sample preparation steps. At a low 8.5x sample dilution used in our tests, ICP-OES is capable of analyzing higher abundance elements such as S, V, and Ni (and others) in some crude oils or refined derivatives and then aliquots of the same samples can be used to introduce into the ICP-MS system for analysis of low-abundance elements. It should be emphasized that low- and high-abundance elements are not consistent or predictable in crude oils, which can have a range of compositions even within the same subsurface petroleum-generating system depending on factors such as source rock depositional setting, thermal maturity, or biodegradation. For example, some heavy marine-sourced crude oils from euxinic basins may have >6% S by weight and 100–1000 µg/g V and Ni, which must be

analyzed by ICP-OES, whereas others such as thermally mature shale oils, lucustrine oils, or condensates can have very low microgram-per-gram concentrations of S, V, and Ni that are better suited for the more sensitive triple-quadrupole ICP-MS.

The triple-quadrupole ICP-MS technology is a more recent development and includes an additional quadrupole before an octapole collision–reaction cell and the analyzer quadrupole. This first quadrupole acts as a simple mass filter to allow only the analyte masses to enter the cell, while rejecting all other masses. With all nonanalyte, plasma, and sample matrix ions excluded from the cell, sensitivity and interference removal efficiency is significantly improved compared to traditional collision–reaction cell (CRC) systems coupled with a single-quadrupole mass analyzer. In this very innovative CRC technology, different collision–reactive gases can be used to reduce the polyatomic interference through ion–molecule chemistry in the octopole cell, which is then used to pass all the product ions formed into the analyzer quadrupole and separate and select the mass or masses of interest. The benefit for analyzing and characterizing crude oil and petroleum samples is that notoriously difficult elements like silicon, phosphorus, and sulfur (and many others) can be determined at significantly lower levels and with higher accuracy than a conventional single-quadrupole instrument. This means that a larger elemental suite can be determined, which can potentially increase the knowledge used to identify the source and the origin of the crude oil sample.



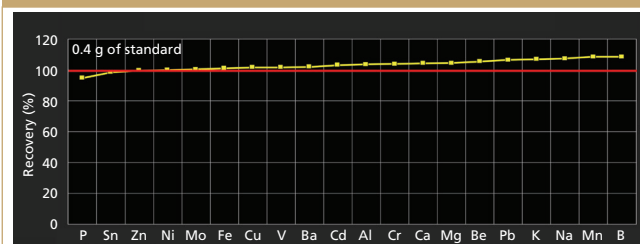
In our comparative studies, we found that using a single-quadrupole ICP-MS and ICP-OES, we could routinely analyze and quantify up to ~47 elements with our digestion techniques, but with triple-quadrupole ICP-MS and ICP-OES we are able to routinely analyze and quantify up to 57 low- and high-abundance elements, mainly because of sensitivity increases and more control over the polyatomic spectral and other interferences. For example, with increasing focus on more stringent environmental management of pollutant emissions from heating oils and vehicle liquid fuels, sulfur, and other elements will be increasingly subject to environmental regulations and low-abundance elemental quantitation in fuel samples will be absolutely critical. This need will necessitate the use of the more advanced ICP-MS spectral reduction techniques to characterize the suite of elements at such low levels.

Recovery Tests and Accuracy

There are very few multielement certified natural crude oil standards, and typically they are certified for a very limited number of elements. We therefore used three approaches to examine recovery and accuracy: a certified synthetic organometallic multielement standard, a 57-element spike recovery test of a base oil blank, and a more limited test on reported NIST SRM oil values for the method developed.

Recovery tests of 20 elements were conducted on a commercially available Conostan (SCP Science) multielement organometallic standard digested with our microwave protocols and then analyzed by

Figure 3: Recoveries of 20 elements in a multielement organometallic standard using microwave digestion and determined by ICP-OES or ICP-MS.



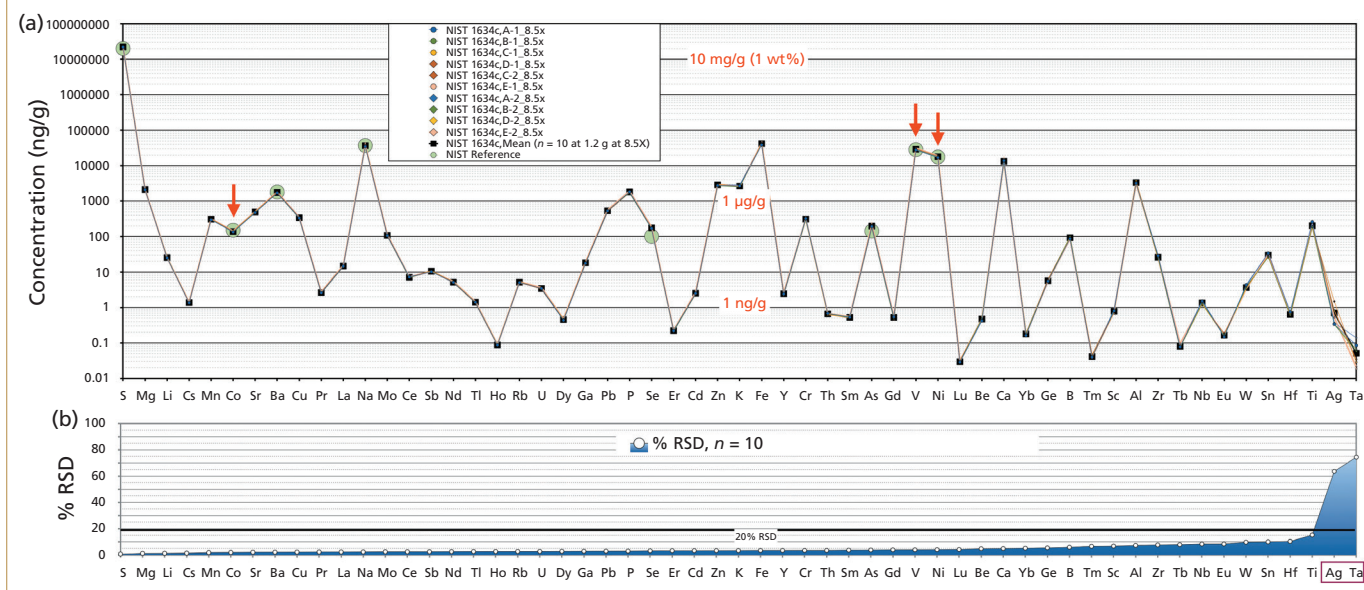
ICP-OES and ICP-MS. **Figure 3** shows that the recoveries for all 20 elements are in the range of 95–107%.

These results were augmented with our own tests in which 500 ng of 57 analyte elements were added to 400 mg of Conostan 75cSt base oil before microwave digestion to conduct a comprehensive recovery test for all elements routinely analyzed in the laboratory. These microwave-assisted digestion recovery results were superior to those obtained using all other digestion methods tested for the same suite of 57 elements and produced on average recoveries of 90–110%. Notably, there was good recovery of tested elements with known volatility issues, such as B, Be, Sn, As, Se, and Sb.

Accuracy Compared to a Standard Reference Material

Accuracy of any method is the agreement between a test result and certified reference values for comparison. Unfortunately, there is no natural oil SRM yet with extensive suites for elements certified to examine accuracy for the majority of elements analyzed. In this study, NIST SRM 1634c No.6 residual fuel oil

Figure 4: Log-scale spidergram of concentrations (ng/g) of 10 replicated analyses of 57 elements measured in NIST SRM 1634C fuel oil, determined by ICP-OES or ICP-MS, together with the RSD of each measurement.



was digested using our method and analyzed by the ICP-OES and ICP-MS techniques outlined for 57 elements. Results include five digestions run separately with two analyses for each digestion. The results shown in **Figure 4** are a log-scale spidergram of concentrations (in nanograms per gram) for five digestions at different times with two analyses of each digestion, making 10 replicates in total.

The precision data underneath the spidergram shows the precision (% RSD) for all elements. It can be seen that all elements were well below 20% RSD even though some elemental abundances were near their MQL. Exceptions include Ag and Ta (far right), both with concentrations less than 1 ng/g, which showed far greater scatter with high RSD. Elemental concentrations ranged widely from more than 2% (20

mg/g) by weight for S and 1–40 $\mu\text{g/g}$ for V, Ni, K, and Na requiring quantitation by ICP-OES, to sub nanogram-per-gram concentrations requiring the remainder of elements to be quantified by triple-quadrupole ICP-MS.

The highlighted green circles represent superimposed NIST “certified” values for Co, Ni, and V as well as “reference” values for As and Se, and “information” values for Ba, Na, and S. The accuracy assessment of our mean achieved values could only realistically be compared to NIST certified values shown in **Table I**, which include Co (9.4%), Ni (1.4%), and V (2.4%). Non-certified values are also listed in Table I for further information. Compared to NIST noncertified “reference” values reported for As and Se, elements known to have volatility issues were somewhat higher in our analyses (27%

Table I: Mean concentration values of NIST SRM 1634c fuel oil, RSDs, and accuracy estimates.

Element	Units	NIST Certified*, NIST Referenced†, NIST Information‡, Elemental Abundances for NIST SRM 1634c Fuel Oil	% RSD	UH-Mean Abundances (Five Repeated 1.2-g Digestions, 8.5 x Dilutions, Replicate Analysis) N = 10	% RSD N = 10	% Accuracy/ NIST	UH-Analytical Techniques	NIST Analytical Techniques
Co*	µg/g	0.1510	3.3	0.138	2.0	9.4	ICP-MS [§]	ICP-MS, INAA
Ni*	µg/g	17.54	1.1	17.8	4.1	1.4	ICP-OES	ID-ICP-MS, LEI
V*	µg/g	28.2	1.3	28.9	4.0	2.4	ICP-OES	ICP-AES, INAA
As†	µg/g	0.142	4.4	0.197	3.8	27.9	ICP-MS [§]	FIA-HAAS, INAA
Se†	µg/g	0.102	3.7	0.175	3.2	41.7	ICP-MS [§]	FIA-HAAS, INAA
Ba†	µg/g	1.8		1.7	2.1	5.8	ICP-MS [§]	INAA
Na†	µg/g	37		36.48	2.4	1.4	ICP-MS [§]	INAA
S†	wt%	2		2.22	0.7	9.9	ICP-OES	ID_TIMS

Note: Only Co, Ni, and V are certified (*), while As and Se (†) are reference values and Ba, Na, and S (‡) are for informational purposes only. [§]Triple-quadrupole MS.

and 42%, respectively) than NIST values although precisions were <4%. Testing by Wondimu and Goessler (8) based on a closed-system rotor-based microwave digestion on the same standard also reported similarly higher values than “reference” values listed by NIST with precisions <5%. The reason is unclear, but higher values could indicate more complete recovery and higher measurement values are associated with closed microwave digestions, or may be related to the differences in analytical techniques used. All “information” values of Ba, Na, and S compare well with the NIST results reported (<10%). Note that many of the NIST analytical methods in Table I differ from the two ICP instrumental techniques and digestion procedures used in our evaluation. Developments and further definition of “true” values for noncertified “reference” and “information” values will require further inter-laboratory comparisons, and NIST statistical testing to allow the potential of future compliance with NIST certification criteria.

It should also be emphasized that the NIST 1634c SRM was chosen for this study because of the comparatively larger number of elements reported by NIST (eight in total), which are measurable by our chosen ICP techniques. The achieved mean concentration results, RSDs, and accuracy estimates compared with NIST reported certified, reference, and informational values are shown in Table I.

Within-Laboratory Precision, Repeatability, and Reproducibility

Within-laboratory precisions of our analyses can be estimated on the basis of the 10 replicate determinations of 57 elements for NIST SRM 1634c. As previously mentioned, the concentrations and the % RSD or variance for each element are plotted in Figure 4. The % RSD of the mean of each element is shown (10 analyses of the SRM) with elements listed in order of increasing RSD value. Analyses of this standard involved five separate microwave digestions (A–E) over time with replicate analysis of each digestion (for example, A1 and



A2). Results are plotted as concentrations in nanograms per gram. Of the 57 elements measured, 42 elements had RSDs ranging from 0.7% to 4.9%, 12 elements had RSDs ranging from 5.2% and 10.0%, and two elements had RSDs ranging from 10.4% to 15.3%, meeting our imposed RSD limits of <20% of acceptability even at sub-nanogram-per-gram levels. Two elements, Ag and Ta, were <1 ng/g in abundance and showed more significant heterogeneity, with RSDs of 63.7% and 74.5%, respectively, and did not meet stricter quantitation criteria. Whereas RSDs are generally low for the 55 elements quantified, the exceptions on these runs were Ag and Ta. Poorer Ag precision sometimes observed for repeat measurements of samples and for NIST 1634c may be a consequence of the low concentration, which is at or near the MQL of 0.03 ng/g and the fact that Ag is also known for its tendency to form matrix-dependent salts over time in solutions, especially at low concentrations. Both factors could contribute to the variability observed. The higher RSD for Ta may also result from matrix-dependent solubility issues, because the element has been observed to drop out of solution over time (~4 weeks) in prepared low-abundance multielement standard solutions. Investigations to better optimize these elements and procedures are underway, although variance is commonly lower in other samples tested.

Poor repeatability is a well-known problem for a number of analytical tech-

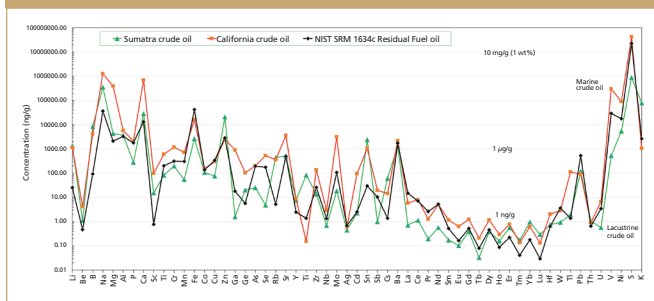
niques used to analyze digests of crude and fuel oils (1). However, in our duplicate digestions and replicate analyses presented here, 55 of the elements that are significantly above the MQL show good within-laboratory RSDs of 0.7-15%. We have also observed the same consistency in other NIST crude oil standards with many replicate digestions and with the natural crude oils analyzed for up to 57 element when analyses were repeated by various laboratory investigators, at various times, and with different reagent batches. In addition to within-laboratory repeatability tests, future studies will involve interlaboratory comparisons to examine the ruggedness of methods. Interlaboratory precision predictions can, however, be made from the Horwitz empirical method and reproducibility curve (11). Based on our repeatability tests and intermediate method precision data, it can be predicted that the overall method should be robust in interlaboratory comparisons for most all of the analytes measured.

Examples of Crude Oil Fingerprints

In **Figure 5**, we show two examples of natural crude oil fingerprinted by our analytical method in comparison with NIST 1634c fuel oil results on a log-scale spidergram. These three analyses illustrate distinct fingerprints for each oil with many elements varying by more than 2–3 orders of magnitude. One of the natural oils was relatively lighter and generated in a subsurface lacustrine source rock environment in Sumatra,



Figure 5: Results obtained using the developed method for fingerprinting two natural crude oils—one from a lacustrine source rock in Sumatra (green) and the other from a marine euxinic environment off the coast of California (orange)—compared with the NIST SRM 1634c residual fuel oil (black).



while the other was a heavier oil generated in a marine euxinic environment off the coast of California.

All element abundances are at or above MQL. They are readily distinguished by distinct ratios and abundances of V and Ni and other elements that can allow oil–oil or oil–source rock correlations to be made by oil exploration scientists. We are also able to distinguish crude oils from different wells in the same fields by this fingerprinting technique. In all, there are 57 element abundances and more than 3000 ratios that can be utilized by upstream explorationists for fingerprinting, oil–oil and oil–source rock correlation, organic matter typing, depositional environment typing, and maturation and biodegradation studies of oils or source rock organic matter (12–16). As in crude oil organic geochemistry, elemental abundances and ratios can also be useful in reservoir management, production allocation, and

transportation and flow assurance engineering (17,18). In addition, downstream refiners have needs to characterize natural or comingled crude oils, feedstocks, and refined products to identify catalyst poisons and corrosive metal species, to control refinery costs, maintenance schedules, and for quality assurance purposes to meet more stringent regulatory requirements and industry standards for refined products (19).

Summary

Recent significant developments in microwave digestion technologies and ICP-MS analytical instruments show significant promise in resolving many of the past issues related to the rapid multielement analysis of crude oil and derivative products. Whereas dilute-and-shoot industry-standard methods will continue to have significant applications, we regard the oil chemical fingerprinting analytical methods developed here as a potential pathway forward to more-routine, lower-cost multielement analysis with a more comprehensive elemental list if the industry is to meet progressively more complex and challenging needs. These more-extensive target analytes include those currently well-accepted and designated as important and useful to the upstream and downstream petroleum industries, as well as low-abundance, poorly documented elements (such as rare earths) whose routine testing is yet to be fully realized. This more-comprehensive elemental list may lead to more sophisticated applica-



tions of elemental analysis for crude oil and derivatives, with benefits extending from exploration and production to refining, product monitoring, and regulatory and compliance efforts. With the optimization in sample preparation and the types and numbers of dedicated instruments required for more complete high-to trace-level elemental characterization, the lower expenditure will translate into an overall reduction in operational and discovery costs.

Disclaimer

Robert Thomas, the editor of the “Atomic Perspectives” column would like to emphasize, that although he contributed to the writing of this month’s column, he does not endorse any of the commercial products mentioned herein.

References

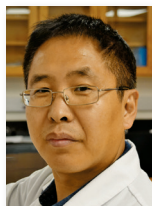
- (1) C. Duyck, N. Miekeley, C.L.P. Silveira, R.O. Aucélio, R.C. Campos, P. Grinberg, and G.P. Brandão, *Spectrochim. Acta, Part B* **62**, 939–951 (2007).
- (2) J.F. Casey and Y. Gao, “Triple Quadrupole ICP-MS and ICP-OES Fingerprinting of Up to 57 Trace and Minor Elements in Crude Oil Using a Single Sample Preparation Method,” available at: http://cen.acs.org/media/webinar/agilent_102015.html (2015).
- (3) J.F. Casey, Y. Gao, and W. Yang, “Analysis of Low Abundance Trace Metals and 50V/51V Isotopes in Crude Oils: New Methods for Characterization and Exploration” presented at the Goldschmidt 2015 conference, Prague, 2015.
- (4) C. Duyck, N. Miekeley, C.L.P. Silveira, and P. Szatmari, *Spectrochim. Acta, Part B* **57**, 1979–1990 (2002).
- (5) C.J. Lord III, *Anal. Chem.* **63**(15), 1594–1599 (1991).
- (6) G.S. Ortega, C. Pécheyran, G. Hudin, E. Marosits, and O.F. Donard, *Microchem. J.* **106**, 250–254 (2013).
- (7) T.A. Yasnygina, S.V. Rasskazov, M.E. Markova, A.E. Zharov, Y.M. Malykh, E.V. Saranina, and N.N. Fefelov, *Russian Journal of Pacific Geology* **9**(2), 109–119 (2015).
- (8) T. Wondimu and W. Goessler, *Bull. Chem. Soc. Ethiop.* **14.2**, 99–113 (2000).
- (9) C.N. Duyck, N. Miekeley, T.C.O. Fonseca, P. Szatmari, and E.V. dos Santos Netob, *J. Braz. Chem. Soc.* **19**(5), 978–986 (2008).
- (10) J.S.F. Pereira, D.P. Moraes, F.G. Antes, L.O. Diehl, M.F.P. Santos, R.C.L. Guimarães, T.C.O. Fonseca, V.L. Dressler, and É.M.M. Flores, *Microchem. J.* **96**(1), 4–11 (2010).
- (11) W. Horwitz, L.R. Kamps, and K.W. Boyer, *J. Assoc. Off. Chem.* **63**, 1344 (1980).
- (12) M.D. Lewan, *Geochim. Cosmochim. Acta* **48**(11), 2231–2238 (1984).
- (13) A.J.G. Barwise, *Energy Fuels* **4**(6), 647–652 (1990).
- (14) R.H. Filby, *Geological Society*, London, Special Publications 78, 203–219 (1994).
- (15) F. Galarraga, K. Reategui, A. Martinez, M. Martinez, J. Llamas, and G. Márquez, *J. Pet. Sci. Eng.* **61**, 9–14 (2008).
- (16) R. Nakada, Y. Takahashi, G. Zheng, Y. Yamamoto, and H. Shimizu, *Geochem. J.* **44**(5), 411–418 (2010).
- (17) M.A. McCaffrey, H.A. Legarre, and S.J. Johnson, *AAPG Bulletin* **80**, 898–913 (1996).
- (18) R.J. Hwang, D.K. Baskin, and S.C. Teerman, *Org. Geochem.* **31**, 1463–1474 (2000).
- (19) J.G. Gary and G.E. Handwerk, *Chemical Processing and Engineering*, 4th. Ed. (Marcel Dekker Inc., New York, 2001).
- (20) W. Yang, J. F. Casey, and Y. Gao, *Fuels* (in review).
- (21) J.F. Casey, Y. Gao, W. Yang, and K.A. Bissada, *Geological Society of London*, special edition “From source to seep: Geochemical applications in hydrocarbon systems,” in review.



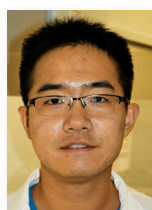
Robert Thomas is principal of Scientific Solutions, a consulting company that serves the application and writing needs of the trace element user community. He has worked in the field of atomic and mass spectroscopy for more than 40 years and has written over 80 technical publications including a 15-part tutorial series on ICP-MS. He recently completed his third textbook entitled Practical Guide to ICP-MS: A Tutorial for Beginners. He has an advanced degree in analytical chemistry from the University of Wales, UK, and is also a Fellow of the Royal Society of Chemistry (FRSC) and a Chartered Chemist (CChem).



John F. Casey is a Professor in the Geology Department at the University of Houston in the Earth and Atmospheric Sciences Department. He serves as the Director of a University core facility, the Center for Advanced Analytical Geochemistry (CAAG). He has worked in the field of trace element and isotopic geochemistry of terrestrial and marine geological materials since the early 1980s. He is the author of more than 100 peer-reviewed articles in the geosciences.



Yongjun Gao is a Research Associate Professor at the University of Houston in the Department of Earth and Atmospheric Sciences. He has 15 years of experience in conducting geochemistry research in various fields and has published more than 40 peer reviewed research articles.



Weihang Yang is a PhD candidate and teaching assistant of Geology in the Earth and Atmospheric Sciences Department at the University of Houston.

*This article was first published in Spectroscopy, **31**(10), 11–22 (2016).*



Simultaneous Mixed-Batch Sample Preparation for Metals Testing of Medical Cannabis

Single Reaction Chamber (SRC) Technology ensures maximum productivity and ease of use.

Technical Application Note

Introduction

The medical cannabis industry is currently one of the fastest growing industries in the United States and becoming more prevalent worldwide. Although systems for growing, producing, and selling medical cannabis and related products are well established, the regulation and enforcement of quality and safety testing have lagged. As the industry matures, many challenges are being faced, such as ensuring consumer safety and providing products free from potential contaminants such as heavy metals.

Like all plants, cannabis absorbs metals from its environment, a result of normal plant metabolism. Some of these metals are naturally occurring and leach into groundwater. Others precipitate in rainwater or may be introduced into the plant's environment as constituents of fertilizers, pesticides, herbicides, and fungicides used to increase crop yield. Regardless of their prevalence, when metabolized, metals are absorbed and transported through the plant roots and into plant tissue. Cannabis is so effective at absorbing metals from its

environment that it has been referred to as a hyperaccumulator of trace metals, including lead, cadmium, copper, chromium, arsenic, mercury, and cobalt. This leads to concern that these elements may occur in high concentrations in cannabis plants.

State governments and private laboratories are focusing on product safety testing with a special emphasis on As, Cd, Hg and Pb, as they are extremely hazardous to human health, even at low levels.

The combination of ICP-MS and Milestone's UltraWAVE with SRC technology allows cannabis analytical testing labs to analyze a broad variety of matrices on which metals determination could be very different, toxic elements in some cases and nutrients in others.

Milestone's SRC microwave digestion is a revolutionary new approach, incorporating all the benefits of closed vessel microwave digestion while making sample preparation fast, easy and efficient. SRC technology operates at very high temperature and pressure (up to 300 °C and 199 bar, respectively), allowing for complete



digestion of even the largest sample size (up to 3–5 g) and difficult-to-digest matrices. Samples can be weighed directly into disposable glass vials, eliminating the need for acid cleaning and vessel assembly. Furthermore, SRC technology eliminates the need to batch samples, as mixed sample types, masses, and acid chemistries can be successfully processed in the same run. This technical note describes how a variety of samples from the cannabis industry were digested simultaneously without sample-to-sample cross contamination.

Experimental Instrument

The UltraWAVE meets the requirements of the new medical cannabis regulations, thanks to its unique benefits, such as:

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

Developed and patented by Milestone, the UltraWAVE with SRC technology utilizes high-performance stainless steel, allowing for higher pressures and temperatures to be reached and any type of acids to be used. Disposable vessels eliminate the need to assemble, disassemble, or clean between processing. Just as important, dissimilar samples can be processed simultaneously using any mixture of disposable glass, quartz, or TFM vials, thus saving time and money. The UltraWAVE is simply the fastest, easiest and most efficient digestion system ever made!



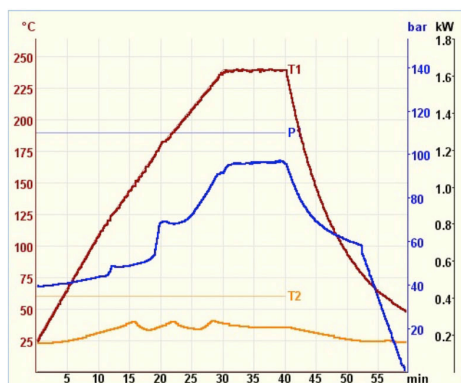
Results and Discussion

The performance of the Milestone UltraWAVE was evaluated through a recovery study on samples of interest for the medical cannabis industry, from plant material to edibles, concentrates, and soil. As cannabis-containing representatives of the above categories, plant material, CBD oil, a vape cartridge, cannabis salve, cookies, gummy bears, and even soil were digested as a mixed batch, simultaneously, with the UltraWAVE and subsequently analyzed via ICP-MS.

Cannabis plant material, CBD oil, vape cartridge, salve, cookies, and gummy bears were fortified with spike solutions containing 20 ppb of As, Cd, Pb, Ag, Ba, Co, Cr, Cu, Mn, Ni, Se, V, Zn, and 10 ppb of Hg. A soil reference material (SRM 2711a) was also included in this study as a quality control sample. The analytical results are shown in **Table 2** with recoveries of all analytes between 80–120% and RSDs be-

Analytical Procedure	
Sample	UltraWAVE - SRC 4 mL of HNO ³ 65%, 1 mL HCl
Cannabis flower	1g
CBD oil	1g
Cannabis vape cartridge	1g
Cannabis salve	1g
Cannabis flavored cookies	1g
Cannabis flavored gummy bear	1g
Soil (SRM 2711a)	1g

Table 1. Sample amount and acid mixture used for the microwave digestion run.



Microwave program used to digest samples:				
Step	Time	Temp	P	Power
1	00:20:00	240 °C	110 bar	1500 W
2	00:10:00	240 °C	110 bar	1500 W

Final dilution: 50 mL with deionized water

low 3%. This demonstrates the robustness and reproducibility of microwave digestion using the UltraWAVE with SRC technology.

Conclusion

The data shown in this technical note demonstrates full recovery of the most common elements occurring in cannabis plants. In addition to full analyte recovery, microwave digestion using Milestone’s SRC technology provides the highest level of reproducibility, even for volatile elements such as As and Hg.

Due to its higher sample capacity, use of disposable vials and faster cool down time, sample processing throughput is 2 to 3 times higher than conventional closed vessel digestion systems. The ability to digest different sample types together and larger sample weights with minimal acid volume

Quantification	
ICP-MS Instrumental Parameters:	
RF Power	1600 W
Sampling depth	10 min
Carrier gas	0.8 L/min
Sweeps/Reading	20
Readings/Replicate	1
Number of replicates	3
Integration time	1000 ms
Dwell time per AMU	50 ms
Mode	KED
Scan mode	Peak hopping
Cell Gas A	0.6
RP a	0
RP q	0.25



Table 2. Data of the recovery study.

		As	Cd	Hg	Pb	Ag	Ba	Co	Cr	Cu	Mn	Ni	Se	V	Zn
Cannabis plant material	Recovery (n=3) (%)	91.7	93.0	98.7	88.3	88.6	93.0	96.5	93.7	-*	-*	91.3	95	94.5	-*
	RSD (%)	1.9	2.1	2.1	2.6	1.5	1.3	2.3	2.4	-*	-*	91.3	1.6	2.1	-*
CBD oil	Recovery (n=3) (%)	95.8	98.5	97.6	89.7	92.7	99.7	93.0	88.2	91.0	91.2	96.2	102.7	90.2	95.8
	RSD (%)	1.8	2.3	1.1	2.2	2.2	2.5	2.2	2.0	2.8	2.4	1.4	0.7	1.9	2.7
Cannabis vape cartridge	Recovery (n=3) (%)	90.8	87.3	91.8	92.0	89.2	91.2	93.2	87.7	94.4	94.8	92.2	96.8	89.7	95.9
	RSD (%)	1.1	2.0	1.2	1.5	2.0	1.9	2.0	1.8	2.1	1.6	1.5	2.6	2.5	1.4
Cannabis salve	Recovery (n=3) (%)	95.8	91.5	94.3	95.3	87.0	90.0	92.2	86.8	92.9	90.4	94.8	100.8	91.3	90.1
	RSD (%)	0.3	1.1	1.4	2.2	1.5	1.0	2.0	1.1	2.4	2.5	2.4	1.8	0.7	0.3
Cannabis flavored cookies	Recovery (n=3) (%)	92.8	93.8	96.1	93.3	89.0	94.0	94.2	98.2	-*	-*	92.8	92.8	89.5	-*
	RSD (%)	2.8	0.7	1.3	1.4	2.4	1.2	1.8	1.0	-*	-*	2.4	2.6	0.6	-*
Cannabis flavored gummy bear	Recovery (n=3) (%)	90.2	89.5	94.1	91.8	90.7	91.5	95.5	91.3	96.4	95.8	90.5	91.2	89.5	92.2
	RSD (%)	2.1	2.0	1.0	2.2	2.4	2.6	2.3	1.4	2.3	2.8	1.5	0.8	1.0	1.1

* The ratio between spiked/unspiked concentration was too low.

		As	Cd	Hg	Pb	Ag	Ba	Co	Cr	Cu	Mn	Ni	Se	V	Zn
Soil (SRM 2711a)*	Recovery (n=3) (%)	90.4*	94.1*	98.7*	93.3*	92.1*	42.0*	89.2*	35.6*	97.8*	89.4*	90.8*	98.9*	47.9*	92.1*
	RSD (%)	2.1	1.9	1.6	1.1	1.0	0.6	1.2	2.4	0.9	1.5	1.8	1.9	0.6	0.9

*The recoveries were calculated according to the total element content and represent the leachable fraction (please, refer to NIST Certificate of Analysis for SRM 2711a for further details).

makes it the optimal technique to perform sample prep for all cannabis related products, from the plant material to edibles, concentrates and even soil samples.

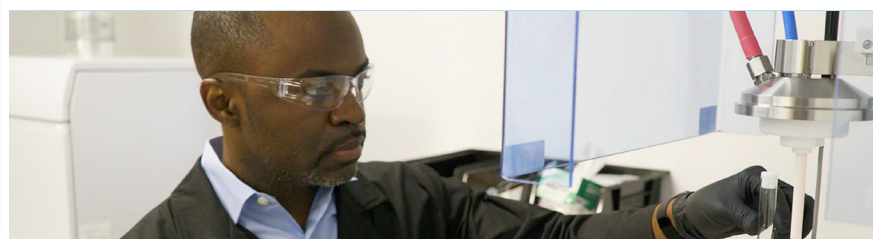
This new era of acceptance and legalization has opened new opportunities for labs.

Standardization of these methods for the industry will give regulators the resources they need to include sensible requirements for regulation and legislation that are being crafted to monitor and control the use of medical cannabis within the United States.



SPONSOR'S CONTENT: USER PROFILE

Milestone's UltraWAVE allows Cannabis Lab to Streamline Heavy Metals Testing





Any Sample, Any Time: The Benefits of Single Reaction Chamber Microwave Digestion for Trace Element Analysis

ON-DEMAND WEBCAST

**Register for free at <http://www.spectroscopyonline.com/spec/benefits>
Can't make the live webcast? Register now and view it on-demand after the air date.**

This webcast will present the fundamental principles and real-world benefits of single reaction chamber (SRC) microwave digestion compared to traditional sample preparation techniques for carrying out trace element analysis by atomic spectroscopy techniques. To be explored are SRC technology capabilities such as those described below, which uniquely address sample digestion challenges and requirements across a broad range of industries:

- Simultaneous digestion of widely different sample matrices
- High volume sample throughput
- Direct temperature and pressure control on every sample
- Reliable digestion regardless of the matrices or acid chemistry
- Maximized ICP-MS performance through reduction of residual carbon content of organic-based samples
- Improved recoveries for highly volatile elements such as mercury
- Lower running costs

KEY LEARNING OBJECTIVES

- Create audience understanding of the technology behind single reaction chamber (SRC) microwave digestion and the overall advantages compared to traditional sample preparation techniques including:
 - Virtual elimination of vessel handling
 - Simultaneous digestion of mixed sample matrices simultaneously
 - Higher pressure capabilities with ability to accommodate large amounts of high organic matrices (API's, excipients, crude oils, foods, polymers)
 - Higher temperature digestion to address challenging samples (ceramics, PGE's)
 - Higher productivity and lower operating costs
- How the unique advantages available using SRC technology are used to effectively address specific sample digestion challenges associated with a wide-range of industries including pharmaceutical/nutraceutical, chemical, food/agriculture, petrochemical; in both in-house and contract lab settings.

WHO SHOULD ATTEND

Analytical chemists who want a better understanding of how to maximize the digestion of a wide variety of differing sample matrices when carrying out trace element analysis using plasma spectrochemical analytical techniques.

PRESENTERS



Robert Thomas
Principal Consultant
Scientific Solutions



**Laura Thompson,
M.Sc.**
National Sales
Manager
Milestone Inc.



MODERATOR
Laura Bush
Editorial Director
Spectroscopy

Sponsored by

MILESTONE



HELPING
CHEMISTS

Presented by

Spectroscopy
Solutions for Materials Analysis

For questions contact Kristen Moore at Kristen.Moore@ubm.com