Microwave Acid Digestion of Crude Oil Samples Using a New High Performance Vessel

Abstract

Microwave digestion is the preferred sample preparation technique for crude oil samples prior to heavy metals analysis. Samples are digested in a concentrated acid matrix in a closed vessel and heated in a commercial microwave digestion oven where the speed of thermal decomposition of the sample and the solubility of metals are increased. Once these metals are in solution, their concentration can be quantified through spectroscopic techniques. The MARS 6 acid digestion process routinely cuts the time of sample preparation by 50 – 75% as compared to hot plates and hot block.

Introduction

The analysis of metals in crude oil prior to refining is of vital importance to the oil refining industry. V and Ni, for example, can act as catalyst poisons affecting the distillation process while toxic elements such as As and Se must be monitored due to environmental concerns. Traditionally, microwave digestion systems have been limited to smaller sample sizes due to the amount of NO_x gases produced in the digestion process.

This application note will focus on the use of the CEM MARS 6 microwave digestion system using a recently introduced high performance vessel to better handle the gaseous digestion byproducts. A mix of crude oil samples and NIST 1634c (Trace Metals in Fuel Oil) will be prepared and analyzed for As, V and Ni. A One Touch Method™ was created with a target temperature of 240 °C and a 20 min hold.

Experimental Conditions

A CEM MARS 6 microwave digestion system equipped with iWave contactless temperature control and iPrep digestion vessels were used to prepare the samples and standards.

iWave is a novel Light Emitting Technology™ that measures the temperature of the actual sample solution inside the vessel and does not require an internal probe.

Figure 1 illustrates the iPrep vessel, a simple to use, three piece vessel which only requires an ergonomic hand held torque device to properly seal it. The patented dual-seal design provides for higher temperatures and fine control of the vent and reseal process necessary for these sample types.

Each sample and standard was weighed and added to an iPrep liner along with 9 mL HNO_3 and 1 mL HCl. The vessels were capped, assembled, and placed in the MARS 6 for digestion.

The pre-loaded Crude Oil Method was chosen on the onboard touchscreen. The MARS 6 then verified the number of samples, identified the proper vessel type and then applied the precise power necessary to complete the digestion. Complete digestion of 12 samples was achieved in 45 minutes.

Samples were diluted to a 50 mL volume and analyzed on a Thermo Fisher Scientific iCAP Q ICP-MS system with settings shown in **Table 1**.

Table 1. iCAP Q Settings

PLASMA/RF
· Forward Power – 1198.8 W
· Interface Temp – 26.13 °C
· Cooling water Flow – 3.00 L/min

GAS FLOW
· Cool Gas Flow – 12.923 L/min
· Auxiliary Gas Flow – 0.7889 L/min
· Nebulizer Gas Flow – 0.8974 L/min

PERISTALTIC PUMP
· Pump Speed – 40.0 rpm
· Mode - Normal
· Direction - Clockwise

Results

The MARS 6 with iWave temperature control was able to precisely control the power in order to prevent any exothermic reactions which can be common with highly organic materials such as crude oil as illustrated in **Figure 2**. The result of the digestion was a clear and colorless solution as seen in **Figure 3**. Results of the ICP-MS analysis are shown in **Table 2**.

Conclusions

The MARS 6 system with iWave technology and iPrep vessels is an ideal solution for digesting difficult crude oil samples for heavy metals analysis.
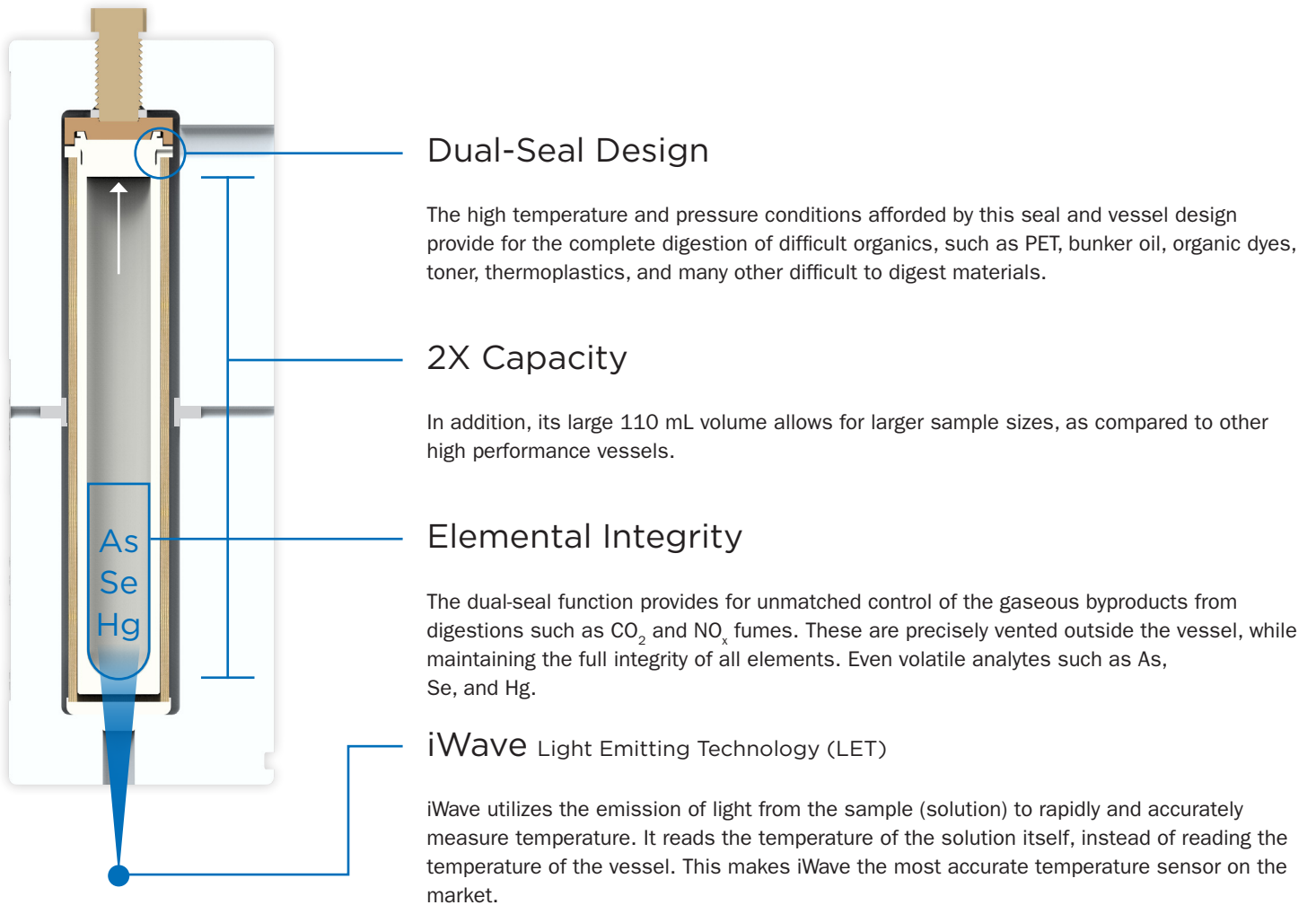
Figure 1. The iPrep Vessel

Dual-Seal Design

The high temperature and pressure conditions afforded by this seal and vessel design provide for the complete digestion of difficult organics, such as PET, bunker oil, organic dyes, toner, thermoplastics, and many other difficult to digest materials.

2X Capacity

In addition, its large 110 mL volume allows for larger sample sizes, as compared to other high performance vessels.

Elemental Integrity

The dual-seal function provides for unmatched control of the gaseous byproducts from digestions such as CO_2 and NO_x fumes. These are precisely vented outside the vessel, while maintaining the full integrity of all elements. Even volatile analytes such as As, Se, and Hg.

iWave Light Emitting Technology (LET)

iWave utilizes the emission of light from the sample (solution) to rapidly and accurately measure temperature. It reads the temperature of the solution itself, instead of reading the temperature of the vessel. This makes iWave the most accurate temperature sensor on the market.
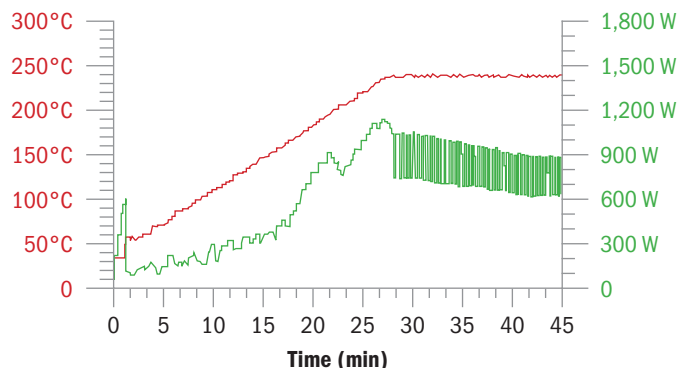
Figure 2. Temperature & Power Graph of Digestion of Crude Oil


The iWave contactless temperature control system automatically adjusts the power (green line) in order to prevent any exothermic reactions from the crude oil samples.

Table 2. Heavy Metal Results from ICP-MS Analysis

NIST 1634c	75As ppm	58Ni ppm	51V ppm
Sample 1	0.172	16.336	28.631
Sample 2	0.159	16.412	29.182
Sample 3	0.181	15.380	28.645
Average	0.171	16.042	28.819
% Recovery	108.05	91.46	102.23
STD DEV	0.0111	0.575	0.314
%RSD	0.0648	0.0359	0.0109

Figure 3. Before and After Digestion of Crude Oil
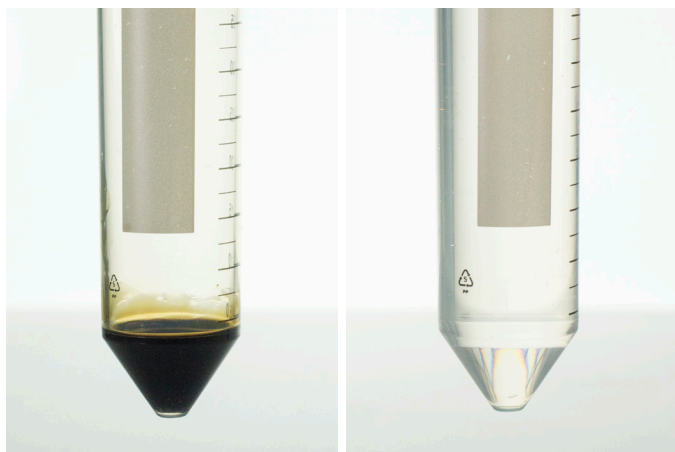
The high temperatures achieved using the iPrep vessels resulted in clear solutions when diluted to 50 mL