Acid Digestion of Difficult Oils and Plastics

Abstract

Sample preparation of heavy oils and thermoplastics for trace metals analysis presents a challenge to analytical laboratories. Traditionally, these types of samples were flamed off using a Bunsen burner or other device and then placed in a muffle furnace for several hours. Once the sample was flamed off and ashed successfully, it was then reconstituted in a weak acid solution. This method is not only lengthy, but also introduces the possibility of contamination. Microwave digestion has been used with some degree of success, however, varying sample types could not always be batched together.

CEM recently pioneered a major advancement in microwave digestion technology. Combining a single mode cavity (SMC) with rapid vortexing, the BLADE™ automated microwave digestion system can digest these difficult samples and many more quickly and completely. The BLADE automatically loads each sample into the microwave cavity for acid digestion and cooling. Once completed, it is returned to its original rack position and the next sample is processed. Each vessel can contain a different material and acid combination, providing ultimate flexibility for laboratory work flow.

Introduction

As we are in the midst of an energy transition, renewable power and electric vehicles are getting cheaper and the energy grid is getting greener. Oil production, however, still represents nearly 12 million barrels per day (BPD) in the United States alone according to data available from the Energy Information Administration.[1] Up to 42.5 gallons of oil products are produced from a single barrel of crude oil, with gasoline being the highest volume product (19.5 gallons or 46% of the crude oil), followed by diesel and heating oil. Following the top three are kerosene, jet fuel, and heavy residual fuel oils such as bunker oil.[2]

Approximately 4% of the world's oil production goes into the production of virgin plastics.[3] This represents more than 400 million metric tons of material being produced each year. Plastics are derived from naptha, which is created from the distillation process of crude oil. Naptha is then converted to ethene through the cracking process. The ethene is polymerized and then eventually extruded into plastic pellets, ready to be turned into one of the many plastic products used every day around the world. Plastics represent the profit center for the petrochemical industry and will continue to do so for the foreseeable future.

Materials and Methods

Instrumentation

The BLADE, an automated microwave digestion system from CEM, was used to prepare a variety of petrochemical samples. (**Figure 1**) The BLADE is a high-performance system that combines speed, simplicity, and automation to process samples sequentially. Samples were weighed into the 60 mL quartz vessel and acid was added. A simple snap-on cap was used, which simplified vessel assembly. The vessels were then loaded into one of two digestion racks. The system then automatically loaded the vessel into the cavity where it was digested and cooled and returned to its original rack position. Once complete, the next sample was processed. Every sample was under individual temperature and pressure control, which was documented and stored. A unique camera feature allows for visual monitoring of the digestion process, which is a great tool to confirm digestion, or for method development. Since samples are processed sequentially, any combination of sample and acid types can be placed into the rack for digestion. Samples were analyzed on an Agilent 7850 ICP-MS (Agilent Technologies, Santa Clara, CA).

Figure 1. BLADE System with Quartz Vessels

Sample Preparation

The samples for this study included a variety of oils and plastics. Oils ranged from lighter fractions such as mineral oil, to the heaviest of material such as bunker oil. The plastics included samples from the easier to digest polyethylene, to the much more robust polyethylene terephthalate (PET). The structure of this thermoplastic is shown in **Figure 2**. PET is widely used in industry, particularly for plastic beverage bottles. A total of three SRMs were digested to validate methodology. These standards included Wear Metals in Lubricating Oil (NIST SRM 1085c) as well as Additive Elements in Polyethylene (NIST SRM 2855 II and III). Sample weights were approximately 0.25 grams, and all samples were digested in triplicate. All digestion parameters are listed in **Table 1**. The samples, both pre and post digestion, are shown in **Figure 3**. The digested samples were all clear, colorless and particle free upon dilution to a final volume of 50 mL with DI H_2O.

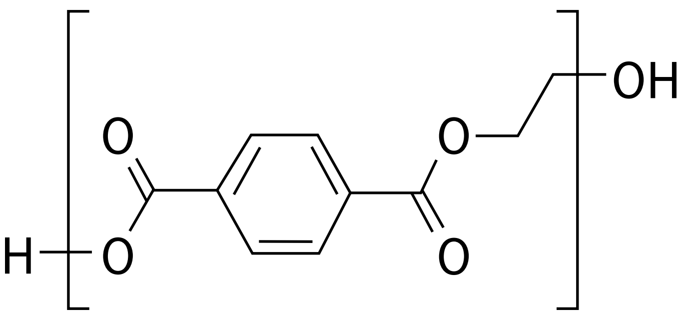

Figure 2. Molecular Structure of PET

Table 1. Digestion Parameters of Various Types of Oils and Plastics

Sample	Acid (s)	Temp. Required	Ramp Time (min)	Hold Time (min)
HDPE	5 mL HNO_3	220 °C	4:00	6:00
PVC	5 mL HNO_3	220 °C	4:00	6:00
Motor Oil	5 mL HNO_3	220 °C	4:00	6:00
Mineral Oil	5 mL HNO_3	220 °C	4:00	6:00
SRM 1085c	5 mL HNO_3	220 °C	4:00	6:00
SRM 2855 II	5 mL HNO_3	220 °C	4:00	6:00
SRM 2855 III	5 mL HNO_3	220 °C	4:00	6:00
PET	8 mL HNO_3	240 °C	5:00	8:00
Bunker Oil	8 mL HNO_3+ 2 mL H_2SO_4	240 °C	5:00	8:00

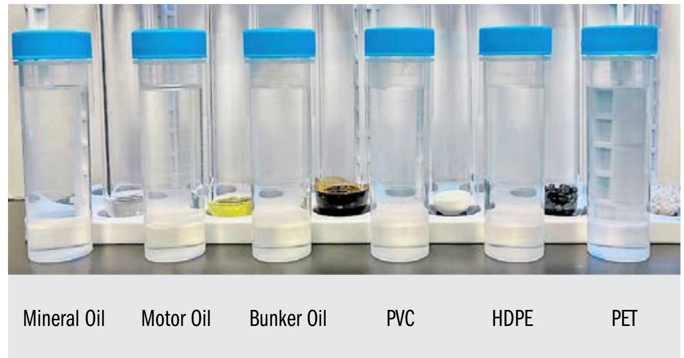

Figure 3. Samples Pre and Post Digestion (After Dilution)

Analysis

The metals of interest were selected based upon the availability of SRMs, as well as industry concerns regarding trace metal contaminants. Samples were analyzed on an Agilent 7850 ICP-MS with conditions listed in **Table 2**. The conditions listed were used to analyze all elements except Ca, which was analyzed using "H_2" tuning mode. The following elements were used as internal standards: Li, Sc, Ge, In, Rh, and Tb. No gas dilution techniques were used for this study.

Table 2. Instrument Conditions of the Agilent 7850 ICP-MS

Parameter	Value for [He] Mode
RF Power (W)	1550
Sampling Depth (mm)	8
Carrier Gas (L/min)	1.05
Dilution Gas	N/A
Helium Cell Gas (mL/min)	5.0
Energy Discrimination (V)	5.0

Results and Discussion

The results for NIST SRM 2855 II and III are shown in **Table 3** (page 3). The certified elements are the same for both, but concentration levels for zinc and calcium are roughly double. All results were excellent as compared to the certified values. The same was true for NIST SRM 1085c, which was certified for additional elements. These results are shown in **Table 4** (page 3).

Table 3. Percent Recoveries for NIST SRM 2855 II and 2855 III

2855 II Additive Elements in Polyethylene (N=3)		
Element	**Cert Values ppm**	**% Recovery**
Na	16	94.72
Ca	37.6	91.48
Ti	10.4	100.54
Cr	2.4	100.50
Zn	415	93.30

2855 III Additive Elements in Polyethylene (N=3)		
Element	**Cert Values ppm**	**% Recovery**
Na	16.4	95.55
Ca	77.2	92.09
Ti	10.4	100.36
Cr	2.4	112.41
Zn	807	99.58

Table 4. Percent Recoveries for NIST SRM 1085c

1085c Wear Metals in Lubricating Oil (N=3)		
Element	**Cert Values ppm**	**% Recovery**
Na	300	98.13
Ca	299	101.59
Ti	300	94.67
V	285	101.02
Cr	302	95.65
Ni	306	94.49
Cu	298	100.14
Zn	285	106.45
Cd	301	97.62
Pb	303	97.04

Conclusion

The BLADE proved to be both an effective and versatile instrument for preparing a wide range of petrochemical products. The ability to digest all types of plastics and oils (including bunker oil) in a single rack, provides end users with unmatched flexibility, as well as a faster turnaround, compared to other sample preparation methods. The BLADE also helps to streamline the workflow in the laboratory by allowing technicians to load the racks into the system and then attend to other tasks. In addition to oils and plastics, petrochemical labs can also prepare catalysts and other inorganic materials in the BLADE as well.

References

[1] U.S. Energy Information Administration. United States Crude Oil Production. https://tradingeconomics.com/united-states/crude-oil-production (accessed November 07, 2022).

[2] Statista Research Department. Products Produced from One Barrel of Crude Oil Breakdown. [Online] January 1, 2010. https://www.statista.com/statistics/856655/products-made-of-one-barrel-of-crude-oil/#statisticContainer (accessed December 1, 2022).

[3] Prevented Ocean Plastic. The Relationship Between Oil and Plastic and What That Means for Recycling. https://www.preventedoceanplastic.com/the-relationship-between-oil-and-plastic-and-what-that-means-for-recycling/#:~:text=Approximately%204%25%20of%20the%20world%E2%80%99s%20oil%20production%20goes,a%20five-step%20process%2C%20starting%20with%20crude%20oil%20extraction.%3A (accessed November 7, 2022).

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