Automated Microwave Sample Preparation of Difficult Petroleum and Polymer Matrices

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ABSTRACT

Sample preparation for metals analysis of petroleum and plastic products provides many challenges. Materials are difficult to sample and completely digest. Incomplete digestion can lead to background interferences. In addition, the typical sample size of 0.1 grams provides challenges for homogeneity as well as detection limits. Finally, the preparation is normally done in a batch environment that requires a lot of handling with no opportunity to automate the process. We will show a novel automated microwave digestion system and prepare samples such as bunker oil, Kevlar and other thermoplastics at the 0.25 gram range using only nitric acid. Methodologies will be presented and results will be discussed.

INSTRUMENTATION

The Discover SP-D Gold with high purity quartz vessels (HPQ) was used to digest the samples. A total of 24 samples were digested in an eight hour time frame.

The majority of the samples were run unattended overnight. The temperature and pressure of each sample were monitored throughout the digestion process and were recorded for every sample. Samples were analyzed via ICP- OES and ICP-MS.

Discover SP-D Gold

HPQ Vessel

ANALYTICAL PROCEDURE

Samples included NIST SRM 1643 (fuel oil), SRM 2855 (both high and low density polyethylene), Kevlar and bunker oil. Each sample was weighed into an HPQ vessel with stir bar, acid was added and a snap on cap was placed on each vessel.

Sample sizes for Fuel Oil, Bunker Oil, and Kevlar were 0.3 g. Sample size for the HDPE polymer was 0.5 g. Ten mL of HNO_3 were used to digest the HDPE and fuel oil. Nine mL of HNO_3 and 0.5 mL of HCl were used to digest the Bunker Oil and the Kevlar samples. All samples were run in the CEM Discover SP-D Gold microwave digestion system using ramp-to-temperature programs.

Prior to sampling, both the Bunker Oil and Fuel Oil were heated in a boiling water bath in order to decrease the viscosity of the sample and thus obtain a more homogenous sample.

Care was taken to ensure that the Kevlar fiber was completely covered in acid prior to digestion.

The Fuel Oil was analyzed for V, Co and Ni. The LDPE sample was analyzed for As, Cr and Cd, and the HDPE was analyzed for Zi.

The Kevlar was spiked with 0.5 mL of a 50 ppm STD of Al, As, Hg, Fe and Mg and blanks were run with each sample.

Samples were diluted to 50 mL with deionized water, and were run on either ICP-OES or ICP-MS. Digestion conditions and results are listed in Tables 1, 2, 3 & 4 respectively.

Table 1. **Digestion Conditions for Discover SP-D Gold**

Sample Type	Number of Stages	Final Hold Temperature	Total Run Time (Including Cool Down)
Bunker Oil	2	250° C	20 minutes
Fuel Oil NIST SRM 1634c	2	250° C	20 minutes
Kevlar	2	250° C	20 minutes
HDPE NIST SRM 2855	1	210° C	20 minutes
LDPE NIST SRM 2855	1	210° C	20 minutes

Table 2. **Results of NIST SRM 2855 HDPE**

	66 Zn (ppm-STD)	68 Zn (ppm-STD)
Sample 1	425.830	426.230
Sample 2	390.230	390.240
Sample 3	411.230	408.720
Sample 4	397.100	400.100
Average	406.098	406.323
STD DEV	15.795	15.269
RSD	3.89%	3.76%
Actual	415.000	415.000
Recovery	97.850%	97.900%

Table 3. **Results of NIST SRM 1634c Fuel Oil**

	51 V (ppm)	59 Co (ppm)	60 Ni (ppm)
Sample 1	27.971	0.147	16.778
Sample 2	27.893	0.139	16.741
Sample 3	27.837	0.148	16.406
Average	27.900	0.145	16.642
STD DEV	0.0673	0.0049	0.2049
RSD	0.24%	3.41%	1.23%
Actual	28.19	0.151	17.54
Recovery	99.0%	95.8%	94.9%

Table 4. **Spike Recovery Results of Kevlar**

	75 As (ppm)	202 Hg (ppm)	27 Al (ppm)	57 Fe (ppm)	(ppm)
Sample 1	43.35	50.79	59.49	58.69	53.18
Sample 2	43.29	45.78	48.73	59.01	47.88
Sample 3	45.39	45.2	44.07	52.52	42.78
Sample 4	57.83	57.52	40.47	50.83	41.74
Sample 5	42.35	46.18	48.8	59.15	45.38
Sample 6	43.58	42.22	55.96	59.55	51.6
Average	45.965	47.948	49.587	56.625	47.093
Actual	50	50	50	50	50
Recovery	91.93%	95.90%	99.17%	113.25%	94.19%

Table 5. **Results of NIST SRM 2855 LDPE**

	52 Cr (ppm-STD)	111 Cd (ppm-STD)	75 As (ppm-STD)
Sample 1	21.100	17.060	0.243
Sample 2	23.110	17.180	0.246
Sample 3	23.150	17.790	0.259
Sample 4	20.810	17.580	0.246
Average	22.043	17.403	0.249
STD DEV	1.261	0.341	0.007
RSD	5.720%	1.960%	2.870%
Actual	20.200	19.450	0.285
Recovery	109.100%	89.500%	87.300%

Figure 1.
Bunker Oil before & after digestion

DISCUSSION

All of these sample matrices are very difficult to put into solution. Bunker oil is also known as #6 fuel oil. It is a very heavy oil, with a viscosity similar to molasses. Kevlar is five times stronger than steel, and gets its strength from its many interchain bonds. Polyethylene is a thermoplastic polymer consisting of very long chain hydrocarbons.

The polymers were the easiest to digest, requiring just a one-step method. The oils and Kevlar required a two-step procedure, but all were completed in 20 minutes including cool down. All samples were completely digested and clear and colorless digests were obtained after dilution, as shown in Figure 1. Very little volume loss indicated that recoveries of even volatile elements would be ensured. Larger samples can be digested but a slight color may be present after dilution.

CONCLUSIONS

The Discover SP-D Gold provides a new tool for analytical chemists to use to prepare difficult sample types. Using the Discover SP-D Gold we were able to digest difficult matrices such as Oils, Polymers and Kevlar. We were able to obtain clear and particle free digests of all samples. Results show good agreement with certified values. The low blank values prove that the HPQ vessel is a suitable choice for trace metals analysis. The automation of the SP-D Gold frees chemists up to attend to other duties while the system runs completely unattended.