

## Digestion of Petroleum Products and Lubricants in Less than 90 Minutes

Conventional methods for the sample preparation of petroleum products and lubricants like dilution or ashing suffer from severe drawbacks. Microwave-assisted acid digestion according to ASTM D7876 is a beneficial approach to achieve reliable results in a short time frame.



### 1 Introduction

Petroleum products and lubricants are routinely analyzed for their elemental content for various reasons.

In crude and residual oils the concentrations of silicon, aluminum, vanadium, nickel, iron and sodium are used to define their quality and value. Nickel and vanadium in crude oil can deactivate catalysts during processing, but also initiate corrosion in motors and boilers during the combustion when present in fuels. Silicon and aluminum serve as indicators for the presence of abrasive silicate particles, causing harm to the combustion engine. Being present as particles adds the necessity for very thorough high-speed mixing to the sampling and the sample preparation procedures. Otherwise lower recoveries for particle bound elements like silicon and partially aluminum can be experienced.

In unused products like lubricating oils the concentration of additives (which contain metals such as calcium, copper, magnesium, phosphorus, sulfur and zinc) is an important quality control parameter.

There are several standard methods available, which describe the sample preparation prior to elemental analysis in petroleum products. Basically these methods apply two different approaches:

- **Dilution** of the oil with an organic solvent such as xylene and kerosene and direct introduction into an AAS or ICP-OES. This method is fast but not applicable for samples containing metal particles. Typical drawbacks are clogged nebulizers, instable plasma conditions and measurement interferences. Common methods applying dilution are ASTM D4951, D5708 (Test Method A), D5863 (Test Method B), or D5185.
- **Dry ashing** (with subsequent acid digestion) of the sample to eliminate the organic matrix. The inorganic residues (ash) are dissolved with (diluted) acids in an open digestion system and subsequently analyzed as an aqueous solution. This method allows for processing of large sample quantities (> 10 g), but suffers from significant errors related to loss of volatile elements and ashing times of several hours. Common methods for dry ashing are IP 501, ASTM D5708 (Test Method B), or D5863 (Test Method A).

Due to the lower limits of determination, modern measuring techniques such as ICP-OES or ICP-MS do not require several grams of sample to obtain accurate analytical data. This fact opens the door for modern sample preparation techniques like microwave-assisted closed-vessel digestion.

The release of the standard practice ASTM D7876 (which covers sample decomposition by using microwave heating) confirms the increased importance of this sample preparation method in the petrochemical industry.

In order to prove the excellent suitability of microwave-assisted closed-vessel digestion, four different reference materials were digested and the results obtained thereof were compared with conventional methods ASTM D5708, D4951, and D5185.

## 2 Instrumentation



Figure 1: Multiwave 5000

High shear mixing was performed with POLYTRON® System PT 3100 D from KINEMATICA AG with a 10 cm probe.

The digestions were carried out in Multiwave PRO, the predecessor of the present model Multiwave 5000. Using the same rotors, vessels and accessories all methods are reliably adaptable for Multiwave 5000.

All digestions were performed with Rotor 8NXF100. Due to the simultaneous pressure control for all eight vessels, this rotor provides the necessary reaction control for such highly reactive samples.

For comparison purposes, the digested solutions were measured with both ICP-OES and ICP-MS.

For ICP-OES measurements a SPECTRO CIROS VISION was used, equipped with a cross-flow nebulizer, a PFA Scott spray-chamber, and a 1.8 mm aluminum oxide injector.

For ICP-MS an Agilent 7500ce / 7900 was used. Ge, In and Lu were used as internal standard. Prior to ICP-MS measurement, the digested solutions were 10-fold diluted.

## 3 Experimental

### 3.1 Samples

Four representative samples with known trace element concentrations were used for this study:

- Engine Oil Lubricants (Sample ID: LU1301) from an ASTM Inter Laboratory Crosscheck Program
- Crude Oil (Sample ID: CO1011) from an ASTM Inter Laboratory Crosscheck Program
- NIST SRM 1634c "Trace Elements in Residual Fuel Oil"
- Fuel Oil (Sample ID: F61405) from ASTM Committee D-2 Proficiency Testing Program (May 2014)

### 3.2 One-step Digestion Procedure

#### 3.2.1 Direct Digestion with Nitric Acid

Approx. 0.3 g of the respective samples was weighed directly into a 100 mL TFM liner. To investigate the sample homogeneity all samples were processed in triplicates.

After addition of a magnetic stir bar, 7 mL HNO<sub>3</sub> (65%) and 1 mL H<sub>2</sub>O<sub>2</sub> (30%) were added to the vessel.

The vessels were closed, the rotor loaded and the digestion program (see Table 1) was started. After cooling, the samples were transferred into 50 mL tubes, filled up, and analyzed.

#### 3.2.2 Digestion with Fluoride

For a complete dissolution of silicon, addition of hydrofluoric acid (or a fluoride salt like ammonium fluoride) might be required.

For this reason a second set of digestions was performed as described in chapter 3.2.1. Prior to digestion additionally 200 µL of a 50% (wt/wt) NH<sub>4</sub>F solution (1 g NH<sub>4</sub>F diluted in 1 mL deionized water) were added to the vessels. In this way HF is generated in situ, while direct handling of concentrated hydrofluoric acid is avoided.

The samples without HF (3.2.1) were measured on ICP-OES only, whereas the samples with HF (3.2.2) were analyzed on both ICP-OES and ICP-MS.

	Step	Power/ Temp.	Time [min]	Fan	Stirring
1	Hold	350 W	20:00	1	high
2	Ramp	800 W	15:00	1	high
3	Hold	800 W	30:00	1	high
	Cooling	70°C		3	off

Table 1: Digestion program

IR temperature limit: 240°C

Pressure limit: 60 bar

Max. pressure increase rate: 0.3 bar/s

**Note:** This program is suitable for 4 vessels. When using 8 vessels increase the power from 350/800 W to 500/1200 W, respectively.

### 3.3 Two-step Digestion Procedure

#### 3.3.1 Principle

Depending on the sample weight the pressure control limits the achievable temperature. If there are stable and difficult-to-digest components in the sample, the temperature might not be sufficient to break down all resins, aromatic- and poly-aromatic substances, a yellow color will remain. Depending on the robustness of the sample introduction system, this will affect the nebulization efficiency of the analytical instrument and cause a problem to the sensitivity of the calibration function.

An approach to overcome this effect and to further increase the sample size could be the "Two-step digestion procedure":

- During the first digestion most of the reactive organic matrix is destroyed.
- Careful venting after the first digestion step releases the reaction gases that limit the heating of the sample.
- Freshly added oxidant and a higher end temperature achievable in the 2<sup>nd</sup> step help to destroy even the stable residues from the 1<sup>st</sup> digestion step.

#### 3.3.2 Procedure

A 10 mL subsample of fuel oil was drawn from the original 1.1 L metal can after heating to 60°C and vigorously shaking of the can. The taken subsample was subsequently exposed to high-shear mixing. Afterwards approx. 0.6 g sample was weighed directly into a 100 mL TFM liner.

##### First step:

For the first step 8 mL of HNO<sub>3</sub> and 1 mL of H<sub>2</sub>O<sub>2</sub> were added.

	Step	Power/ Temp.	Time [min]	Fan	Stirring
1	Hold	600 W	10:00	1	off
2	Hold	900 W	40:00	1	off
3	Cooling	60 °C		3	off

Table 2: First step - digestion program

Experiment conditions: 0.5 bar/sec.

**Note:** This program is suitable for 8 vessels. When using 4 vessels decrease the power from 600 W to 400 W.

After cooling down to 60°C the venting screws were opened carefully to slowly remove the reaction gases.

##### Second step:

For the second step 2 mL of fresh HNO<sub>3</sub> and 2 mL of H<sub>2</sub>O<sub>2</sub> were added. The addition of H<sub>2</sub>O<sub>2</sub> generated gas bubbles which removed the NO<sub>x</sub> from the liner.

If 200 µL 50 % (wt/wt) NH<sub>4</sub>F was needed for the digestion, it was added immediately before closing the vessels.

	Step	Power/ Temp.	Time [min]	Fan	Stirring
1	Ramp	1500 W	10:00	1	off
2	Hold	1500 W	30:00	1	off
3	Cooling	70 °C		3	off

Table 3: Second step - digestion program

Experiment conditions: 0.5 bar/sec.

**Note:** This program is suitable for 8 vessels. When using 4 vessels decrease the power from 1500 W to 1100 W.

## 4 Results

### 4.1 Digestion with One Step

The element contents of NIST residual fuel oil (Table 4) are compared with the certified value.

Element	D7876 ICP-OES [µg/g]	D7876 ICP-MS [µg/g]	Certified Value [µg/g]
Al	3.6 ± 0.6	-	-
Co	-	0.14 ± 0.05	0.1510 ± 0.0051
Fe	49.5 ± 1.5	47.8 ± 2.9	-
Mg	2.0 ± 0.1	-	-
Na	42 ± 2	33 ± 2	37 *)
Ni	15.7 ± 0.2	17.3 ± 0.3	17.54 ± 0.21
V	27.1 ± 0.4	28.6 ± 0.2	28.19 ± 0.40

Table 4: Results for Residual Fuel Oil (NIST SRM 1634c)

ICP-OES: n = 6 (mean of digestions with and without HF)

ICP-MS: n = 3 (only digestions with HF)

\*) only for information

The measured element content of engine oil lubricants (Table 5) and crude oil (Table 6) are compared with the values obtained during the ASTM inter laboratory crosscheck, using the respective ASTM standard practice.

Element	D7876 ICP-OES [µg/g]	D7876 ICP-MS [µg/g]	D4951 ICP-OES [µg/g]	D5185 ICP-OES [µg/g]
<b>Al</b>	4.1 ± 1.1	-	-	-
<b>B</b>	-	249 ± 1	229 ± 26	-
<b>Ca</b>	2130 ± 70	2170 ± 10	2400 ± 100	2390 ± 200
<b>Fe</b>	0.7 ± 0.1	< 3.5	-	-
<b>Mg</b>	9.0 ± 0.5	-	-	-
<b>Mo</b>	79.9 ± 1.5	78.5 ± 0.4	77.0 ± 6.0	74.3 ± 10.1
<b>Na</b>	< 10	< 10	-	-
<b>Ni</b>	0.49 ± 0.12	< 5	-	-
<b>P</b>	-	831 ± 16	761 ± 38	743 ± 66
<b>S</b>	-	2830 ± 90	2950 ± 220	2830 ± 370
<b>Ti</b>	94.5 ± 1.8	-	-	-
<b>V</b>	1.1 ± 0.1	-	-	-
<b>Zn</b>	690 ± 20	837 ± 7	837 ± 42	825 ± 76

Table 5: Results for Engine Oil Lubricants (LU1301)

ICP-OES: n = 6 (mean of digestions with and without HF)

ICP-MS: n = 3 (only digestions with HF)

Element	D7876 ICP-OES [µg/g]	D7876 ICP-MS [µg/g]	D5708 (A) ICP-OES [µg/g]	D5708 (B) ICP-OES [µg/g]
<b>Fe</b>	6.7 ± 0.6	8.4 ± 0.3	5.4 ± 0.6	6.2 ± 1.2
<b>Mg</b>	2.3 ± 0.3	-	-	-
<b>Mo</b>	1.1 ± 0.1	0.98 ± 0.02	-	-
<b>Na</b>	60 ± 13	54 ± 3	-	-
<b>Ni</b>	57.8 ± 0.3	65.2 ± 0.9	63.6 ± 7.4	59.8 ± 6.0
<b>S</b>	-	2.707 ± 0.034 [%]	-	-
<b>Si</b>	81 ± 6 *)	-	-	-
<b>Ti</b>	2.08 ± 0.05	-	-	-
<b>V</b>	263 ± 1	255 ± 4	267 ± 30	255 ± 27

Table 6: Results for Crude Oil (CO1011)

ICP-OES: n = 6 (mean of digestions with and without HF)

ICP-MS: n = 3 (only digestions with HF)

\*) n=3 (only digestions with HF)

The measured values after microwave digestion according to ASTM D7876 are in good agreement with the data obtained from conventional methods, which have been determined in an inter laboratory crosscheck (engine oil lubricants and crude oil) as well as are stated on the NIST certificate (residual fuel oil).

Moreover, additional elements (which have not been considered in the inter laboratory crosschecks or the NIST certificate) have been measured for comparison purposes. For most of these elements the values from ICP-OES and ICP-MS are well comparable, indicating a reliable sample preparation procedure.

Results for ICP-OES measurement were combined from both acid mixtures (mean value of digestions with and without NH<sub>4</sub>F), as - except for silicon in crude oil - no significant differences could be observed. The low standard deviations observed for the 6 independent digested samples indicate a homogeneous sample and show that 0.5 g of sample, instead of the >10 g conventionally used, are sufficient to achieve representative results.

Silicon could be determined only from the solutions containing NH<sub>4</sub>F, and did work on the ICP-OES only due to its HF-resistant layout. For the solutions without NH<sub>4</sub>F, results for silicon were in the range of the background level. With the ICP-MS, silicon could not be measured due to the high blank values observed.

Based on these data no clear suggestion can be given for the use of NH<sub>4</sub>F. It will depend on the amount and type of silicon present in the sample, and will require investigation for individual samples.

## 4.2 Digestion with Two Steps

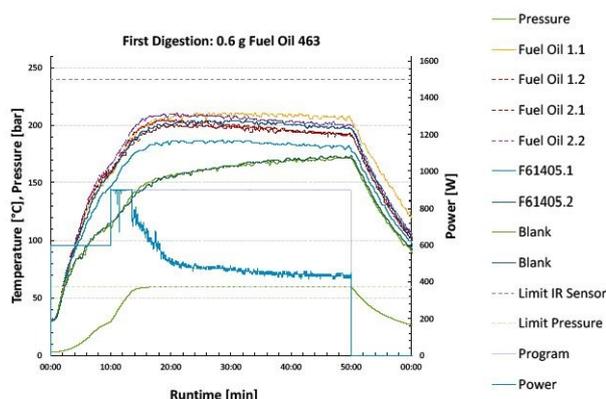


Figure 2: Two-step digestion procedure: first digestion

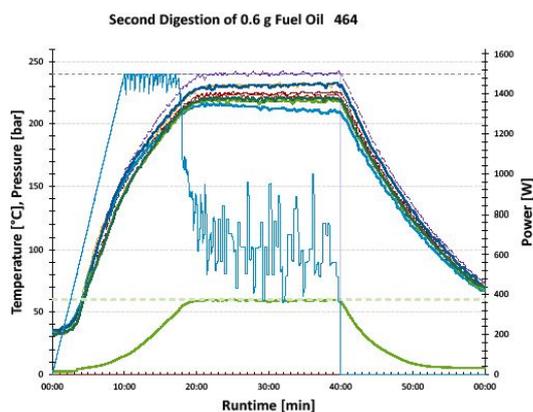


Figure 3: Two-step digestion procedure: second digestion

Data chart in Fig. 2 shows strong exothermic reaction with quick buildup of pressure due to the generation of reaction gases. Shortly after the power step to 900 W the pressure limit is reached and the power limited. The temperature cannot increase any more.

After cooling down, releasing the reaction gases and filling up with fresh oxidants again, there are much less organic substances present than in the 1<sup>st</sup> digestion step. A more drastic heating program can be used to achieve highest possible digestion temperatures.

The second run is finally IR temperature controlled. All samples are kept at an IR temperature between 210 °C and 240 °C, which is equivalent to an internal temperature of about 260 °C. This is sufficient to digest even the most stable substances in fuel oils.

	Reference [µg/g]	Two-step [µg/g]	Two-step with NH <sub>4</sub> F [µg/g]
<b>Al</b>	7.5 ± 1.1	8.10 ± 0.6	8.1 ± 0.4
<b>Si</b>	15 ± 2.2	10.23 ± 0.6	4.2 ± 2.2
<b>Ca</b>	13 ± 2.5	48 ± 27	23.8 ± 1
<b>Fe</b>	53 ± 12	86 ± 12	76.7 ± 7
<b>Na</b>	22 ± 4.3	26.8 ± 1.4	25.8 ± 0.9
<b>Ni</b>	39 ± 2.7	39.3 ± 6.7	37.2 ± 3.9
<b>V</b>	78 ± 4.3	80.8 ± 9.3	78.5 ± 5.6

Table 7: Results of Residual Fuel Oil (ASTM F61405)

The results for Al, Ni, Na, V show very good agreement with the reported values from the lab proficiency testing exercise in 2014. Positive and erratic deviations of Fe and Ca may be attributed to contamination by storage container (Fe) and laboratory environment (Ca). The low recoveries for Si cannot be improved by NH<sub>4</sub>F addition to the digestion acid of the second step. Also spectroscopic issues can be excluded.

Moreover there are reports that Si values at that low level are in good agreement even after digestion with HNO<sub>3</sub> only. So a possible reason can be an incomplete homogenization of the sample within the storage container prior to taking a smaller subsample for the high-shear mixer. So there are good chances that with appropriate care in sampling and mixing the three mentioned elements will also be determined correctly.

## 5 Conclusion

Multiwave 5000 with Rotor 8NXF100 is the ideal solution when it comes to microwave-assisted digestion of various petroleum products and lubricants according to ASTM D7876.

The unique simultaneous pressure control in all vessels allows for digestion of sample weights up to 0.5 g. The high digestion temperature provides reproducible digestion conditions, thus accurate results, within a reasonable time frame (less than 1.5 hours incl. cooling time) compared to conventional methods. The closed-vessel design minimizes the risk of contamination and loss of volatile analytes, and it requires small amounts of reagents only. This reduces both the consumption of expensive reagents and the expensive disposal of hazardous waste.

The sample weight is limited due to high carbon content and possible excessive reaction behavior. For a few types of raw oil samples it is possible to increase the sample weight to about 0.8 g. For residual fuel oils or F6 marine fuels or vacuum residues the first digestion step will probably not

achieve sufficient digestion quality to vent the vessels without foaming and sample losses.

Considering the detection power and small sample consumption of modern simultaneous ICP-OES equipment, transfer of samples into a final measuring solution of 15 – 20 mL is sufficient. From the aspect of the detection limit this is equivalent to triple the sample weight with a dilution to a final volume of 50 mL.

To avoid handling of concentrated hydrofluoric acid, the use of solid  $\text{NH}_4\text{F}$  provides a convenient and safer workaround.

Due to its robustness this system can be applied to a variety of petrochemical samples and facilitates demanding sample preparation for subsequent routine analysis.

## 6 References

ASTM D7876-13, Standard Practice for Practice for Sample Decomposition Using Microwave Heating (With or Without Prior Ashing) for Atomic Spectroscopic Elemental Determination in Petroleum Products and Lubricant

ASTM D-7455-14, Standard Practice for Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis

ASTM D4951-14, Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

ASTM D5185-13e1, Standard Test Method for Multi-element Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

ASTM D5708-12, Standard Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry

ASTM D5863 - 00a(2011), Standard Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry

IP 501: Determination of aluminum, silicon, vanadium, nickel, iron, sodium, calcium, zinc and phosphorous in residual fuel oil by ashing, fusion and inductively coupled plasma emission spectrometry

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