



Less than 90 Minutes Turnaround Time for Trace Metal Analysis on Petroleum Products

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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 which achieves reliable results in a short time frame.

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. The presence of silicon and aluminum in residual fuel oils causes abrasion within the combustion engine. Before use, products like lubricating oils are tested to determine the concentration of additives (which contain metals such as calcium, copper, magnesium, phosphorus, sulphur and zinc) as this is an important quality control parameter.

Standard Methods

There are several standard methods available which describe the sample preparation prior to elemental analysis in petroleum products. These methods mainly apply two different approaches. The first method incorporates the dilution of the oil with an organic solvent and direct introduction into an AAS or ICP-OES (ASTM D4951, D5708 – A, D5863 – B, D5185). This method is fast but not applicable for samples containing larger particles. Typical drawbacks are clogged nebulisers, instable plasma conditions and measurement interferences. The second frequently used method is dry ashing (with subsequent acid digestion); dry ashing burns off the organic matrix of the sample. The inorganic residues, the ashes, are dissolved with acids in an open digestion system and subsequently analysed as an aqueous solution (IP 501, ASTM D5708 – B, or D5863 – A). This method allows for processing of large sample quantities (> 10 g) but suffers from significant errors related to loss of volatile elements and results in turnaround times in the range of 10 hours.

Current Change of Technology

More and more laboratories are changing their analytical measuring equipment from FAAS to modern measuring techniques such as ICP-OES or ICP-MS. There are several advantages provided by these techniques: they are rapid, provide multi-elemental capability and, especially for ICP-MS, have a wide dynamic range. Additionally, they have much lower limits of determination and therefore 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 new 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.

Microwave-Assisted Closed Vessel Digestion

Using microwave-assisted closed-vessel digestion, the sample is decomposed with concentrated acids under pressure resulting in a clear aqueous solution with low residual carbon content. Due to the application of closed vessels which withstand an operating pressure of up to 80 bar, the temperature is not restricted to the boiling point of the acids. According to the Arrhenius Law, a 10 °C increase in temperature means a 2-fold acceleration of the reaction and halving of the reaction time. As a result of the achievable high temperature the time required for complete digestion is significantly reduced. Microwaves are the perfect heating source as they heat the liquid bulk directly while the surroundings, such as vessels, remain comparably cool. As a consequence, microwave heating is fast and energy-efficient, saving additional process time. Further advantages of this modern sample preparation technique are no loss of volatiles and a minimised risk of contaminations. Based on the precise documentation, the sample preparation procedure is highly reproducible.

Proof of Principle

In order to compare conventional methods such as ASTM D5708, D5863, D4951, D5185 and IP 501 with microwave-assisted closed-vessel digestion an engine oil lubricant, a crude oil sample and a "NIST standard reference material 1634c – trace elements in fuel oil" were investigated. The engine oil lubricant and the crude oil sample were part of an ASTM interlaboratory cross-check program. Anton Paar's Multiwave PRO with Rotor 8NXF100 was used to digest the samples. Approximately 0.5 g of the respective samples were digested under stirring for 65 minutes with a temperature limit of 260 °C and a pressure limit of 60 bar using a mixture of HNO₃ (65 %) and H₂O₂ (30 %) as reagents (see Fig. 1). To investigate the sample homogeneity, even when small sample amounts are used, all samples were processed in triplicates. For a complete dissolution of silicon, the addition of hydrofluoric acid (or a fluoride salt like ammonium fluoride) might be required. For this reason a second set of digestions was performed after adding a 50 % NH₄F solution to the reagent mixture. In this way HF is generated in situ, while direct handling of concentrated hydrofluoric acid is avoided. The samples without NH₄F were measured on ICP-OES only, whereas the samples with NH₄F were analysed on both ICP-OES and ICP-MS. Prior to measuring with ICP-MS the samples were diluted 1 + 9.

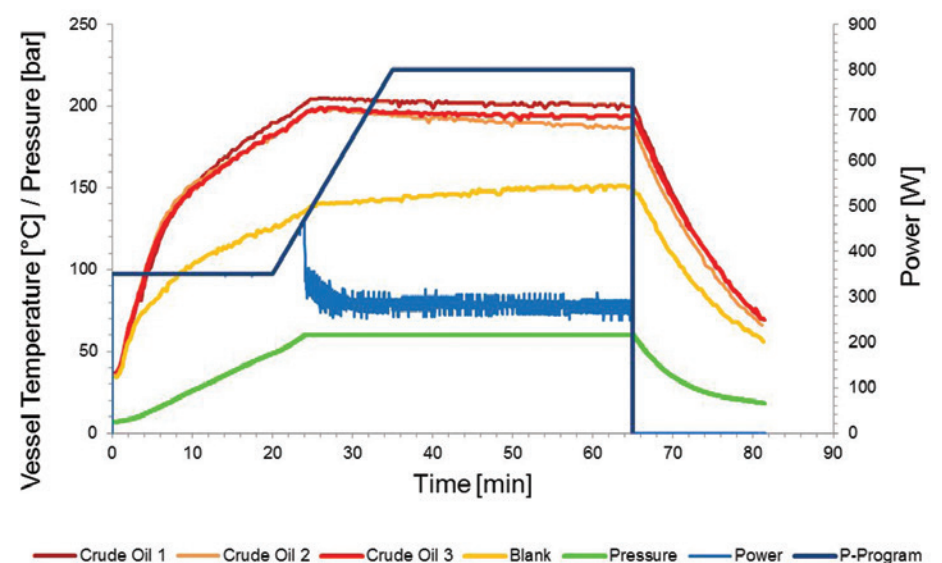


Fig. 1: Digestion program of crude oil samples. The introduced microwave power (blue line) follows the preset power program until the pressure limit of 60 bar (green line) is reached in any of the monitored vessels. If this is the case, the power is reduced accordingly. The three crude oil samples reach a vessel surface temperature of about 200 °C; the blank vessel temperature (yellow line) is lower as no reaction happens inside. As the vessels are continuously cooled to remove overheat and to minimise material stress, the surface temperatures are lower compared to the internal temperatures (digestion temperatures). If the inner temperature is requested, an immersion temperature probe can be used for the digestion. It can be clearly seen that reactive samples such as oil create a high pressure and high temperature during digestion. Therefore, a prerequisite for results is a microwave instrument which withstands both high temperature and high pressure at the same time.

Results

The measured element contents of engine oil lubricants, shown in Table 1, and of crude oil, shown in Table 2, are compared with the values obtained during the ASTM interlaboratory cross-check. The element contents of NIST fuel oil, shown in Table 3, are compared with the certified value.

Table 1: Results for Engine Oil Lubricants

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

ICP-OES: n = 6 (mean of digestions with and without NH_4F)

ICP-MS: n = 3 (only digestions with NH_4F)

Table 2: Results for Crude Oil

	D7876 ICP-OES [$\mu\text{g}\cdot\text{g}^{-1}$]	D7876 ICP-MS [$\mu\text{g}\cdot\text{g}^{-1}$]	D5708 (A) ICP-OES [$\mu\text{g}\cdot\text{g}^{-1}$]	D5708 (B) ICP-OES [$\mu\text{g}\cdot\text{g}^{-1}$]
Fe	6.7 ± 0.6	8.35 ± 0.27	5.4 ± 0.6	6.2 ± 1.2
Mg	2.3 ± 0.3			
Mo	1.1 ± 0.1	0.98 ± 0.02		
Na	60 ± 13	54 ± 3		
Ni	57.8 ± 0.3	65.2 ± 0.9	63.6 ± 7.4	59.8 ± 6.0
S		2.71 ± 0.03 [%]		
Si	81 ± 6*			
Ti	2.08 ± 0.05			
V	263 ± 1	255 ± 4	267 ± 30	255 ± 27

ICP-OES: n = 6 (mean of digestions with and without NH_4F)

ICP-MS: n = 3 (only digestions with NH_4F)

*) n = 3 (only digestions with NH_4F)

Table 3: Results for Residual Fuel Oil (NIST SRM 1634c)

	D7865 ICP-OES [$\mu\text{g}\cdot\text{g}^{-1}$]	D7865 ICP-MS [$\mu\text{g}\cdot\text{g}^{-1}$]	Certified Value [$\mu\text{g}\cdot\text{g}^{-1}$]
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	17.2 ± 0.3	17.54 ± 0.21
V	27.1 ± 0.4	28.6 ± 0.2	28.19 ± 0.40

NICP-OES: n = 6 (mean of digestions with and without NH_4F)

ICP-MS: n = 3 (only digestions with NH_4F)

*information value

The measured values after microwave digestion are in good agreement with the data obtained from conventional methods. Additional elements (which have not been considered in the interlaboratory cross-checks or the NIST certificate) have been measured for comparison purposes. For most of these elements the values from ICP-OES and ICP-MS are 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_4F) as no significant differences could be observed. The low standard deviations observed for the 6 independently digested samples indicate a homogenous sample and shows 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_4F and this determination only worked on the ICP-OES due to its HF-resistant layout. Generally, it depends on the amount and type of silicon present in the sample whether NH_4F (HF) has to be used or not.

Why Use Anton Paar's Multiwave PRO Plus Rotor 8NXF100?

Multiwave PRO combined with Rotor 8NXF100 can hold a temperature of 260 °C and simultaneously withstands a pressure of 60 bar for a time frame of more than 2 hours. These combined specifications are required to obtain complete digestions for petroleum products. Petroleum products are highly reactive; they create a lot of pressure and heat during the digestion. To prevent damage to the equipment it is essential to have the temperature and pressure under full control. The Rotor 8NXF100 provides wireless pressure (Fig. 2) and temperature control of each vessel. The pressure is measured 50 times per second and is simultaneously monitored in all reaction vessels. If the pressure or the pressure increase rates exceed the preset limits the microwave power is immediately shut off and, if necessary, the vessels are cooled via a guided airflow along the vessel surface.

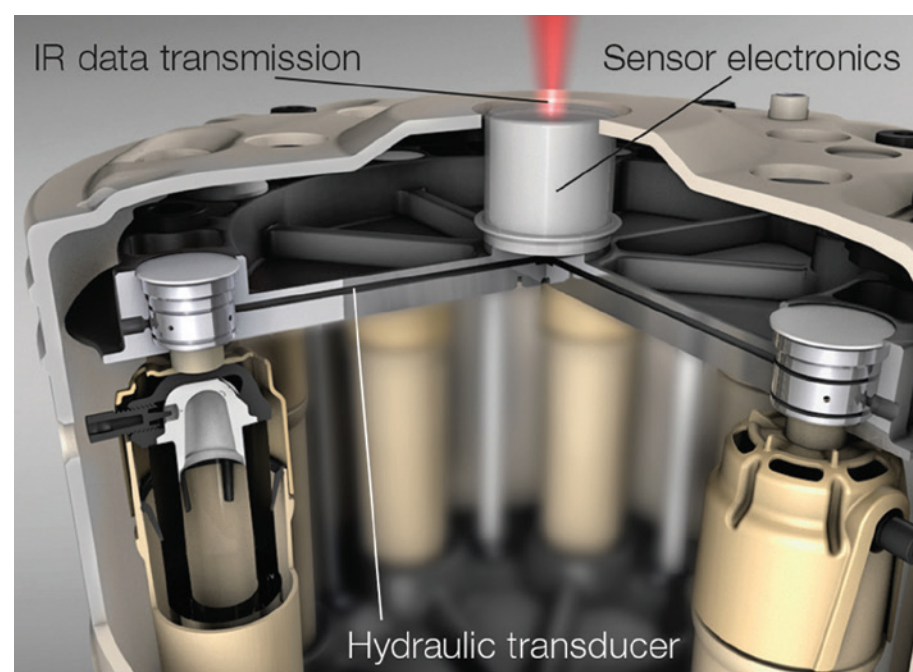


Fig. 2: Schematic of the pressure measurement of Rotor 8N

Conclusion

Multiwave PRO 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 reaction control in all vessels allows for digestion of comparably high sample weights. The high digestion temperature provides reproducible digestion conditions and therefore accurate results, within a reasonable time frame (less than 1.5 hours incl. cooling time). The closed-vessel design minimizes the risk of contamination and loss of volatile analytes, and requires small amounts of reagents only. This reduces both the consumption of expensive reagents and the costly disposal of hazardous waste. To avoid handling concentrated hydrofluoric acid, the use of solid NH_4F instead provides a convenient and safer workaround. Low sample amounts of 0.5 g are enough to obtain representative results. Due to its robustness this system can be applied to a variety of petrochemical samples and facilitates demanding sample preparation for subsequent routine analysis.

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