Routine Trace Metal Analysis of Marine Fuels Using Microwave Acid Digestion

Multiwave PRO

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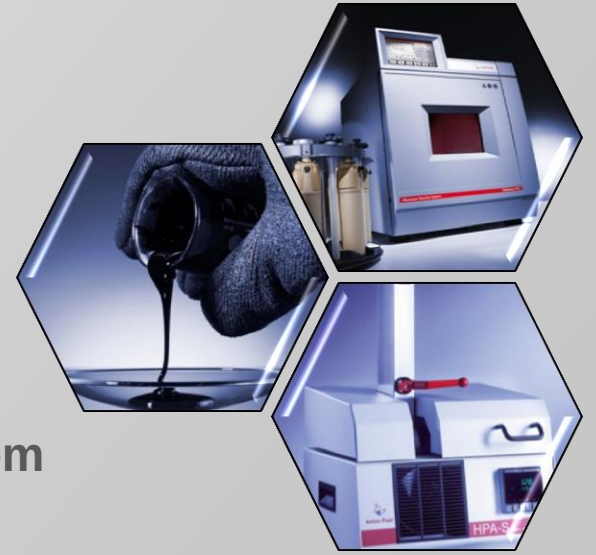

Anton Paar – Company Profile

Establishment	1922
Owner	Charitable Santner Foundation
CEO	Dr. Friedrich Santner
Chairman of the Board	DI Ulrich Santner
Number of employees (*as of the end of 2015)	967* Headquarters 2.259* worldwide
Turnover 2015	~ 260 million Euros
Export share	93 %
Investment in R&D	20 % of the annual turnover

Company Presence - Worldwide

Trace Metal Determination in Petro Products

- .. to define the quality
- .. to prevent deactivation of catalysts
- .. to monitor and analyze contaminations
- ...to follow regulations and much more…

Common sample preparation techniques:

- Dry ashing with open vessel acid digestion (e.g. IP 501, ASTM D5708-B, or D5863-A)
- Direct dilution using organic solvents (e.g. ASTM D4951, D5708-A, D5863-B, D5185)
- Microwave-assisted acid digestion (ASTM D7876)

Trace metal determination
ICP-OES, ICP-MS, FAAS

Limitations of Conventional Methods

- Dilution Method:
  - Metal particles > 5 µm cannot be measured with the dilution method
  - Clogged nebulizers
  - Employed organic solvents interfere with modern measuring systems
  - Special measuring equipment required

- Dry Ashing & Open vessel digestion
  - Losses of volatile elements
  - Increased risk of contamination
  - Time consuming (in the range of 6 hrs to 1.5 days)

- **Multiwave PRO - The Master of Sample Preparation**
  - Possible Applications:

- **Acid Digestion / Leaching**
- Oxygen Combustion
- UV – Digestion
- Protein Hydrolysis
- Solvent Extraction
- Acid Evaporation
- Drying
- Synthesis

Multiwave PRO

- Shortest process times
- Reliable acid digestions up to 300 ºC @ 80 bar (1160 psi)
- No losses of volatiles & minimized risk of contamination
- Minimized reagent consumption
- Full reaction control:
  - Wireless temperature control in each position
  - Wireless pressure control in each vessel
- Easy data transfer via USB, LAN
- Safety – CE, GS & NRTL approval

Why High Temperature? – Complete Digestions

Samples: 300 mg Lubrication Oil

170 ºC 190 ºC 230 ºC 260 ºC

Same holding time, different temperatures

Higher temperature and pressure → Better digestion result!

High Performance Rotor 8N

- 8 vessels for high performance
- Unique pressure sensor system for simultaneous control of all reaction vessels
- Wireless data transmission
- Robust rotor upper plate
- Temperature control on all positions (via IR sensor)
- T-sensor in one reference vessel (optional)

- **XF100: 260 ºC @ 60 bar**
- XQ80: 300 ºC @ 80 bar
- p_{MAX}: 140 bar

Pressure Measurement for Full Reaction Control & Safety

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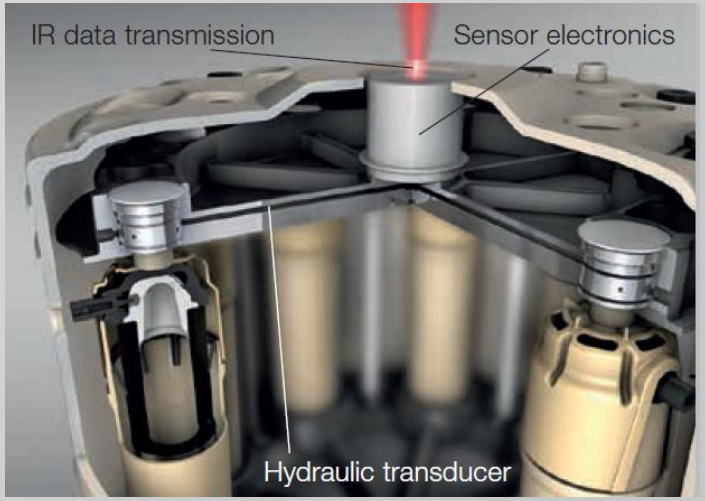
Quick & simultaneous

- Measures pressure (p)
- Measures pressure increase rate

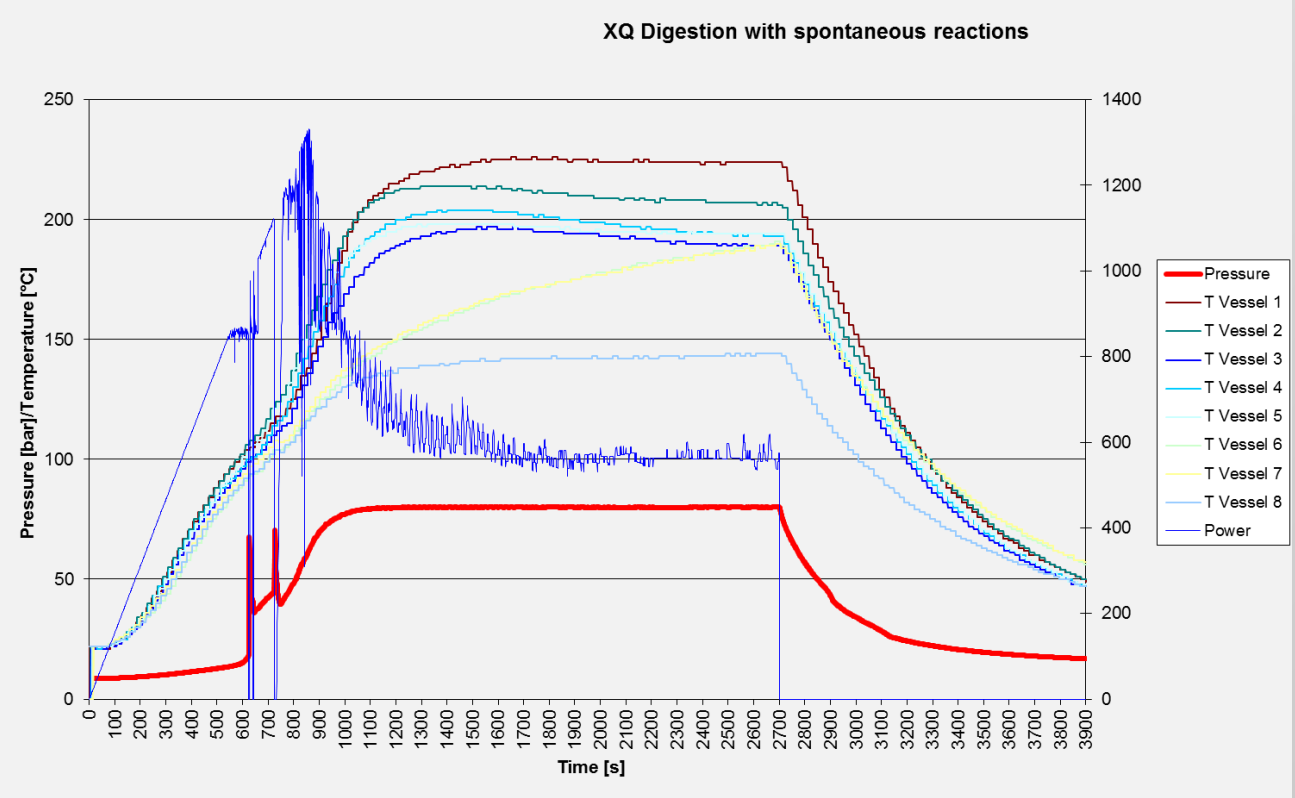
} → Every 20 milliseconds

If limits are exceeded:

- MW Power is reduced
- Cooling is increased



High-speed pressure sensing in action



- @ 10 + 12 min: p-jump of 35 bar
- Controlled by power cut and cooling up
- No indication of vessel number, probably different vessels
- Normal process continuation afterwards

Full Compliance with Standard

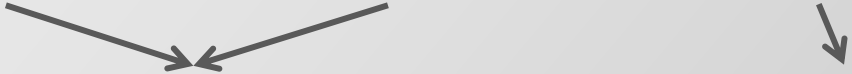
- ASTM D7876
  - Standard Practice for Sample Decomposition Using Microwave Heating (With or Without Prior Ashing) for Atomic Spectroscopic Elemental Determination in Petroleum Products and Lubricants.

Applicable to:

- Petroleum products and lubricants
  - Greases
  - Additives
  - Lubricating oils
  - Gasolines
  - Diesels
- Fossil fuel products:
  - Coal
  - Fly ash
  - Coal ash
  - Coke
  - Oil shale

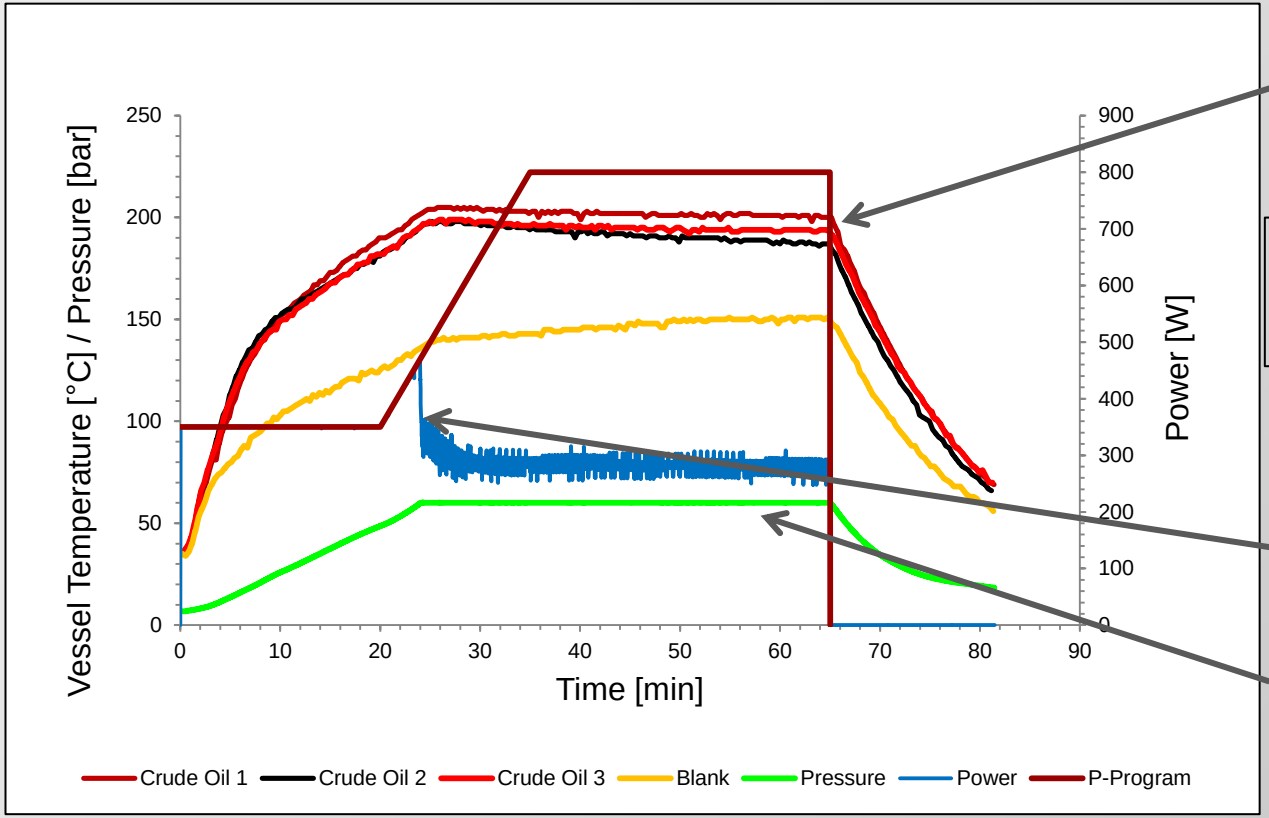
Comparison of Methods

- ASTM D4951, ASTM D5185, ASTM D7876
- 3 Samples:
  Engine Oil Lubricant, Crude Oil, Residual Fuel Oil



  ASTM Interlaboratory Crosscheck NIST SRM 1634c
- Multiwave PRO equipped with Rotor 8NXF100
- Two digestion reagents:
  1.) 7 mL HNO_3 (65%) + 1 mL H_2O_2 (30%)
  2.) 7 mL HNO_3 (65%) + 1 mL H_2O_2 (30%) + 200 µL of a 50% NH_4F
- Solutions measured with ICP-OES (1+2) and with ICP-MS (2)

Digestion Program of Crude Oil Samples



Vessel surface temperatures ~ 200 °C

Digestion conditions:
T > 200 ºC & p ~ 60 bar

Power is reduced as p-Limit is reached

Pressure of 60 bar

Residual Fuel Oil (NIST SRM 1634c)

	D7876 ICP-OES [µg·g^{-1}]	D7876 ICP-MS [µg·g^{-1}]	Certified value [µg·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

ICP-OES: n = 6 (mean of digestions with and without NH_4F)
ICP-MS: n = 3 (only digestions with NH_4F)
*...information value

Residual Fuel Oil (ASTM F61405)

	2-step, 0.6 g [µg·g^{-1}]	2-step + NH_4F 0.6 g [µg·g^{-1}]	Referencevalue [µg·g^{-1}]
Al	8.1 ± 0.6	8.1 ± 0.6	7.5 ± 1.1
Si	10.2 ± 0.3	4.2 ± 2.2	15 ± 2.2
Ca	48.7 ± 27.6	23.8 ± 0.9	13 ± 2.5
Fe	86.1 ± 0.8	76.7 ± 7.0	53 ± 12
Ni	39.3 ± 6.7	37.2 ± 6.7	39 ± 2.7
Na	26.8 ± 1.4	25.8 ± 0.9	22 ± 4.3
V	80.8 ± 9.3	78.5 ± 5.6	78 ± 4.3

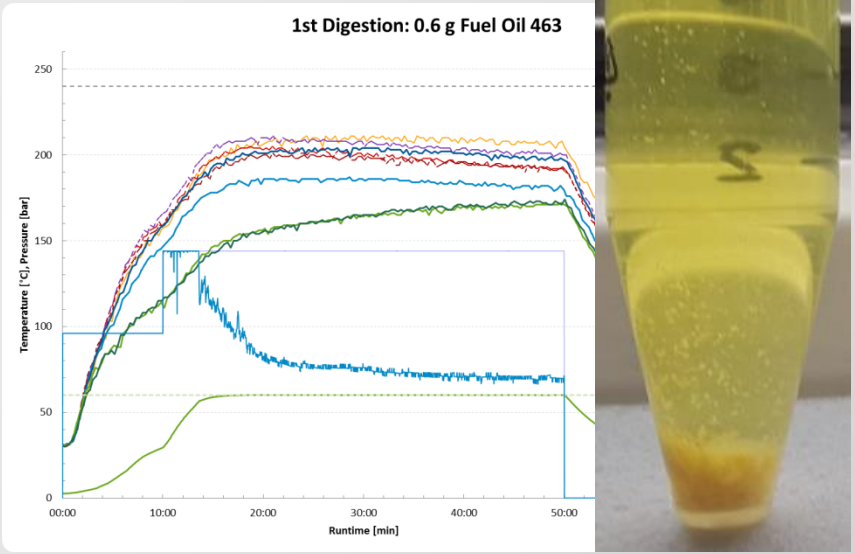
- Good agreement for most elements
- Si: problem with sampling heterogeneity?
- Ca, Fe contamination issues

Summary of Results

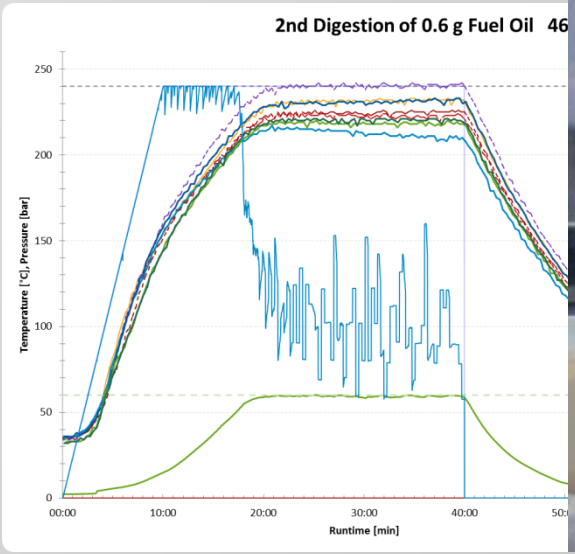
- Measured values are in a good agreement
- Values from ICP-OES and ICP-MS are well comparable → reliable sample preparation procedure
- Low standard deviations for the 6 samples → 0.5 g of sample are sufficient to achieve representative results.
- Digestion time reduction from typically **6-8 hours to < 90 minutes**
- Time for 2-step procedure less than 120 min incl. handling

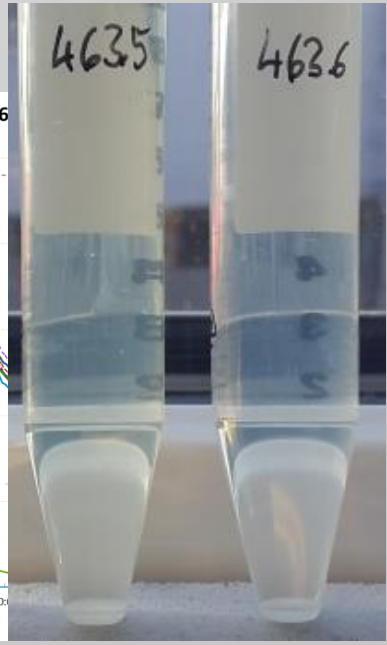
Run Data - 2-Step Procedure

Pre-reaction



2nd step





Multiwave PRO – Summary

- Highest temperatures (300 ºC) → lowest interferences during measurement
- Complete digestions of demanding samples
- Closed vessel digestion: No losses of volatiles & minimized risk of contamination
- Fast sample preparation method
- Minimized reagent consumption
- Full reaction control for highly reactive samples