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Elemental Analysis as Easy as It Can Be – From Ultra-Low Sulfur to Catalyst Elements at Refineries, to Lubricants and Wear Metals in Engine Oils

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Bruker offers best-in-class turnkey elemental analysis solutions for the entire petrochemical industry – from feedstock at refineries, to catalyst elements in fluid catalytic cracking (FCC) processes, to final process and quality control – contributing to an increase in productivity and profit.

Turnkey Solutions for Refineries

Elemental analysis is a crucial process control tool for the petrochemical refining industry. The quantification of over 30 elements by XRF in all kinds of hydrocarbons is easily possible with the universal calibration package PETRO-QUANT. Whether XRF is employed as a technique to quantify sulfur from the crude oil to refined products, or to analyze refinery process impurities such as metals and catalysts, PETRO-QUANT is your tailor-made solution!

Since X-ray Fluorescence (XRF) spectrometry enables direct analysis of petrochemical samples, without digestion or dilution, it is widely employed as monitoring technology: Sulfur levels in fuels are regulated, and norm-compliant analysis can be performed with the **S6 JAGUAR**, Bruker's benchtop Wavelength Dispersive XRF (WDXRF)**;** e.g., ASTM D2622 and ISO 20884. For the lowest detection limits as well as for the analysis of solids such as petcoke, the **S8 TIGER** WDXRF spectrometer (Figure 1) is the optimal choice. Results of trace element analyses in coke are listed in Table 1. In comparison to many other spectroscopic techniques, X-ray fluorescence requires no or only very little sample preparation, making daily routine analysis simple and fast.

Figure 1: WDXRF S8 TIGER Series 2 with PETRO-QUANT as ready to analyze solution for 30 elements

Table 1: Results of a repeatability test. Anode coke was measured 10 times on the WDXRF S8 TIGER

Element	Average	Std. Dev.	Rel. Std. Dev.	Certified Conc.
S [%]	0.57	0.00	0.85	0.60
Ni [PPM]	3.4	0.5	14.4	4
Si [PPM]	78.8	12.0	15.3	70
Fe [PPM]	127.0	0.8	0.6	130.0
Na [PPM]	36.0	0.0	0.0	n.a.
Al [PPM]	45.4	1.5	3.3	50
Ca [PPM]	65.7	0.5	0.7	63
K [PPM]	13.8	0.6	4.3	12
Mg [PPM]	5.2	0.4	7.7	6
Cl [PPM]	241.5	1.7	0.7	230
Cr [PPM]	9.0	0.1	1.1	1
Mn [PPM]	6.0	0.6	10.5	6.0
P [PPM]	21.1	0.3	1.4	11
Pb [PPM]	448.8	1.1	0.2	450
Ti [PPM]	9.9	0.7	7.1	4
Zn [PPM]	569.3	0.8	0.1	570
C [%]	99.26	0.00	0.0	99.3

Equipped with polarized optics, the **S2 POLAR** (Figure 2) – a benchtop Energy Dispersive XRF (EDXRF) spectrometer – is the ideal analytical tool for refineries and regions where regulatory compliance for sulfur and Ultra-Low Sulfur (ULS) can be fulfilled with EDXRF. The S2 POLAR allows for norm compliant analysis according to ISO 13032, ASTM D7220 and D4294. It is being used to perform routine tasks along the downstream supply chain in oil terminals, tank farms, petrol stations, or service labs. The data in Table 2 highlights the excellent performance of the S2 POLAR for sulfur analysis.

Figure 2: Easy-to-use EDXRF S2 POLAR with integrated TouchScreen

The polarized excitation of the S2 POLAR reduces the background for elements like S, P and Cl substantially, resulting in excellent Lower Limit of Detections (LLD). For the determination of Ultra-Low Sulfur in automotive fuels, a LLD of 0.5 ppm S in about 5 minutes proofs the analytical performance of this compact benchtop EDXRF spectrometer. This performance allows fully norm-compliant determinations of low sulfur and ULS in automotive fuels according to latest international norms. Due to the multi-element capability, the instrument is also able to quantify Ni and V or Cl in crude oils according to ASTM D8252 and ASTM D4929C, respectively.

Table 2: Repeatability of gasoline analyses, measured on the polarized EDXRF S2 POLAR

# Measurement	S [ppm]
1	**10.1**
2	**10.0**
3	**10.2**
4	**10.9**
5	**10.4**
6	**10.4**
7	**10.3**
8	**10.4**
9	**10.1**
10	**10.2**
Average	**10.3**
Abs. Std. Dev.	**0.24**
Rel. Std. Dev. [%]	**2.34**

Oil & Lubricants – Elemental Analysis

Oils and lubricants need to fulfill different tasks in engineering. Beside lubrication they are needed to cool pistons in car engines and while metal milling, to protect against corrosion and to bind particles: Precise and reliable analysis of additives at the minor and trace level is the key for high product quality. Moreover, accurate analyses allow to use expensive additives sparsely and thus to safe production cost, while ensuring the performance requirements of the product. XRF is the most important analytical method for the analysis of additives and impurities, no matter if oils, greases, or waxes need to be qualified (ASTM D6443 and D4927) and to detect engine debris in the form of wear metals (DIN 51399). The norm-compliance to ASTM D6443 of the S6 JAGUAR is demonstrated in Table 3. These norms are fulfilled by WDXRF instrumentation, while the EDXRF S2 PUMA meets the requirements for the ASTM D6481 and D7751. The later one covers 7 key additive elements including Mg, Ca, and Mo in lubricating oils.

Table 3: Stability, precision, accuracy, and norm compliance data according to ASTM D6443 with S6 JAGUAR

Measurement #	Mg [wt.%]	P [wt.%]	S [wt.%]	Cl [wt.%]	Ca [wt.%]	Cu [wt.%]	Zn [wt.%]
Rep 1	0.0786	0.0501	0.2781	0.0505	0.2034	0.0203	0.0503
Rep 2	0.0797	0.0513	0.2802	0.0505	0.2039	0.0203	0.0501
Rep 3	0.0780	0.0494	0.2782	0.0501	0.2028	0.0201	0.0501
Rep 4-12	…	…	…	…	…	…	…
Rep 13	0.0790	0.0511	0.2789	0.0516	0.2041	0.0199	0.0505
Average	0.0787	0.0501	0.2793	0.0507	0.2037	0.0201	0.0503
Abs. Std. Deviation	0.0006	0.0006	0.0010	0.0004	0.0014	0.0001	0.0001
ASTM D6443 passed	✓	✓	✓	✓	✓	✓	✓
Rel. Std. Deviation [%]	0.71	1.23	0.37	0.86	0.66	0.70	0.27
Certified Composition	0.0800	0.0500	0.2754	0.0500	0.2024	0.0200	0.0501
Difference	0.0013	0.0001	0.0039	0.0007	0.0013	0.0001	0.0002
Rel. Difference [%]	1.62	0.20	1.43	1.40	0.64	0.50	0.38

Figure 3: Petrochemical samples require no or only very little sample preparation, making daily routine analysis simple and fast

Figure 4: From compact EDXRF benchtop instruments to high-end, full-power floor-standing WDXRF instrumentation (from left to right: S2 POLAR, S2 PUMA, S6 JAGUAR, S8 TIGER)

Conclusion

There is a huge variety of raw, intermediate, and final petrochemical, from incoming feedstock at refineries to intermediate process streams and final automotive fuels or lubricants. The materials vary significantly with respect to their physical properties, from highly volatile such as gasoline to viscose or even solid as greases and waxes. Each of these products do require precise and reliable elemental analysis. This article demonstrates the suitability and benefits of EDXRF and WDXRF instruments for multiple key applications in the petrochemical industry.

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