QUALITY & PROCESS CONTROL WITH XRF: FROM FEEDSTOCK IN REFINERIES TO FUELS, LUBRICANTS AND POLYMERS

Bruker provides comprehensive solutions for the elemental analysis of petrochemical materials, like crude oil, fuels, lubricants, catalysts, and petcoke. The analytical results provide vital information for process and quality control. This contributes to an increase in productivity and profit.

Process and Quality Control at Refineries – from Feedstock to Final Products

Elemental analysis is crucial for process control in the petrochemical refining industry. X-ray Fluorescence (XRF) spectrometry is widely used to quantify many elements in all kinds of hydrocarbon materials. It enables direct analysis of petrochemical samples, without acid digestion or dilution. For examples, Sulfur (S) levels in fuels are regulated, and norm-compliant analysis according to ASTM D2622 and ISO 20884 can be performed with the S6 JAGUAR (Fig. 1), Bruker's benchtop wavelength dispersive XRF (WDXRF) spectrometer. The instrument is equipped with a 400 W HighSense™ X-ray tube making it the most powerful benchtop WDXRF. Modern software with enhanced fundamental parameter algorithms and state-of-the-art hardware enables excellent analytical performance. It achieves outstanding sensitivity for a wide range of elements (F to U), and the different configuration options allow to optimize the system for the various analytical needs.

Fig. 1: Compact benchtop WDXRF spectrometer S6 JAGUAR, available as 24-position XY-loader configuration for high sample throughput or manual sample loading

Table 1: Results of a repeatability test of 20 QC gasoline measurements on the WDXRF S6 JAGUAR, according to ASTM D2622

Measurement #	S Concentration [ppm]	Difference between consecutive replicates [ppm]	Max. allowed difference according to ASTM D2622 [ppm]
# 1	10.09		
# 2	10.19	0.10	0.93
# 3	10.31	0.12	0.93
# 4	10.30	-0.01	0.93
...	...	...	...
# 17	10.31	0.09	0.93
# 18	10.18	-0.13	0.93
# 19	10.15	-0.03	0.93
# 20	10.21	0.06	0.93
Mean Value [ppm]	10.20		
Std Dev [ppm]	0.16		
RSD [ppm]	1.61		

As an example for the analytical performance of the S6 JAGUAR, the calibration details and results for the analysis of S in automotive fuels according to ASTM D2622 are shown in Fig. 2 and Table 1, respectively.

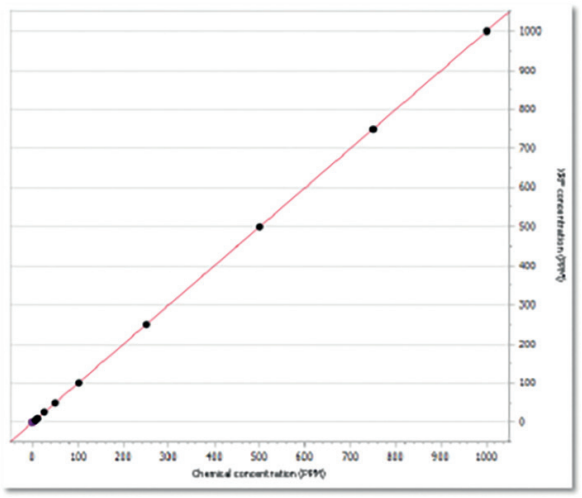

Fig 2: Calibration curve for S showing here the calibration range up to 1000 ppm S of ASTM D2622 on the WDXRF S6 JAGUAR.

The calibration of low sulfur in mineral oil was performed according to ASTM D2622. All standards were traceable to NIST. For the measurements, seven grams of material was pipetted into a liquid cup equipped with a 3.6 µm Mylar film. The samples were measured directly after preparation, and results were available within minutes after starting a sample.

The results reveal the excellent repeatability of the measurements. The maximum allowed difference between two consecutive measurements was 0.93 ppm, but the typical difference of the S6 JAGUAR was much better, around 0.1 ppm S. The lower limit of detection (LOD) is 0.7 ppm S and confirms the outstanding performance of the S6 JAGUAR.

The S6 JAGUAR is also suitable for the analysis of intermediate refinery products and final products such as Pb and Mn in gasoline (ASTM D5059). Beside liquid products, also solids such as material from the fluid catalytic cracking process (FCC), petcoke, and bitumen can be easily analyzed.

Elemental Analysis in Oil & Lubricants

The elemental analysis of oils and lubricants is also of wide interest in the petrochemical industry. It helps in determining the chemical composition of the oils and lubricants. This is essential in engineering, not only for lubrication but also for cooling pistons in car engines and protecting against corrosion and binding particles. Precise and reliable analysis of additives at the minor and trace level is key for high product quality. Accurate analyses allow for the sparing use of expensive additives, thus saving production costs while ensuring the performance requirements of the product. XRF is the most important analytical method for the analysis of additives and impurities, whether 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 S6 JAGUAR is norm-compliant with all elements defined in DIN 51399, including those of further interest, as demonstrated for a selection of these 24 elements in Table 2.

Table 2: Stability, precision, and accuracy data for the WDXRF S6 JAGUAR are complying with DIN 51399

Measurement	Al [PPM]	Si [PPM]	S [%]	Fe [PPM]	Ni [PPM]	Cu [PPM]	Mn [PPM]	V [PPM]	Ti [PPM]	K [PPM]	Zr [PPM]	W [PPM]
1	99.8	50.7	0.0896	50.2	49.1	49.1	49.4	52.6	55.4	49.9	53.1	46.0
2	96.0	53.4	0.0895	50.6	49.3	49.7	49.8	52.3	56.8	49.3	51.9	46.5
3	100.4	55.0	0.0896	51.0	49.2	49.0	50.4	53.8	54.9	48.3	52.3	47.2
4	99.5	51.3	0.0889	50.6	49.4	49.6	51.1	52.1	55.1	48.2	52.5	46.3
...	...	...	...	...	...	...	...	...	...	...	...	...
17	99.6	51.8	0.0895	50.7	49.0	49.8	51.1	53.9	54.5	49.5	51.7	47.0
18	104.3	48.6	0.0900	51.2	49.3	49.8	51.2	52.6	54.5	51.5	51.6	46.9
19	95.7	50.2	0.0898	50.9	49.2	49.6	51.6	52.7	56.0	50.3	51.9	47.8
20	102.6	51.8	0.0905	50.6	49.9	49.9	51.5	52.5	56.6	50.4	51.3	48.9
Certified Value	100.0	50.0	0.0865	50.1	50.1	50.0	50.0	50.1	50.0	50.0	50.0	50.0
Average	100.4	51.6	0.0897	50.7	49.5	49.4	50.5	52.3	55.6	49.4	52.4	47.1
Std. Dev.	2.8	2.0	0.0006	0.5	0.5	0.4	0.7	0.8	0.9	1.1	0.7	0.9
Rel. Std. Dev. [%]	2.79	3.83	0.62	1.01	0.94	0.71	1.33	1.51	1.66	2.23	1.31	1.90

Table 3: Measurement results of an ABS polymer control sample. Comparison of measured concentration vs. certified values of the different RoHS elements

Element	Measured Concentration [ppm]	Certified Concentration [ppm]
Br	28	25
Cd	99	100
Cr	14	16
Hg	58	63
Pb	947	954

Additives and Fillers in Polymers & Plastics

There is a growing demand for polymers and plastics worldwide, and with the increasing production volume, there is also a need for fast and reliable process and quality control. XRF with its capability to analyze different materials such as powders, granules, and disks, and with the simple sample preparation without material dissolution, is a frequently used technique for elemental analysis in polymers and plastics quality control. Common XRF applications also include raw material analysis such as additives, fillers, pigments, or catalysts.

Quite important to monitor are also the elements covered in the EU RoHS (Restriction of Hazardous Substances) directives which regulate the use of hazardous materials in electronic devices and components. Targeted elements include Pb, Hg, Cd, Cr, and Br. Other regulations to follow cover Waste of Electrical and Electronic Equipment (WEEE), or heavy metal content in used cars, or toy safety aspects. Calibration data and analytical data on RoHS elements for the S6 JAGUAR are shown in Fig.3 and Table 3.

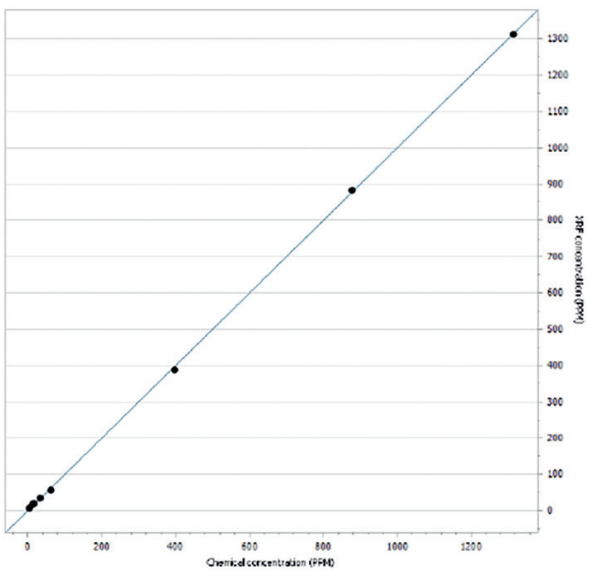

Fig 3.: Calibration curve for the determination of Hg in polymers on the S6 JAGUAR, showing here the curve for the entire calibration range of the method.

Conclusion

The S6 JAGUAR enables time-efficient and accurate analysis of elements in fuels & oils, contaminants, and wear metals in fuels, lubricating and polymers. When installed at refineries and oil-production plants, it can easily test the quality of incoming materials and optimize the used additives from day one. It ensures that all elements are analyzed at best performance with highest accuracy and precision combined with low cost of ownership.

Some petrochemical applications only require a smaller, more compact energy dispersive XRF (EDXRF) instruments. For such measurements Bruker offers either the S2 PUMA with direct excitation or the S2 POLAR with polarized excitation. Other, more demanding applications, e.g. when there is a need to measure lower traces or for higher sample throughput in central labs, the floor standing WDXRF S8 TIGER with up to 4 kW power is perhaps the first choice (Fig. 4).

Fig. 4: Bruker's innovative XRF Portfolio, from compact EDXRF benchtop instruments to high-end, full power floor standing WDXRF instrumentation (S2 POLAR, S2 PUMA, S6 JAGUAR, S8 TIGER, from left to right)

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