THE INDISPENSABLE ANALYTICAL TOOL IN PETROCHEMICAL LABORATORIES FOR QUANTITATIVE TRACE ELEMENT ANALYSIS

Accurate and precise trace element determination in petrochemicals is vital in all relevant application areas to ensure highest product quality, optimal performance of engines and a clean environment. When it comes to reliable process control by element detection there is no other method than XRF enabling users to get accurate and precise information in a short time.

Figure 1: WDXRF spectrometer S8 TIGER optimal for petrochemical applications

XRF is unique regarding simple and robust sample preparation and handles solid and liquid sample direct without the need for lengthy digestion or dilution. At the same time especially wavelength dispersive X-ray fluorescence spectrometry (WDXRF) offers optimal analytical performance one would need for petrochemi¬cal laboratories in industry and research:

- **Sulphur determination in automotive fuels**

  Environmental regulations are enforcing lower levels of hazardous elements in automotive fuels. Nowadays the sulphur concentration in fuels is globally reduced down to 10 ppm. New legislation is enforcing lower levels in heavy ship fuels. Following ASTM D 2622 or ISO 20884 with WDXRF quality control on sulphur can be done very precisely with typically less than 5 % rel. standard deviation. When producing biofuels the monitoring of additional elements such as Si, P, Fe etc., can be done In addition at the same time.

- **Cost efficiency and performance for lubricants**

  Additives in lubricants and polymers are expensive; therefore the accurate control of concentration levels will achieve cost savings while maintaining a high product quality at the same time. Based on ASTM D 6443 all typical additives elements are tracked by WDXRF precisely enabling producers to keep their products in tight specifications.

- **Wear metal analysis for long engine life**

  Modern fuel-saving engines contain more and more parts made out of light alloys. The high performance requires a strict focused development to make bearings and pistons last longer. Early warnings on engine break downs are based on the precise analysis of wear metals in the trace level. Therefore the analysis of metals in engine oils supports car manufacturers and helps to decrease the necessity of maintenance. With modern WDXRF spectrometers such as Bruker's S8 TIGER early warnings for engine breakdowns are done quickly by detecting both dissolved elements but also larger particles at the same time, spotting severe failures.

- **XRF to support regulatory compliance for consumer product safety and environmental protection**

  The analysis of catalyst residues and hazardous elements down to the sub-ppm level are a key application today following the strict rules for active pharmaceutical ingredients.
  The same applies for alternative fuels used in cement production and power generation.

Ready-to-analyse – standard compliance made easy

Sulphur in automotive fuels has been a source of toxic air pollutants like sulphur dioxide and sulphates. Legislation enforces lower residual sulphur concentrations in fuels, like the actual limit of 10 ppm in Europe. Future regulations may drive these limits down even further. Wavelength-dispersive X-ray fluorescence (WDXRF) analysis is today the method of choice for accurately and precisely analysing low sulphur concentrations in petroleum products. The outstanding analytical performance of the S8 TIGER exceeds the requirements of actual standards like ASTM 2622 and already meets future demands – a safe investment.

With the flexible and compact beampath, high-performance X-ray tube and advanced analyser crystals, the S8 TIGER offers superior analytical performance in detection limits, precision and accuracy. The S8 TIGER is optimised for highest instrument uptime, lowest cost of ownership and ultimate reliability. SampleCareTM with 4x protection (including the unique vacuum seal) reduces the helium consumption and protects spectrometer components against damage from droplets or particles, even during measurements.

Bruker provides the fully calibrated, standard compliant S8 TIGER spectrometers to match the needs of your laboratory. In order to make sure that the analyser delivers the optimal performance independent from operators. After the on-site installation, the spectrometer can perform routine applications on the spot with no need for highly trained personal, saving lots of time and money, e.g. such as EN ISO 20884, ASTM D2622, ASTM D6443, ASTM D5059 and others.

The calibration of low sulphur in mineral oil according to ASTM D 2622-10 was performed

Figure 2: Sample cups for WDXRF measurements using Mylar foils

Table 1: Precision test results for low sulphur in automotive fuels at 5 ppm with the S8 TIGER ECO

Measurement	S (PPM)
12:53 PM	4,7
1:00 PM	4,8
1:07 PM	4,8
1:14 PM	5,0
1:22 PM	5,2
1:31 PM	4,7
1:38 PM	5,1
1:46 PM	4,8
1:52 PM	5,1
1:59 PM	4,8
2:06 PM	4,7
2:16 PM	5,1
Average	4,9
Abs.Std.Dev.	0,2
Rel.Std.Dev.	3,8%
Minimum	4,7
Maximum	5,2
Range	0,5

on the S8 TIGER in ECO configuration with seven standard samples prepared by using commercially available standards covering a concentration range from 0 – 100 ppm for the low range. The high precision of the S8 TIGER ECO is shown in Table 1. The prepared samples are shown in fig.2.

The analysis of ultra low sulphur concentrations in petroleum products according to ASTM D 2622-10 with the S8 TIGER is reliable, precise and accurate. The optimised excitation and the intensity optimised beam path with the germanium crystal leads to an unmatched analytical performance. The determination of ultra low sulphur concentrations allows driving the production of low sulphur automotive fuels with the S8 TIGER ECO in the most efficient way. It ensures that the actual and future limit values of sulphur in fuels are not exceeded along the supply chain.

PETRO-QUANT BASIC – Versatile and Efficient, One Universal Calibration for all kinds of Petrochemical Samples

Typically accurate quantitative elemental analysis with X-ray fluorescence requires conventional calibrations. When calibrating a spectrometer, a set of reference samples are analysed with an optimised set of measurement parameters. After the calibration is computed it is then used for the analysis of unknown samples. If an analyser for various sample matrices such as lube oils and fuels is calibrated, highly trained specialists are required.

The universal PETRO-QUANT BASIC calibration enables the analysis of petrochemical samples without the need for further sample matrix information. Time consuming calibrations for each application are not necessary. The universal calibration is pre¬pared in the factory by our experienced method developers. This makes the start of routine analysis faster and safer than ever. The universal calibration is based on the powerful 'variable alphas' correction model. It helps to cover various sample types with just one calibration. This reduces the calibration effort to a minimum. PETRO-QUANT BASIC gives you an accurate and precise analysis of 30 elements in hydrocarbon samples with standard errors and 3 sigma detection limits in the lowest possible ppm-range. One example for a PETRO-QUANT calibration and the compensation of matrix effects is shown in fig 3.

Typical materials to be routinely analysed "standardless" are automotive fuels, wear metals in engine oils, additives in polymers, lubricants, grease, catalyst residues in polymers, trace elements in pet coke and coal and other elements in hydrocarbons.

The analysis of wear metals is critical to predict engine performance, schedule maintenance and reduce costs when operating expensive machinery such as mining trucks, racing cars or in motor development. Fast measurements and the simultaneous detection of dissolved elements and elements bound in particles are vital not to miss sudden failures of bearings or other devices. PETRO-QUANT for the S8 TIGER applies optimal measurement parameters for the S8 TIGER, by using the XS-55 multilayer optic for Na and Mg, the PET crystal for Al and Si, the XS-GE-C for P, S, and Cl and finally the LiF 200 for all elements from K – U. The application is easily customised by selecting the relevant elements from the 30 calibrated elements. Based on the measurements PETRO-QUANT even selects the optimal set

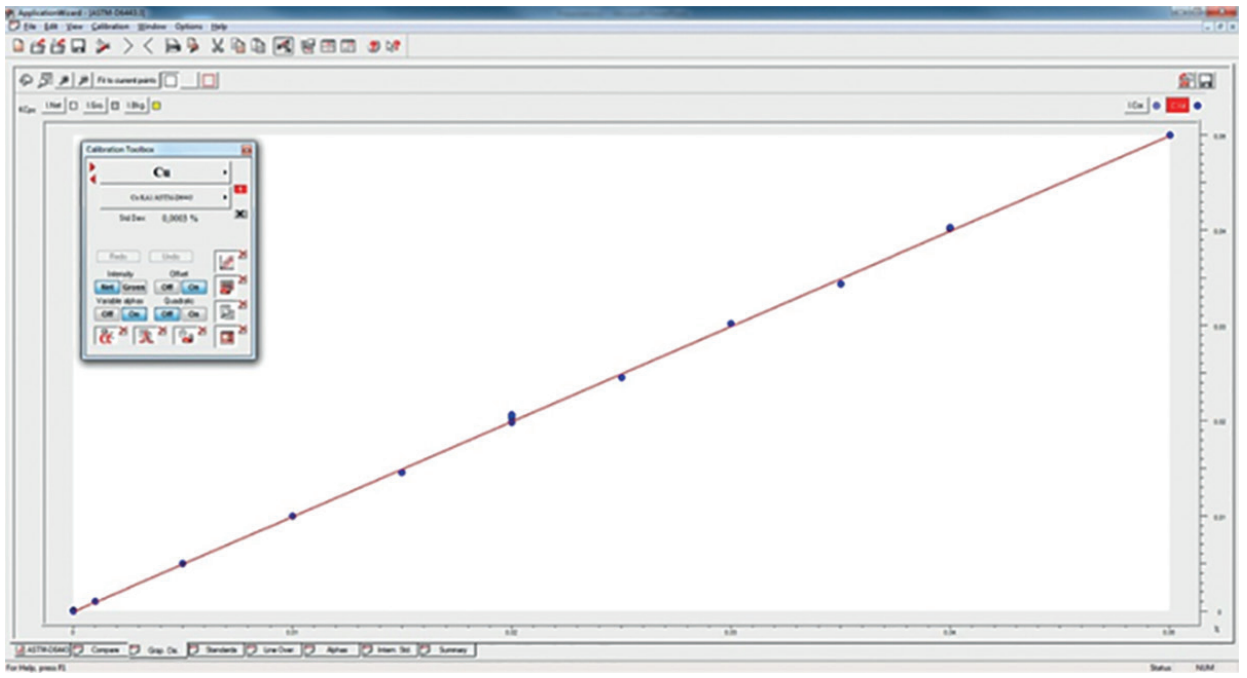

Figure 3: PETRO-QUANT calibration for Calcium covering the lower ppm-concentration range

of conditions according to the concentration range. Changes is sample weight and material composition are covered by the powerful fundamental parameter algorithm, even unknown oxygen concentrations are compensated with the Aut-O-Matic functionality. This becomes important when analysing aged engine oil or biofuels. The PETRO-QUANT solution is shown in figure 4.

Figure 4

In table 2 the analytical precision for the analysis of wear metals in engine oils is shown by analysing a 10 ppm multielement standard. The elements of focus were Mg, Al and Si coming from the light-weight engine body. Another set of elements can be related to pistons, bearings and other parts in gear boxes.

The high analytical precision of the S8 TIGER with PETRO-QUANT with typically less than 1 ppm at very low trace levels are enabling

Figure 5: Engine oils – a critical application, but not for WDXRF with PETRO-QUANT

users to early recognise engine problems avoiding higher costs for repairs or frequent maintenance. The implementation of the S8 TIGER in test facilities close to maintenance centers is simple and straight forward using the factory calibrated S8 TIGER and its easy-to-use interface shown in fig 1.

PETRO-QUANT is optimised for the wavelength disper¬sive X-ray fluorescence spectrometer S8 TIGER. All S8 TIGERs provide unsurpassed analytical performance with excellent precision and accuracy for the analysis of traces in petrochemicals. The S8 TIGER 1 K offers attrac¬tive low cost of operation without the need of cooling water and low power consumption while the S8 TIGER 3 and 4 K deliver shortest time to result.

Table 2: Precision test on wear metals in engine oils analyzed by the S8 TIGER 4 kW with PETRO-QUANT, certified concentrations are 10 ppm, maximum measurement time 10 minutes total

Sample	Mg (PPM)	Al (PPM)	Si (PPM)	P (PPM)	Ca (PPM)	Ti (PPM)	V (PPM)	Cr (PPM)	Fe (PPM)	Ni (PPM)	Cu (PPM)	Zn (PPM)	Mo (PPM)	Sn (PPM)	Pb (PPM)
1	12,5	8,9	7,6	8,8	12,1	9,2	10,3	10,7	10,5	11	10,2	9,9	9,8	9,8	9,1
2	11,2	6,7	8,4	8,9	10,1	10,6	10,4	10,9	9,7	9,9	10	9,9	9,3	11,8	9,8
	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
11	10,6	8,5	5,9	8,9	11,1	9,8	10,3	10	9,1	10,5	10,3	9,9	10	9,4	9,7
12	8,4	8,3	6,5	9,3	12,5	10,4	11,2	10,3	10,4	10,3	10,4	9,9	9,8	10	10
Mean	10,3	7,9	8,6	9,3	11	10,3	10,5	10,3	9,9	10,3	10,2	9,9	9,4	10,1	9,7
Std. Dev.	1,6	1,1	1,9	0,7	1	0,6	0,5	0,5	0,6	0,4	0,2	0,2	0,6	1,8	0,3

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