

Lab Report XRF 80

S8 TIGER[™]

Low Sulphur Analysis of Petroleum Products According to ASTM 2622

Introduction

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 analyzing low sulphur concentrations in petroleum products. WDXRF is a non-destructive method that is easily integrated into industrial environments such as refineries and laboratories. Simple sample preparation, reliability, ease-of-use and accurate analytical results are the main advantages of WDXRF.

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. This report shows how the S8 TIGER excels at low sulphur analysis of petroleum products.

Instrument

The S8 TIGER WDXRF spectrometer is the perfect solution for performing elemental analysis for the hydrocarbon processing industry. With to the most flexible and compact beam path, high-performance X-ray tube and advanced analyzer crystals, the S8 TIGER offers superior analytical performance in detection limits, precision and accuracy.

The S8 TIGER is optimized for highest instrument uptime, lowest cost of ownership and ultimate reliability. SampleCare[™] 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.

For the determination of low sulphur concentrations in petroleum products, the S8 TIGER is equipped with a 4 kW rhodium X-ray tube, two collimators (0.23° and 0.46°) and four analyzer crystals to cover the elemental range from N to U. The curved germanium crystal XS-GE-C provides 20-40% more intensity for the elements P, S and Cl, and is the best choice for the analysis of sulphur in fuels.

Standard and Sample Preparation

Calibration according to ASTM 2622 was performed with ten standard samples prepared by using mineral oil and di-n-butyl sulfide covering a concentration range from 0 – 1000 ppm. The standards are commercially available and traceable to the NIST reference sample SRM 1616 a – sulphur in kerosene.

Seven grams of the standard or sample were pipetted into a liquid cell prepared with a 3.6 µm Mylar film support. The samples were measured directly after preparation.

Measurement

Measurements were performed on the S8 TIGER using the curved germanium crystal XS-GE-C, 0.46° collimator and 4 kW excitation with the settings 30 kV and 135 mA. Peak intensities were recorded to an amount of 1×10^5 counts to meet the desired statistical error.

The adjusted peak position of S Kα1 for the XS-GE-C crystal was set to a 2θ value of 110.698°, the background position was set at 115.22°. The measurement time was set to 25s for the peak and 25s for the background.



Figure 1: Curved germanium crystal XS-GE-C

The reliable and precise analysis of trace elements requires the highest sensitivity and best possible resolution. Laterally curved crystals are focussing the emitted fluorescence radiation towards the center of the detector. This arrangement achieves for elements with high reflection angles more intensities and an increased resolution in comparison to the flat crystal geometry. The analyzer crystal XS-GE-C is based on a curved Ge(111) crystal and offers the enhanced analytical performance for the elements P,S, Cl.

Results

The calibration curve was calculated from the intensity of the ten standard samples by multiple regression. Calibration details are shown in Table 1, the curve is shown in Figure 2.

Table 1: Calibration Details for low sulphur in fuels

Analyte	S Kα1 [XS-GE-C]
Peak [° 2θ]	110.698
Bkg [° 2θ]	115.220
Sensitivity [kcps/%]	387.2
Cal.Offs. [ppm]	0.4
Cal. Dev. [ppm]	2
r ²	0.999961
LLD [ppm - 3σ, 100 s]	0.2
LoD [ppm - 3σ, 25 s]	0.4

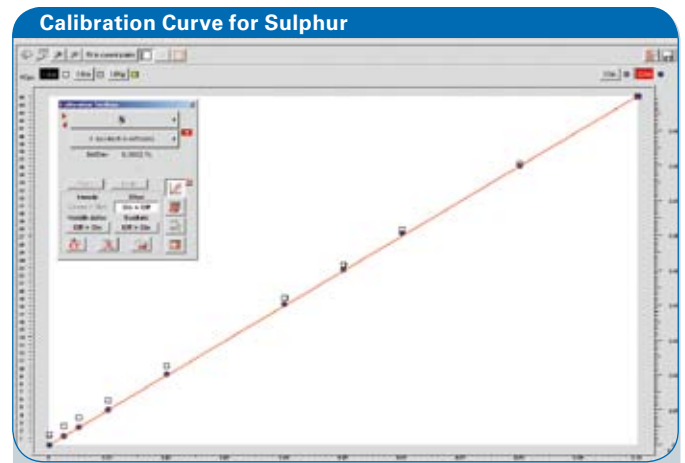


Figure 2: Calibration curve for sulphur in petroleum products of concentration range 0 – 1000 ppm

The detection limit is calculated according to

$$LLD = \frac{3}{m} \sqrt{\frac{I_b}{T_b}}$$

where m = sensitivity of analyte in kcps/mass%

I_b = background intensity for analyte in kcps

T_b = counting time in seconds at the background angle

To test the precision of the method, two samples with sulphur concentrations of 5 and 25 ppm were measured twenty times. The results and the statistical parameters are shown in Table 2 and Figure 3.

Table 2: Precision data for sulphur in fuels at two concentrations

Sample	Sample 1 [5 ppm]	Sample 2 [25 ppm]
Rep 1	5.2	25.3
Rep 2	5.0	24.7
Rep 3	4.6	25.1
Rep 4	5.5	24.8
Rep 5	5.2	24.9
Rep 6	5.3	25.2
Rep 7	5.0	25.2
Rep 8	5.8	24.8
Rep 9	5.1	25.2
Rep 10	4.9	25.2
Rep 11	4.5	24.8
Rep 12	4.8	25.1
Rep 13	5.6	24.7
Rep 14	4.9	25.3
Rep 15	4.6	25.4
Rep 16	5.0	25.2
Rep 17	5.4	25.1
Rep 18	4.6	24.8
Rep 19	5.0	25.3
Rep 20	4.7	25.2
Mean Value	5.0	25.1
Abs. Std. Dev.	0.4	0.2
Rel. Std. Dev.	7.2	0.9

Conclusions

The analysis of low sulphur concentrations in automotive fuels with the S8 TIGER is fast, precise and accurate. The high analytical performance with the optimized excitation and the increased sensitivity using the new analyzer crystal XS-GE-C speeds up the analysis considerably. The presented data prove that today's and future regulations can be mastered by the S8 TIGER. The high precision of the S8 TIGER allows the safe identification of fuel sample very close to the federal limit values. The process to reduce the sulphur level in fuel therefore can be controlled better and doesn't require high safety ranges – a big cost advantage.

The S8 TIGER is the perfect tool for elemental analysis of hydrocarbon samples especially in laboratory and industrial environments, due to the ease-of-use with TouchControl™ and the 4x protection of spectrometer components by SampleCare™.

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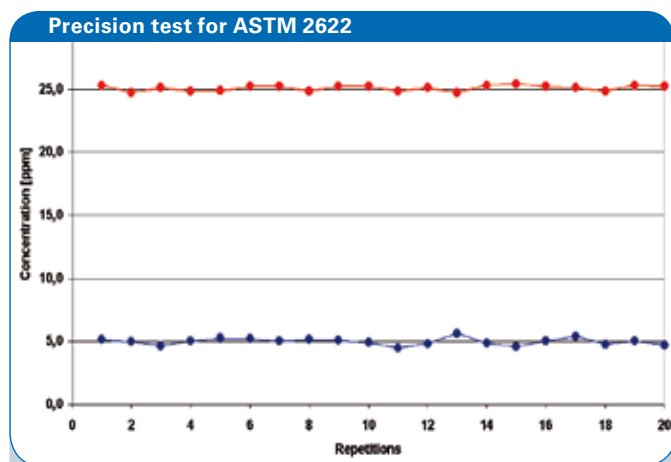


Figure 3: Precision data for sulphur in fuels at two concentration levels

All configurations and specifications are subject to change without notice. Order No. DOC-L80-E00080.
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