Lab Report XRF 113

S8 TIGER ECO "Petro"

Optimal analysis of ultra low levels of sulfur in automotive fuels and mineral oils according to ASTM D 2622-10

Introduction

Sulfur in automotive fuels has been a source of toxic air pollutants like sulfur dioxide and sulfates. The international legislation enforces today very low residual sulfur concentrations in fuels, like the actual limit of 30 ppm for diesel in the US. The EU directive 2003/17/EC regulates the maximum allowed level in the European Union to be max. 10 ppm. Future regulations may drive these limits down even further. And more countries will join the sulfur reduction initiative.

Wavelength-dispersive X-ray fluorescence (WDXRF) analysis is actually the method of choice for accurately and precisely analyzing low sulfur concentrations in petroleum products. WDXRF instruments are easily integrated into industrial workflows such as in refineries and commercial service laboratories due to its simple sample preparation, reliability, ease-of-use and accurate analytical results. At the same time they offer compelling analytical performance making WDXRF far superior than other analytical methods.

The S8 TIGER ECO "Petro" brings additional advantages for the analysis of low sulfur in hydrocarbons and is easily satisfying the requirements of ASTM D 2622-10. It has been optimized to combine low cost of ownership by reducing the energy and helium consumption with an optimal spectrometer configuration for dedicated performance.

This report will outline the analytical performance of the S8 TIGER ECO "Petro" for ASTM D 2622-10 and describes the specific benefits for this analytical task.

Figure 1: Ultra low sulfur automotive fuel

Instrument

The S8 TIGER ECO "Petro" for ASTM D 2622 is the optimal solution for performing analysis of sulfur in hydrocarbon matrices such as gasoline, kerosene, diesel and mineral oil. Traces of sulfur can be analyzed at ultra low detection limits and optimal precision due to the compact beam path: High sensitivity for sulfur is achieved with the close coupling between X-ray tube and sample. The germanium analyzer crystal ensures optimal analytical sensitivity and resolution. The measurement of peak and background positions in sequential mode ensures that for each matrix the accurate net intensity is determined.

The S8 TIGER ECO "Petro" for ASTM D 2622 is optimized for highest instrument uptime, lowest cost of ownership and ultimate reliability. The unique vacuum seal of the S8 TIGER ECO "Petro" outperforms other conventional WDXRF due to its complete protection of the goniometer and its parts. It locks out fumes from diesel and gasoline which otherwise will enter the spectrometer chamber damaging crystals, motors and detectors. In addition it significantly reduces the helium consumption and therefore the cost of operation, because helium flushing is only required for the small sample chamber, while the goniometer remains always in vacuum. Without the need for an additional external cooling device and no need of compressed air the quick installation and reliable operation is guaranteed for the S8 TIGER ECO "Petro".

Sample preparation

The calibration of low sulfur in mineral oil according to ASTM D 2622-10 was performed with seven standard samples prepared by using commercially available standards covering a concentration range from 0 – 100 ppm for the low range. All standards were traceable to the NIST reference sample SRM 1616 a – sulfur 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 ECO "Petro" for ASTM D 2622 using the germanium crystal combined with the 0.46° collimator. The S Kα signal was detected with the proportional flow counter. The excitation of this line was done with 30 kV and 33 mA. The adjusted peak position of S Kα1 for the germanium crystal was set to a 2θ value of 110.664°, the two background position were set to 108.500° and 113.500°. The measurement time was 100 s for the peak and 60s for each background.

Results

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

Table 1: Calibration Details for low sulfur in fuels.

Parameter	Value
Peak [° 2θ]	110.664°
Bkg 1 [° 2θ]	108.500°
Bkg 2 [° 2θ]	113.500°
Cal.Offs. [ppm]	0
Cal. Dev. [ppm]	0.1
r^2	0.999994
LLD [ppm - 3σ, 100 s]	0.4

The detection limit is calculated according to

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

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 analytical precision of the S8 TIGER ECO "Petro", one sample in the most important level of 10 ppm was measured 10 times one by one and for the long term test ten times within 2 weeks. In addition a second sample at 5 ppm was tested for short term precision.

The results and the statistical parameters are shown in Table 2 and 3 for the sample with 10 ppm S and in Table 4 for 5 ppm.

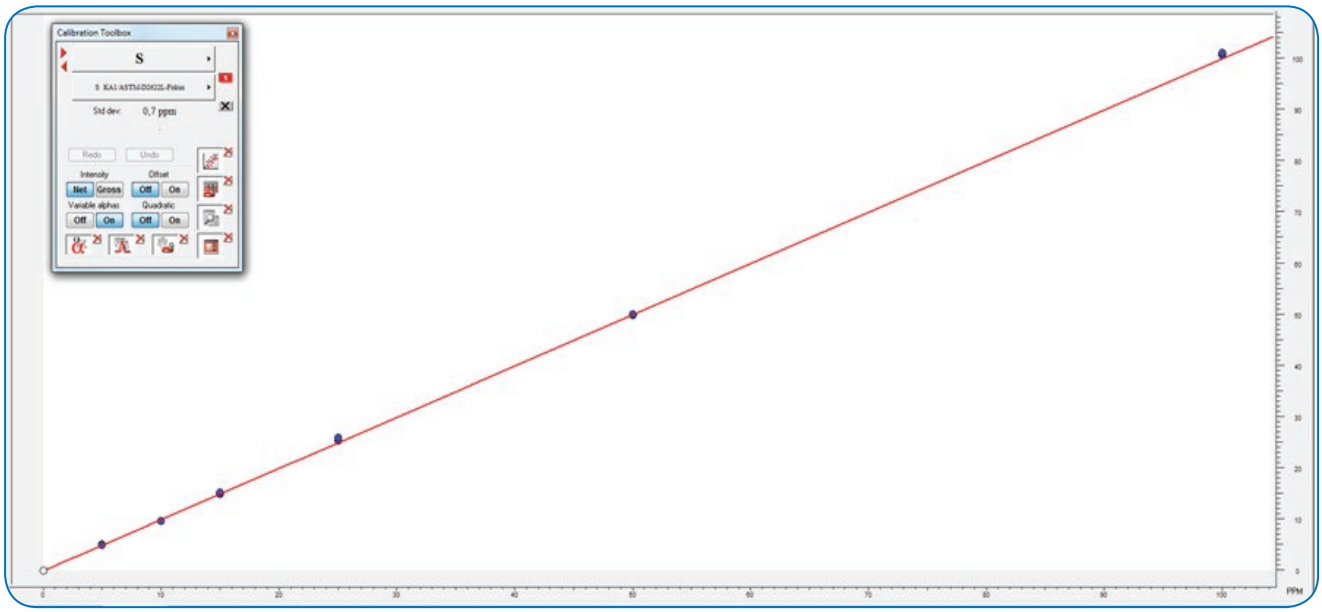

Figure 2: Calibration curve for sulfur in fuels according to ASTM D 2622 covering 0 – 100 ppm

Table 2: Short term repeatability at 10 ppm S in mineral oil

Measurement Finished	S (PPM)	Diff. to prev. [ppm] ASTM max. allow. 0.9 ppm
14:02	10.4	
14:08	10.5	0.1
14:14	10.1	-0.4
14:20	10.2	0.1
14:26	10.2	0.0
14:32	10.2	0.0
14:38	10.1	-0.1
14:44	10.2	0.1
14:50	10.0	-0.2
14:56	10.0	0.0
15:02	10.2	0.2
15:08	9.8	-0.4
Average	**10.2**	
Abs.Std.Dev.	**0.18**	
Rel.Std.Dev.	**1.8%**	
Minimum	**9.8**	
Maximum	**10.5**	
Range	**0.7**	

Table 3: Long term repeatability at 10 ppm S in mineral oil

Measurement Finished	S (PPM)	Diff. to prev. [ppm] ASTM max. allow. 0.9 ppm
21.06.2013 14:02	10.4	
24.06.2013 11:03	10.0	-0.4
25.06.2013 09:34	10.4	0.4
26.06.2013 09:47	10.3	-0.1
27.06.2013 09:22	10.4	0.1
28.06.2013 08:31	10.1	-0.3
01.07.2013 10:21	10.2	0.1
02.07.2013 10:37	9.7	-0.5
03.07.2013 10:39	10.3	0.6
04.07.2013 10:32	10.2	-0.1
05.07.2013 08:59	10.2	0.0
09.07.2013 11:25	9.9	-0.3
Average	**10.2**	
Abs.Std.Dev.	**0.21**	
Rel.Std.Dev.	**2.1%**	
Minimum	**9.7**	
Maximum	**10.4**	
Range	**0.7**	

Table 4: Short time repeatability at 5 PPM S in mineral oil

Measurement Finished	S (PPM)	Diff. to prev. [ppm] ASTM max. allow. 0.5 ppm
12:54	4.7	
13:00	4.8	0.1
13:06	4.8	0.0
13:13	5.0	0.2
13:19	5.2	0.2
13:25	4.7	0.5
13:32	5.1	0.4
13:38	4.8	0.3
13:45	5.1	0.3
13:51	4.8	0.3
13:58	4.7	0.1
14:04	5.1	0.4
Average	**4.9**	
Abs.Std.Dev.	**0.2**	
Rel.Std.Dev.	**3.8%**	
Minimum	**4.7**	
Maximum	**5.2**	
Range	**0.5**	

Conclusions

The analysis of ultra low sulfur concentrations in petroleum products according to ASTM D 2622-10 with the S8 TIGER ECO "Petro" is reliable, precise and accurate. The optimized excitation and the intensity optimized beam path with the germanium crystal leads to an unmatched analytical performance.

The determination of ultra low sulfur concentrations allows driving the production of low sulfur automotive fuels with the S8 TIGER ECO in the most efficient way. It ensures that the actual and future limit values of sulfur in fuels are not exceeded along the supply chain. Due to the unique vacuum seal and the SampleCare™ packages the S8 TIGER ECO "Petro" is an indispensible tool for every refinery and testing lab providing safe and reliable analysis of liquid fuel samples, highest instrument uptime and lowest cost of ownership. With 5 years warranty on the X-ray tube peace of mind is guaranteed.

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