Get More Precision at Trace Level: Sulphur-Analysis in Automotive Fuels According to ISO 20884 and ASTM D 2622 By WDXRF

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In the last years fuel quality has been increasingly regulated by legislation to enforce more stringent automotive emission levels. The most important characteristic is the sulphur concentration in different fuel types. The allowable limit of sulphur in automotive fuels went down to the lowest mg/kg range. A limit of 50 mg/kg sulphur was announced in Europe for 2005, but tax incentives for fuels established even lower levels. Since 2009 Euro V Diesel is enforced with a maximum concentration of 10 ppm sulphur. In the US EPA regulations are enforcing a level of less than 15 ppm for Highway Diesel fuel. The preferred technology to analyse low sulphur at this low level is wavelength dispersive X-ray fluorescence spectrometry (WDXRF). But these low levels are no longer covered by ISO 14596 or ASTM D 2622 for high ranges.

The norm which describes the low sulphur fuels analysis by WDXRF is now ISO 20884 and ASTM D 2622 for the very low range down to 5 ppm. As matrix effects hardly vary when analysing fuels, only ISO 20884 and ASTM D 2622 could be established without an external standardisation. The concentration range is subdivided in a low range (5 - 60 mg/kg) and a high range (> 60 - 500 mg/kg). This report describes how the modern WDXRF spectrometer S8 TIGER analyses effectively the low sulphur type fuels on a daily basis. The high spectral resolution and the enhanced light element determination the wavelength dispersive X-ray fluorescence (WDXRF) spectrometer S8 TIGER easily achieves detection limits down to 0.2 ppm.

Figure 1: WDXRF spectrometer S8 TIGER

Instrument

The S8 TIGER is perfectly suited for the low sulphur analysis in a refinery or a commercial testing lab. Even lowest traces are analysed efficiently and reliably based on the optimum instrument setup. With excitation power of up to 4 kW, a high resolution, high intensity optimised analyser crystal XS-GE-C the S8 TIGER provides optimal analytical performance. The system is optimised for the analysis of liquid samples to make the operation as simple and failsafe as possible:

Liquid samples are automatically detected during the loading and the helium mode is enforced to prevent spillage of the sample and damages on system components. The low temperature X-ray tube head and the unique atmospheric helium mode prevent volatile samples from boiling which finally protects the instrument and ensures the best analytical stability. Finally the SampleCare system ensures with the unique vacuum seal the protection of spectrometer components separating the sample and spectrometer chamber. Fumes and droplets will not enter the spectrometer chamber. This completely protects crystals and detectors versus against damage and avoids frequent system failures like with conventional spectrometers on the market.

The S8 TIGER comes for ISO 20884 and ASTM D 2622 with PETRO-QUANT and the ready-to-analyse solution containing the calibration inclusively the specific set of calibration standards, the optimised measurement method and drift correction samples. For instrument verification and the performance test in addition a quality check sample is supplied with the package. This helps to establish easily the analytical quality routine for audit conformity.

Sample preparation and measurement parameters

7 g of the gasoline sample are filled in a liquid cup with a 3.6 µm Mylar foil. This foil is transparent for the light element radiation, but provides chemical resistance against gasoline.

All data obtained using the following measurement parameters are listed in table 1. The helium mode with atmospheric pressure is applied, because of the high volatility of fuel samples.

Figure 2: SampleCare system to enable safe analysis of liquid samples

Table 1: Measurement Parameters for ISO 20884

Anode	Rhodium
Voltage	30 kV
Current	135 mA
Collimeter	0,46°
Crystal	curved Germanium XS-GE-C
Measuring Time	Peak 30 s, Background 30s
S Line Position	110,738°
Background Position	113,150°
Detector	Flow counter with discriminator settings at 50 - 160%
Optical Path	atm. Helium (with vacuum seal)
FIlm	3.6 µm Mylar®

Calibration of the Low Concentrations Range

The norm compliant calibration is based 5 standards ranging from 5 to 50 ppm plus blank sample, and is based on a linear model. The following graph and table describes the calibration (concentrations in mg/kg):

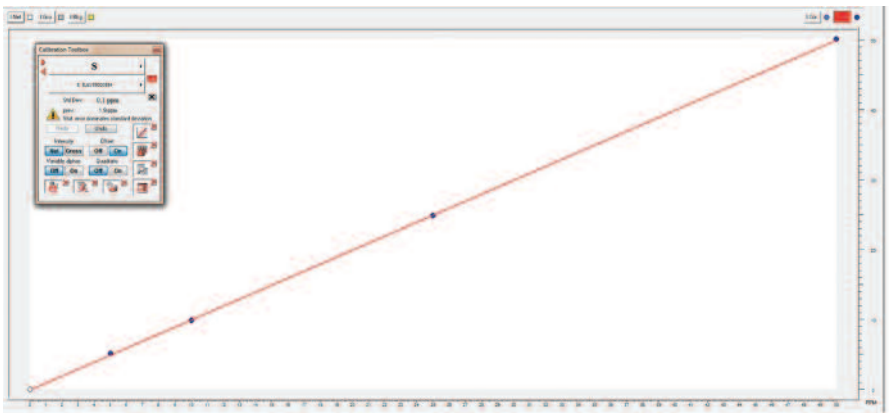

Figure 3: Calibration curve for ISO 20884 low range 5 – 50 ppm

Table 2: Calibration details for ISO 20884 low range

Number	Chem. Conc. [ppm]	XRF Con. [ppm]	Absolute Deviation [ppm]
1	0	0,1	0,1
2	5	5,1	0,1
3	10	9,9	-0,1
4	25	24,9	-0,1
5	50	50,1	0,1

The mean regression deviation of the calibration is less than 0.1 ppm, the squared correlation coefficient is with a value of 0.999957 very close to 1. The detection limit LOD (3s, 24 seconds) is 0.4 ppm.

Repeatability Low Concentration Range

The repeatability of the ISO 20884 method was checked with a 10.3 ppm QC-sample by measuring the sample 22 times. According to ISO 20884, the difference between two consecutive results in the range of 10.3 mg/kg must not exceed 1.9 mg/kg in more than one out of 20 cases. The maximum deviation of two consecutive measurements was 0.9 ppm, finally much less, the relative standard deviation was 0.3 ppm. These results are fully compliant with ISO 20884.

Table 3: Repeatability test for the low concentration range analysing a sample with 10.3 ppm for 22 times

Time	S [ppm]	Deviation from previous [ppm]
2:58 PM	10,5	
3:00 PM	10,7	-0,2
3:02 PM	10,3	0,4
3:05 PM	10,5	-0,2
3:07 PM	10,4	0,1
3:11 PM	9,9	0,5
3:13 PM	9,9	0,0
3:15 PM	10,4	-0,5
3:52 PM	10,4	0,0
3:54 PM	10,5	-0,1
3:56 PM	10,2	0,3
3:58 PM	10,6	-0,4
4:00 PM	10,0	0,6
4:02 PM	10,2	-0,2
4:31 PM	10,8	-0,6
4:33 PM	9,9	0,9
4:35 PM	10,7	-0,8
4:37 PM	10,3	0,4
4:39 PM	10,1	0,2
4:42 PM	10,5	-0,4
4:44 PM	10,2	0,3
4:46 PM	10,3	-0,1
Average [ppm]	10,3	
Abs. Std. Dev. [ppm]	0,3	
Rel. Std. Dev [ppm]	2.7	

Calibration of the High Concentrations Range

The norm compliant calibration is based 6 standards ranging from 50 to 500 ppm plus blank sample and is based on a linear model. The following graph and table describes the calibration (concentrations in mg/kg):

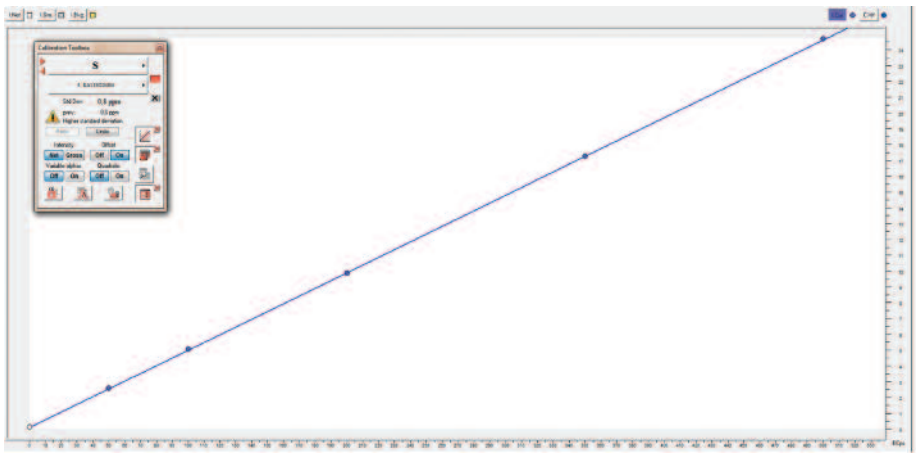

Figure 4: Calibration curve for ISO 20884 high range 50 – 500 ppm

Table 4: Calibration details for ISO 20884 high range

Number	Chem. Conc. [ppm]	XRF Con. [ppm]	Absolute Deviation [ppm]
1	0	0	0
2	50	50,6	0,6
3	100	100,5	0,5
4	200	198,6	-1,4
5	350	349,6	-0,4
6	500	500,6	0,6

The mean regression deviation of the calibration is less than 0.8 ppm, the squared correlation coefficient is with a value of 0.999963 very close to 1. The detection limit LOD (3s, 30 seconds) is 0.4 ppm.

Repeatability Low Concentration Range

The repeatability of the ISO 20884 method was checked with a 150 ppm QC-sample by measuring the sample 22 times. According to ISO 20884, the difference between two consecutive results in the range of 10.3 mg/kg must not exceed 4 mg/kg in more than one out of 20 cases. The maximum deviation of two consecutive measurements was 1.4 ppm, finally much less than described in the standards as maximum difference between two consecutive measurements. The relative standard deviation was 0.5 ppm. These results are fully compliant with ISO 20884 and ASTM D 2622.

Table 5: Repeatability test for the high concentration range analysing a sample with 150 ppm for 22 times

Time	S [ppm]	Deviation from previous [ppm]
11:50	150,7	
11:53	150,5	0,2
11:55	151,4	-0,9
11:57	151,0	0,4
11:59	150,6	0,4
12:38	151,0	-0,4
12:40	151,5	-0,5
12:42	150,7	0,8
12:45	151,8	-1,1
12:48	151,7	0,1
12:50	150,3	1,4
12:52	151,2	-0,9
12:54	150,5	0,7
12:56	151,5	-1
12:58	150,4	1,1
13:00	151,3	-0,9
13:03	150,6	0,7
13:05	151,1	-0,5
13:07	151,4	-0,3
13:09	151,8	-0,4
13:11	150,5	1,3
13:13	150,0	0,5
Average [ppm]	151,0	
Abs. Std. Dev. [ppm]	0,5	
Rel. Std. Dev. [ppm]	0,35%	

Table 6: Summary of results for ISO 20884

	ISO 20884 Low	ISO 20884 High
Calibration		
Range	5 - 50 ppm	50 - 500
Standards	5 incl. Blank	6 incl. Blank
Calib. Regress. Dev.	0.1	0.8
Squared corr. Coeff.	0.999957	0.999963
LOD (3 , 30sec.)	0.4	0.4
Statistical Dev.	0.2	0.2 - 0.5
Precision Test		
Repeatability		
Conc.	10.3 ppm	150 ppm
Min.	9,9 ppm	150 ppm
Max.	10,8 ppm	151.8 ppm
Abs. Std. Dev.	0.3 ppm	0.5 ppm
Rel. Std. Dev.	2.7%	0.35%
Maximum Difference	0,9 ppm	1.4 ppm
Allowed Difference	1.9 ppm	4 ppm

Results and Conclusion

The S8 TIGER with 4 kW excitation power and the curved germanium analyser crystal XS-GE-C easily achieves the analytical performance required for the determination of low sulphur in automotive fuels according to ISO 20884 and ASTM D 2622. It delivers impressive analytical precision allowing a close monitoring of the product quality. The requirements of ISO and ASTM are easily achieved. The results are shown in Table 6.

Therefore the S8 TIGER is perfectly suited for the sulphur test of automotive fuels in refineries, commercial testing labs and for governmental service labs in daily routine. Providing best analytical performance in combination with simple intuitive operation and failsafe handling of liquid sample the S8 TIGER provides peace of mind. The PETRO-QUANT solution package for ISO 20884 and ASTM D 2622 even provides the audit conform long term performance test, so even analytical quality audits are easy to pass.