



## Lab Report XRF 104

# S8 TIGER with PETRO-QUANT SULFUR-ANALYSIS IN AUTOMOTIVE FUELS ACCORDING TO ISO 20884

### Introduction

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

The norm which describes the low sulfur fuels analysis by WDXRF is now ISO 20884. As matrix effects hardly vary when analyzing fuels only, ISO 20884 could be established with an external standardization. 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 analyzes the low sulfur type fuels efficiently on a daily basis. The high spectral resolution and the enhanced light element determination enable the S8 TIGER to easily achieve detection limits as low as 0.2 ppm.

### Instrument

The S8 TIGER is perfectly suited for the low sulfur analysis in a refinery or a commercial testing lab. Even lowest traces are analyzed efficiently and reliably based on the optimum instrument setup. Combining excitation power of up to 4 kW with the high resolution and a high intensity crystal XS-Ge-C the S8 TIGER provides high sensitivity. The system is optimized for the analysis of liquid samples to make the operation as simple as possible: The TouchControl makes the start of samples simple and failsafe.

Liquid samples are automatically detected during the loading and the helium mode is enforced to prevent spillage of the sample and possible damages to 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 SampleCare with the unique vacuum seal ensures 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 damage and avoids frequent system failures which conventional spectrometers on the market have.

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

### Sample preparation and measurement parameters

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

Table 1: Measurement Parameters for ISO 20884

Anode	Rhodium
Voltage	30 kV
Current	135 mA
Collimator	0,46°
Crystal	curved germanium XS-Ge-C
Measuring Time	Peak 30 s, Background 30 s
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 on 5 standards ranging from 5 to 50 ppm plus a blank sample and is based on a quadratic model. The following graph and table describe the calibration (concentrations in mg/kg):

The mean regression deviation of the calibration is less than 0.1 ppm; the squared correlation coefficient is a value of 0.999957, very close to 1. The detection limit LOD (3s, 30 seconds) is 0.4 ppm

### Repeatability Low Concentration Range

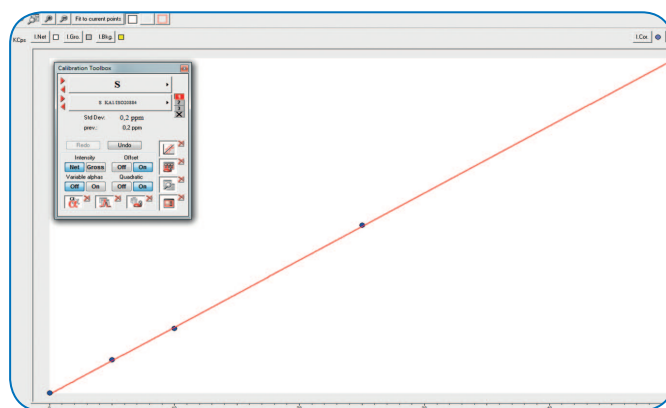


Figure 1: Calibration curve for ISO 20884 low range 5 – 60 ppm

Table 2: Calibration details for ISO 20884 low range

Number	Chem. Conc. [ppm]	XRF Conc. [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 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 analyzing 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
Mean Value	10.3	
Abs. Std [ppm]	0.3	
Rel. Std.	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 quadratic model. The following graph and table describes the calibration (concentrations in mg/kg):

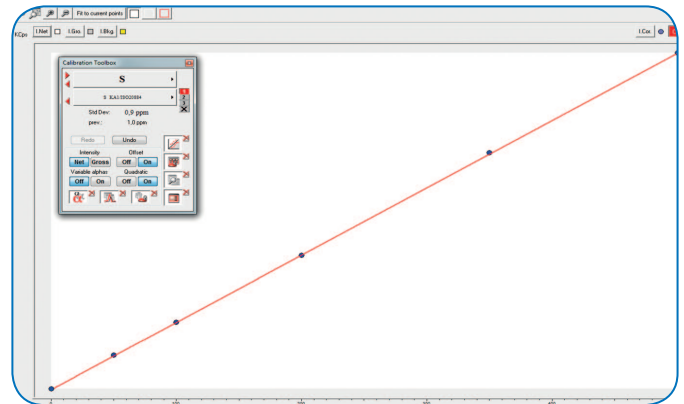


Figure 2: Calibration curve for ISO 20884 high range 60 – 500 ppm

Table 4: Calibration details for ISO 20884 high range

Number	Chem. Conc. [ppm]	XRF Conc. [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.

## Repeatability High 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 > 60 mg/kg must not exceed 4.0 mg/kg in more than one out of 20 cases. The maximum deviation of two consecutive measurements was 1.4 ppm, finally much less; the relative standard deviation was 0.5 ppm. These results are fully compliant with ISO 20884.

Table 5: Repeatability test for the high concentration range analyzing 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	-1.0
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	151.0	
Std.Dev.	0.5	
Rel.Std.Dev.	0.35%	

## Results and Conclusion

The S8 TIGER with 4 kW excitation power and the curved germanium analyzer crystal XS-Ge-C easily achieves the analytical performance required for the determination of

low sulfur in automotive fuels according to ISO 20884 and exceeds impressively the precision requirements. The results are shown in Table 6.

Table 6: Summary of results for ISO 20884

	ISO 20884 Low	ISO 20884 High
<b>Calibration</b>		
Range	5 - 60 ppm	> 60 - 500
Standards	5 incl. Blank	6 incl. Blank
Calib. Regress. Dev.	0.1	0.8
Squared corr. Coeff.	0.999957	0.999963
LOD (3, 30 sec.)	0.4	0.4
Statistical Dev.	0.2	0.2 -0.5
<b>Precision Test</b>		
Repeatability		
Conc.	10.3 ppm	150 ppm
Min.	9,9 ppm	150 ppm
Max.	10,8 ppm	151.8 ppm
Abs. Sd. 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

Therefore the S8 TIGER is perfectly suited for the sulfur 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 samples the S8 TIGER enables peace of mind. The PETRO-QUANT solution package for ISO 20884 even provides the audit conform long term performance test, so even analytical quality audits are easily passed.

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