S4 PIONEER
SULFUR-ANALYSIS ACCORDING ISO 20884

Introduction

In the last years, the allowable limit of sulfur content in fuels went down to the lowest mg/kg range. A limit of 50 mg/kg sulfur was announced in Europe for 2005, but tax incentives for fuels with less than 10 mg/kg S shift routine analyses to a range which is no longer covered by ISO 14596[2] (see Lab Report XRF 62).

As matrix effects hardly vary when analyzing fuels only, ISO 20884[1] could be established with an external standard. The concentration range is subdivided in a low range (5 - 60 mg/kg) and a high range (> 60 - 500 mg/kg).

Sample Preparation

5.0 ± 0.1 g of the sample were poured into liquid cups (inner diameter 3.5 cm) that were covered with a 2.5 µm Mylar® film. Each cup was placed on a printing or weighing paper for a 30 s tightness testing and the sample was subsequently measured.

Measurement Parameters

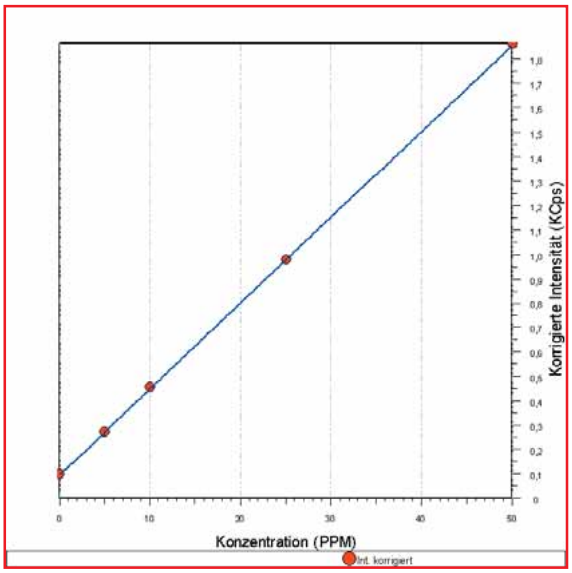
All data were obtained using the following measurement parameters:

Anode	Rhodium
Voltage	30 kV
Current	135 mA
Collimator	0,46°
Crystal	Germanium
S Line Position	110.746°
Measuring Time	24 s
Background Position	113.150°
Measuring Time	24 s
Detector	Flow counter with pulse height analysis
Discrimination Window	50 - 160%
Optical Path	atm. Helium (with vacuum seal)
Film	2,5 µm Mylar®

Because of the high volatility of fuel samples, the helium mode of atmospheric pressure is applied.

Calibration Low Concentrations Range

A norm compliant calibration is based on a quadratic model. The following graph and table describes the calibration (concentrations in mg/kg):



Conc.	Conc. XRF	Absolute Deviation	Count.Stat. Deviation	LOD
0.0	0.0	0.0	0.2	0.6
5.0	4.9	-0.1	0.3	0.6
10.0	10.1	0.1	0.3	0.6
25.0	25.0	0.0	0.3	0.6
50.0	50.0	0.0	0.3	0.6

The calibration can be summarized as follows (concentrations in mg/kg):

Concentration Range	5.0 - 60.0
Number of Standards	5
Intensity Model	Net Intensities
Calibration Model	Quadratic
Regression Minimizes	Relative Errors
Mean Regression Deviation	< 0.1
Counting Statistic Deviation	0.2 - 0.3
Limit Of Detection (LOD) (3 σ, 24 s)	0.6

$$LOD = \frac{3}{m} \cdot \sqrt{\frac{I_{Bgr}}{t_{Bgr}}}$$

m	Sensitivity of sulfur calibration [cps/%(m/m)]
I_{Bgr}	Count rate at background position [cps]
t_{Bgr}	Counting time at background position [s]

Accuracy Low Concentrations Range

As a first step, the accuracy of the calibration was checked by analysis of a few DIN round-robin samples. The results, including respective DIN R/√2 reproducibility ranges, are presented in the following table (concentrations in mg/kg):

Sample	Conc.	DIN R/√2 range	
SOK672	6.8	4.9 – 8.9	✓
JF675	49.1	47.7 – 56.5	✓
SOK681	6.9	5.7 – 9,6	✓
SOK682	5.2	3.9 – 7.5	✓
DK684	26.0	24.0 – 31.4	✓
HEL686	39.3	37.6 – 47.5	✓
OK691	9.5	7.7 – 12.0	✓
SOK692	9.4	7.6 – 12.0	✓
DK693	7.0	5.6 – 9.5	✓
DK694	6.4	5.0 – 8.8	✓
JF696	40.9	37.4 – 47.3	✓

(S)OK (Premium) Gasoline, JF Jet Fuel, DK Diesel Fuel, HEL Light Fuel Oil

All results were found within the demanding round-robin DIN R/√2 ranges.

Repeatability Low Concentrations Range

In addition to the accuracy of the analysis method, the precision had to be tested. Repeatability was determined running the round-robin SOK672 premium gasoline sample 20 times. According to ISO 20884, the difference between two consecutive results in the range of 6.8 mg/kg must not exceed 1.9 mg/kg in more than one out of 20 cases. The results and differences of the respective measurements are given in the following table (n = 20; concentrations in mg/kg):

Date	Concentration	Difference
09.07.2004 09:57	7.1	
09.07.2004 09:59	6.8	-0.3
09.07.2004 10:01	6.9	0.1
09.07.2004 10:03	7.0	0.1
09.07.2004 10:05	7.0	0.0
09.07.2004 10:07	6.6	-0.4
09.07.2004 10:09	6.7	0.1
09.07.2004 10:11	7.5	0.8
09.07.2004 10:13	7.4	-0.1
09.07.2004 10:15	7.6	0.2
09.07.2004 10:18	7.1	-0.5
09.07.2004 10:20	7.6	0.5
09.07.2004 10:22	7.5	-0.1
09.07.2004 10:24	7.5	0.0
09.07.2004 10:26	8.2	0.7
09.07.2004 10:28	8.1	-0.1
09.07.2004 10:31	7.2	-0.9
09.07.2004 10:33	7.1	-0.1
09.07.2004 10:35	7.4	0.3
09.07.2004 10:37	8.2	0.8
Average	7.3	
Mean Abs. Std. Dev.	0.5	
Minimum	6.6	0.0
Maximum	8.2	0.9
Range	1.6	
Maximum Difference of the Norm		1.9
Norm Compliance		✓

The repeatability requirements are easily met with the S4 PIONEER. The maximum deviation is not exceeded in the whole run and the maximum real deviation is less than the half of the specified limit.

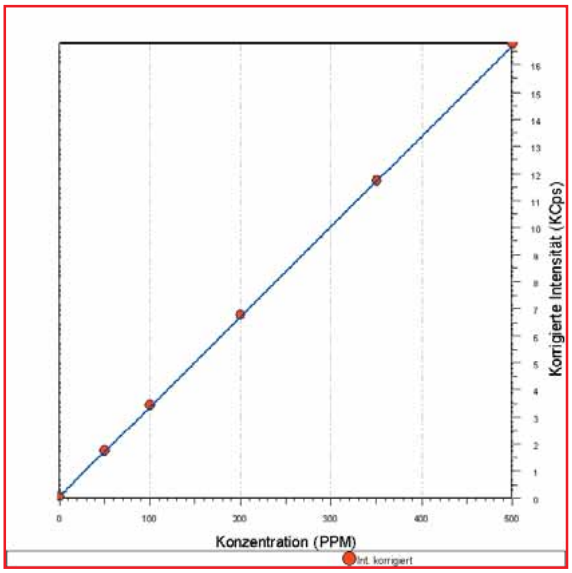
These values demonstrate the excellent short-time stability of the S4 PIONEER. To get additional data for long-time stability the same sample SOK672 was analyzed over a period of 68 days. The results are presented in the following table (n = 21; concentrations in mg/kg):

Date	Concentration	Difference
09.07.2004 09:57	7.1	
12.07.2004 08:46	7.5	0.4
13.07.2004 07:40	6.9	-0.6
14.07.2004 09:01	7.0	0.1
15.07.2004 07:37	7.1	0.1
20.07.2004 09:14	7.3	0.2
21.07.2004 11:08	7.8	0.5
22.07.2004 10:35	7.4	-0.4
23.07.2004 07:43	7.0	-0.4
27.07.2004 07:39	6.6	-0.4
28.07.2004 08:36	7.3	0.7
29.07.2004 07:35	6.2	-1.1
30.07.2004 07:48	7.3	1.1
02.08.2004 07:41	7.2	-0.1
03.08.2004 08:55	7.7	0.5
04.08.2004 07:59	7.0	-0.7
05.08.2004 08:42	7.3	0.3
06.08.2004 07:39	7.2	-0.1
09.08.2004 10:20	7.4	0.2
27.08.2004 09:20	7.6	0.2
15.09.2004 15:02	7.4	-0.2
Average	7.2	
Mean Abs. Std. Dev.	0.4	
Minimum	6.2	0.1
Maximum	7.8	1.1
Range	1.6	
Maximum Difference of the Norm		1.9

Even over a period of 68 days, nearly the same parameters are reached as compared to the short-time stability measurements. Range (1.6 mg/kg in both cases) and mean absolute deviation (0.5 resp. 0.4 mg/kg) are almost the same and the maximum difference of two consecutive measurements is not exceeded at all, even over a period of 68 days. This excellent stability of the S4 PIONEER is, among other features, based on the unique vacuum seal separating sample and spectrometer chamber. This component allows a complete and fast exchange of mode air (sample change) and helium (measurement) in the small sealed volume of the sample chamber. Thus, highest stability conditions are guaranteed from the very beginning of any measurement.

Calibration High Concentrations Range

The calibration for the high concentration range of ISO 20884 is quadratic as well. It is presented in the following graph and table (concentrations in mg/kg):



Conc.	Conc. XRF	Absolute Deviation	Count.Stat. Deviation	LOD
0.0	-0.4	-0.4	0.3	0.6
50.0	50.0	0.0	0.3	0.6
99.9	100.7	0.8	0.4	0.6
200.0	199.9	-0.1	0.5	0.6
349.7	348.8	-0.9	0.7	0.6
499.6	500.1	0.5	0.8	0.6

The calibration can be summarized as follows (concentrations in mg/kg):

Concentration Range	> 60.0 - 500.0
Number of Standards	6
Intensity Model	Net Intensities
Calibration Model	Quadratic
Regression Minimizes	Relative Errors
Mean Regression Deviation	0.6
Counting Statistic Deviation	0.3 - 0.8
Limit Of Detection (3 σ, 24 s)	0.6

Accuracy High Concentrations Range

Again the accuracy of the calibration was checked first analyzing several DIN round-robin samples. Results as well as respective DIN R/√2 ranges are given by the following table (concentrations in mg/kg):

Sample	Conc.	DIN R/√2 range	
JF676	120.4	118.2 – 136.0	✓
DK684	333.8	321.0 – 363.8	✓
JF696	147.0	142.1 – 164.9	✓

JF Jet Fuel, DK Diesel Fuel

As in the low concentrations range the results match the demanding DIN R/√2 ranges in the high concentration range too.

Repeatability High Concentrations Range

The repeatability test for the high concentration range was performed analyzing the DIN round-robin sample JF676. According to ISO 20884, the difference between two consecutive results in the high concentration range must not exceed 4.0 mg/kg in more than one out of 20 cases. The results and differences of this test are presented in the following table (n = 20; concentrations in mg/kg):

Date	Concentration	Difference
09.07.2004 13:17	120.3	
09.07.2004 13:19	121.9	1.6
09.07.2004 13:21	121.1	-0.8
09.07.2004 13:24	121.3	0.2
09.07.2004 13:26	119.9	-1.4
09.07.2004 13:28	120.8	0.9
09.07.2004 13:30	120.6	-0.2
09.07.2004 13:32	120.9	0.3
09.07.2004 13:34	120.2	-0.7
09.07.2004 13:36	119.6	-0.6
09.07.2004 13:38	121.0	1.4
09.07.2004 13:40	120.8	-0.2
09.07.2004 13:42	120.4	-0.4
09.07.2004 13:45	120.1	-0.3
09.07.2004 13:47	121.3	1.2
09.07.2004 13:49	120.2	-1.1
09.07.2004 13:51	120.0	-0.2
09.07.2004 13:53	119.4	-0.6
09.07.2004 13:56	118.9	-0.5
09.07.2004 13:58	119.8	0.9

Average	120.4	
Mean Abs. Std. Dev.	0.7	
Minimum	118.9	0.2
Maximum	121.9	1.6
Range	3.0	
Maximum Difference of the Norm		4.0
Norm Compliance		✓

The maximum deviation is less than half of the specified limit for the high concentration range as well.

The next table gives the data of a long-time stability test (68 days) of ISO 20884 high concentration range with S4 PIONEER (n = 21; concentrations in mg/kg):

Date	Concentration	Difference
09.07.2004 13:17	120.3	
12.07.2004 08:59	120.5	0.2
13.07.2004 07:56	119.4	-1.1
14.07.2004 09:12	120.7	1.3
15.07.2004 07:49	120.7	0.0
20.07.2004 09:25	119.6	-1.1
21.07.2004 11:18	119.0	-0.6
22.07.2004 10:42	119.8	0.8
23.07.2004 07:55	121.4	1.6
26.07.2004 10:08	120.3	-1.1
27.07.2004 07:53	120.1	-0.2
28.07.2004 08:52	120.2	0.1
29.07.2004 07:44	118.3	-1.9
30.07.2004 08:02	120.6	2.3
02.08.2004 07:54	120.4	-0.2
03.08.2004 09:06	121.1	0.7
04.08.2004 08:12	120.5	-0.6
05.08.2004 08:54	119.4	-1.1
06.08.2004 07:53	119.7	0.3
09.08.2004 10:28	118.8	-0.9
27.08.2004 09:33	121.0	2.2
15.09.2004 15:04	119.7	-1.3

Average	120.1	
Mean Abs. Std. Dev.	0.8	
Minimum	118.3	0.0
Maximum	121.4	2.3
Range	3.1	
Maximum Difference of the Norm		4.0

Long-time stability parameters are perfectly comparable to the short-time stability parameters. Ranges (3.0 resp. 3.1 mg/kg) as well as mean absolute deviations (0.7 resp. 0.8 mg/kg) are almost identical. Additionally, the maximum deviation of two consecutive measurements is always clearly below the norm limits.

Conclusion

The S4 PIONEER is perfectly suited to run sulfur analyses according ISO 20884 for the high concentration range (> 60 - 500 mg/kg) as well as for the low concentration range (5 - 60 mg/kg).

The accuracy of the calibrations was verified by the analysis of DIN round-robin samples. All available samples were analyzed and all the results matched the demanding DIN R/√2 range.

The differences of the short-time stability measurements (about 40 min) were far beyond the maximum deviations given by the norm which would even have been allowed to be overcome in one out of 20 cases. Even for long-time stability measurements (68 days), these maximum differences of consecutive measurements were beyond the norm limit and in the same range as the short-time values.

Notes

[1] ISO 20884 (2004-07) Petroleum products – Determination of sulfur content of automotive fuels – Wavelength dispersive X-ray fluorescence spectrometry (ISO 20884:2004); Beuth Verlag GmbH, Berlin.

[2] ISO 14596 (1998-08) Petroleum products - Determination of sulfur content – Wavelength dispersive X-ray fluorescence spectrometry (ISO 14596:1998); Beuth Verlag GmbH, Berlin

The picture of the gasoline isomerisation line Schwedt on page 1 was kindly provided by Deutsche BP.

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