



Lab Report XRF 157

S2 POLAR

- ASTM D4294: Fast and Reliable Analysis of Sulfur in Petroleum and Petroleum Products

Introduction

X-ray fluorescence (XRF) is the perfect method for the fast and reliable analysis of sulfur in petroleum and petroleum products. In comparison to other spectroscopic techniques such as Atomic Absorption (AAS) or Inductively Coupled Plasma (ICP), the sample preparation is easy and straightforward. In addition, in XRF there is no need for daily re-calibrations and no need of high-volume flammable gases or plasma Argon gas which leads to much lower costs per samples for XRF.

The analysis of sulfur in petroleum and petroleum products is often described by international norms. One common, widely accepted norm is ASTM D4294 which covers the determination of S in a concentration range of 16 ppm to 5 % S in automotive fuels, biodiesel, jet fuel, crude oil and similar petroleum products. The benchtop Energy Dispersive X-ray Fluorescence (EDXRF) S2 POLAR fulfills the requirements of all three concentration ranges of ASTM D4294-16 in its latest revision and is therefore fully norm-compliant with it.

Instrument

The EDXRF S2 POLAR (Fig. 1) with its polarizing HighSense™ beam bath is optimized for petrochemical applications. This results into an excellent signal to background ratio especially for elements like sulfur and outstanding detection limits in the sub-ppm range for diesel and gasoline. The instrument is equipped with a Pd X-ray tube and the HighSense ULS silicon drift detector. It is very small in benchtop size, the compact footprint is ideal for space-saving analysis in labs or on-site process control in refineries, at tank farms, and in oil terminals. The easy-to-use multilingual TouchControl™ interface in combination with the factory calibrated application packages for the norm ASTM D4294 provide a 'One-Button' Ready-to-analyze solution (Fig. 2). This enables users with minimal training to run routine samples.



Figure 1: Compact benchtop EDXRF S2 POLAR

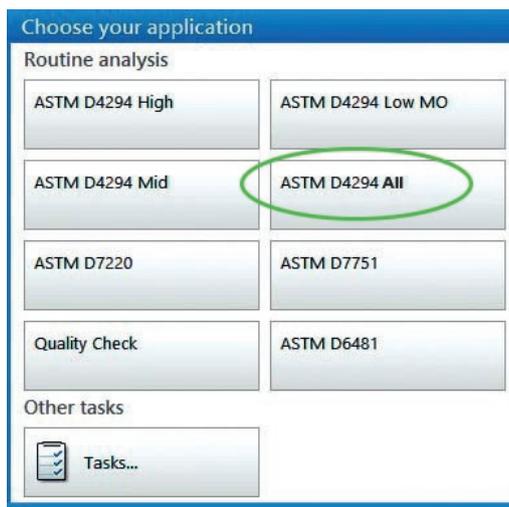


Figure 2: Easy and straightforward to use with factory pre-calibrated One-Button TouchControl™ methods. The norm consists of three concentration ranges (low, mid, and high) that all are covered with one button 'ASTM D4294 All'.

Preparation

The preparation accessory kit for oil samples (K410C215) contains the required parts to prepare liquid cups for the samples. This kit contains liquid cups with 40 mm outer diameter, SampleCare™ cups with 51 mm and Prolene foils with 4.0 μm thickness. The liquid cup preparation tool provided with the S2 POLAR is very helpful to prepare liquid cups in an optimal and efficient way. Due to the standardized liquid cups the costs per sample are low. For sample preparation it is only required to weigh 7 g fuel sample into a liquid cup and place it for the measurement into a larger SampleCare cup. The SampleCare cup itself is also prepared with a 4.0 μm Prolene foil (Fig. 3). The SampleCare cup prevents sample leakages and protects important system components. This guarantees maximum instrument availability, even with high throughput of refinery process samples.



Figure 3: Liquid sample cup (Ø 40 mm) to the left and the larger SampleCare cup (Ø 51 mm) to the right

Measurement

Due to the simple and straightforward sample preparation the analytical results are available within minutes after taking the sample. Table 1 shows the detailed measurement parameters.

Table 1: Measurement parameters

Element	Tube voltage [kV]	Tube current [mA]	Measurement time [s]
S	25	1.7	300

In order to obtain best analytical results for such low sulfur concentrations the measurements have been performed in 'Helium (reduced pressure)' mode. According to the norm samples with a concentration below 100 ppm S are measured as duplicates. All measurements have been performed with SampleCare cup.

Calibration

The ASTM D4294 describes three concentration ranges, starting from 0 - 1000 ppm S, 0.1 – 1.0 % S, and 1 – 5 % S. The Bruker Ready-to-analyze solution ASTM D4294 MO is a factory calibrated application package and consists in total of 23 validated sulfur standards based on mineral oil matrix. With the 'Automatic Line Switch' option of the S2 POLAR software SPECTRA.ELEMENTS the instrument is able to cover the entire ASTM D4294 calibration from 0 to 5 % S in one calibration. Depending on the concentration range the instrument selects fully automatically the calibration curve for the best fitting calibration range. The calibration curve for the lower concentration range is shown in Fig. 4 and overlaid sulfur signals in this calibration range are shown in Fig. 5.

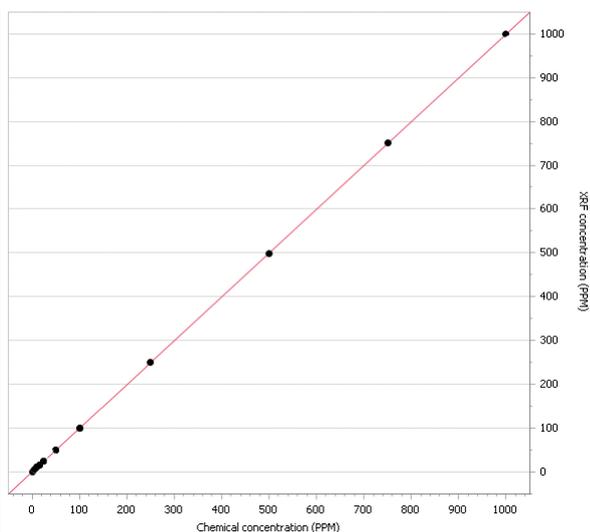


Figure 4: Calibration curve for sulfur in mineral oil for the lower concentration range between 0 to 1000 ppm S

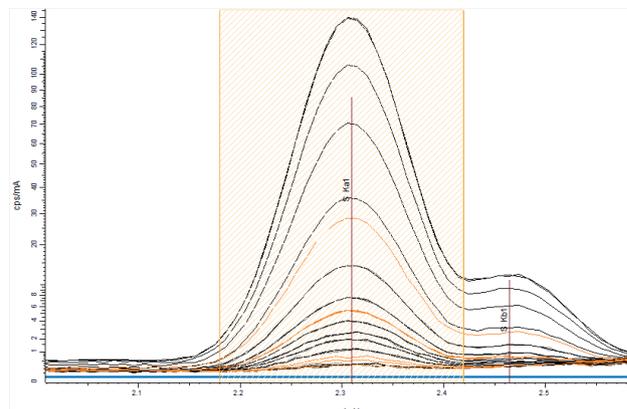


Figure 5: Overlaid sulfur signals in mineral oil between 0 and 1000 ppm S. The integration range is shown in orange.

For ease-of-use the ASTM D4294 MO solution also contains required QC Blank sample, four QC samples at different concentration levels as well as drift correction (DC) samples. There is no need for extensive method set-up and the instrument is immediately ready for routine samples.

Results

The S2 POLAR shows excellent reproducibility for measurements over a longer period of time. Table 2 shows the data of 10 different measurements of the same QC sample over 2 weeks and confirms the excellent analytical performance of the S2 POLAR.

Table 2: Reproducibility of QC sample with 35 ppm S

# Measurement	Date, Time	S [ppm]
1	07.02.2018, 14:26	35.2
2	08.02.2018, 11:37	34.6
3	09.02.2018, 13:23	34.8
4	12.02.2018, 17:42	35.2
5	13.02.2018, 13:18	35.2
6	14.02.2018, 16:32	34.7
7	15.02.2018, 17:06	35.4
8	16.02.2018, 15:23	35.3
9	19.02.2018, 18:12	35.1
10	20.02.2018, 11:39	35.7
Mean		35.1
Abs. Std. Dev.		0.35
Rel. Std. Dev. [%]		0.99

Fig. 5 depicts the repeatability of a 35 ppm S sample for 20 measurements (blue line). The red bars at the bottom show that the difference between successive measure-

ments is for all measurements lower than 1 ppm. The maximum allowed difference is 4.3 ppm S which is easily achieved by the S2 POLAR.

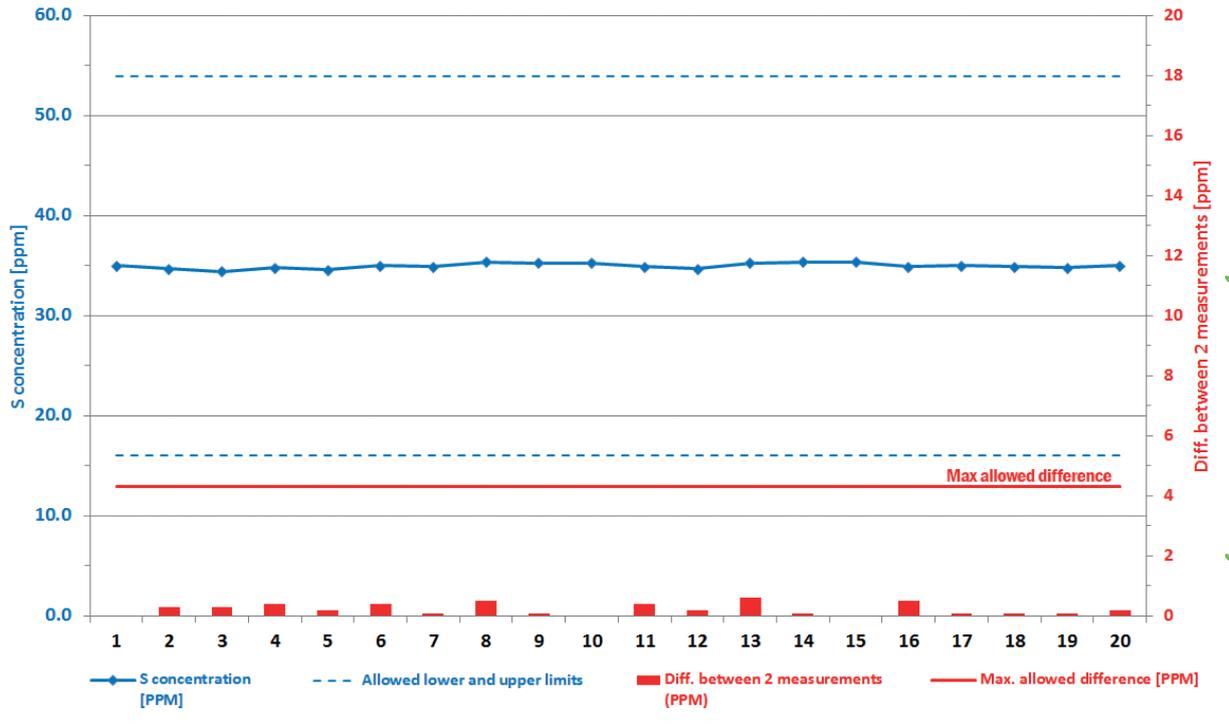


Figure 5: Repeatability of 20 measurements of a mineral oil sample, according to ASTM D4294

Conclusion

With its optimized HighSense beam path the S2 POLAR allows fast and reliable monitoring of sulfur in automotive fuels, biodiesel, jet fuel, crude oil and similar petroleum products. The instrument is fully norm-compliant to all concentration ranges of the international accepted norm ASTM D4294-16. With factory pre-calibrated 'One-Button' TouchControl method and the facilitated sample preparation, routine measurements are easy and

straightforward. SampleCare prevents leakages of liquid samples and protects important system components. This guarantees maximum instrument availability. The compact instrument is suitable for on-site process control in refineries or laboratories as well as for monitoring the downstream supply chain of pipelines, oil terminals, and petrol stations.

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