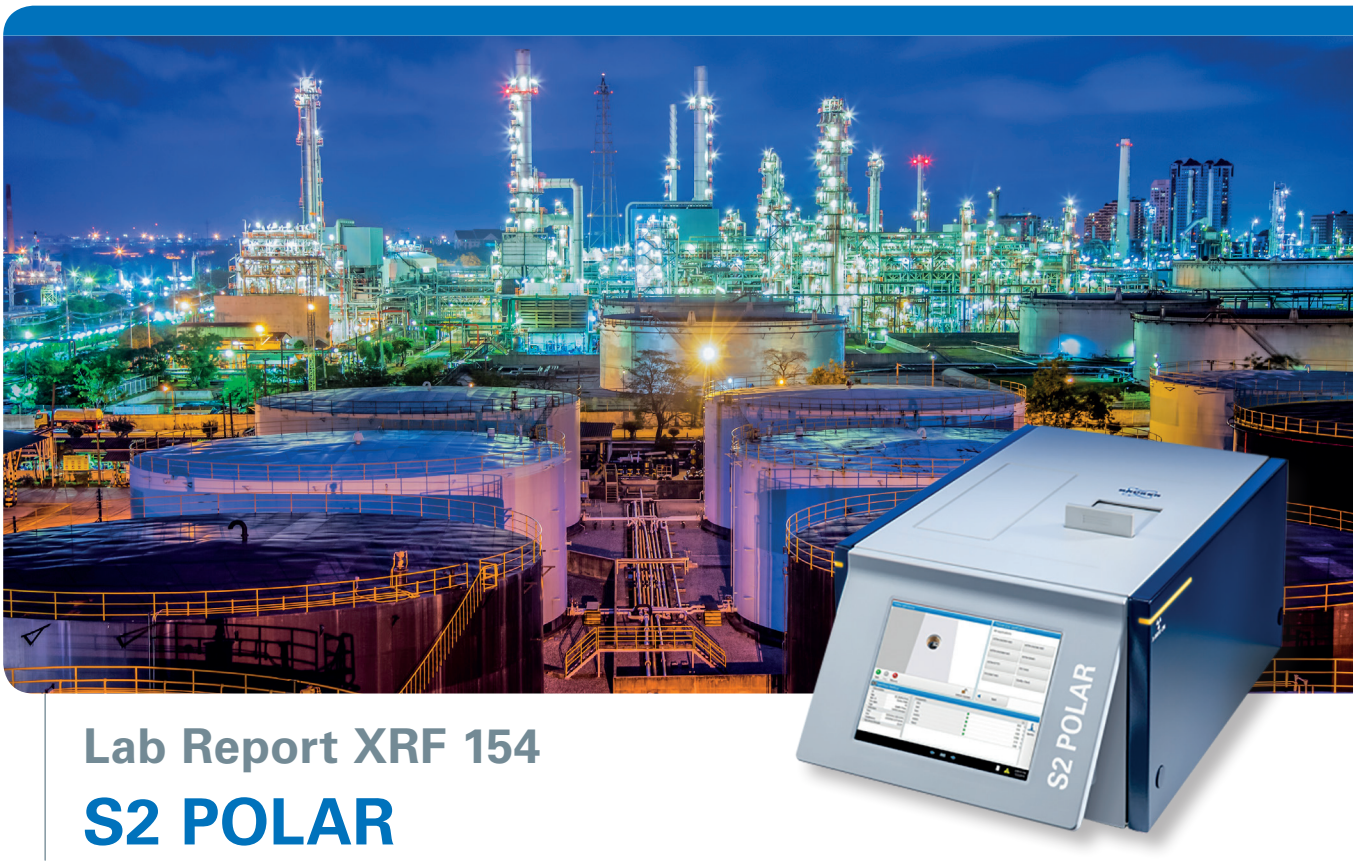

Lab Report XRF 154

S2 POLAR

- ASTM D7220: Accurate and Precise Analysis of Ultra-Low Sulfur (ULS) in Automotive, Heating, and Jet Fuels

Introduction

Sulfur concentrations in automotive fuels are strictly regulated. The current sulfur limit is at a level of 10 to 15 ppm in many countries around the world and others are to follow. Accurate and precise monitoring of the sulfur contents, often below 10 ppm, enhances cost-efficiency and pays back rapidly.

X-ray fluorescence (XRF) is the perfect method for this application: Fast and easy-to-use with straightforward sample preparation. The benchtop Energy Dispersive X-ray Fluorescence (EDXRF) S2 POLAR masters all the requirements for sulfur analysis in automotive, heating, and jet fuels and is fully norm-compliant with ASTM D7220-17. The ASTM D7220 norm is applicable to gasoline, oxygen enriched gasoline, diesel, diesel/biodiesel blends, kerosene, jet fuel, jet fuel/biodiesel blends and No. 2 home heating oil. The scope of the norm covers the concentration range from 3 to 942 ppm S.

Instrument

The EDXRF S2 POLAR (Figure 1) with its polarizing HighSense™ beam bath is optimized for petrochemical applications. This results in an excellent signal to background ratio, especially for elements like sulfur, where outstanding detection limits in the sub-ppm range are achieved. The instrument is equipped with a Pd X-ray tube and the HighSense ULS silicon drift detector. The compact and sturdy design of the S2 POLAR is ideal for small labs or on-site process control at refineries, tank farms, and oil terminals. The easy-of-use multilingual TouchControl™ interface in combination with the factory calibrated application packages for the norm ASTM D7220 provide a 'One-Button' Ready-to-analyze solution (Figure 2). This enables users to run routine sample after minimal training.

Figure 1: S2 POLAR - Compact benchtop EDXRF designed for the fuel industry

Preparation

The dedicated preparation kit for fuel samples contains all required parts to quickly prepare liquid cups for fail-safe fuel sample analyses. The kit contains liquid cups with 40 mm outer diameter, SampleCare™ cups with 51 mm and XRF Mylar® foils with 3.6 µm thickness. The standardized liquid cup solution allows for a cost and time efficient operation. The liquid cup is filled with 7 g of fuel and simply placed into a larger SampleCare cup (Figure 3). The SampleCare cup itself is also prepared with a 3.6 µm Mylar® foil to prevent sample leakage and protect important system components. This guarantees maximum instrument availability, even with high throughput of refinery process samples.

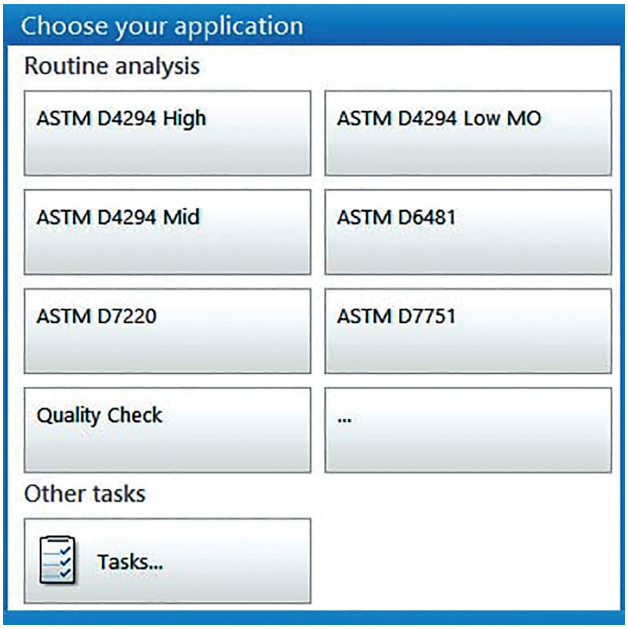

Figure 2: Easy and straightforward to use with factory pre-calibrated 'One-Button' TouchControl™ methods

Measurement

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

Table 1: Instuments 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 'Atmospheric Helium' mode.

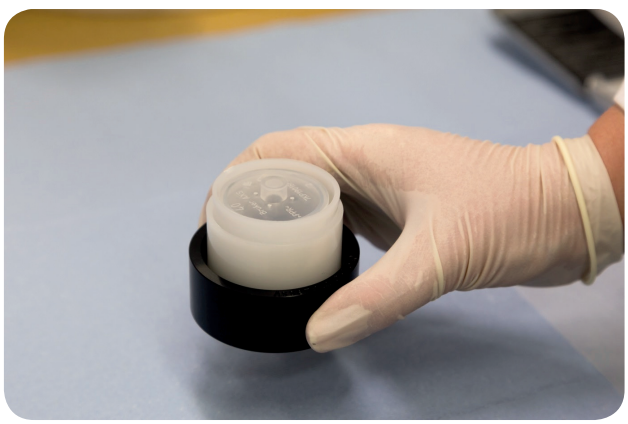

Figure 3: Liquid cup (Ø 40 mm) in SampleCare cup (Ø 51 mm). The liquid cup preparation tool can also be used to transport the sample from lab bench to measurement chamber.

Calibration

Bruker's Ready-to-analyze solution is a factory pre-calibrated application package, which is based on a set of ten validated sulfur standards. The standards contain 0, 5, 10, 15, 25, 50, 100, 250, 500, 750, and 1000 ppm S, respectively. The calibration curve for the lower concentration range is shown in Figure 4 and sulfur signals for 0 to 25 ppm S in gasoline are shown in Figure 5.

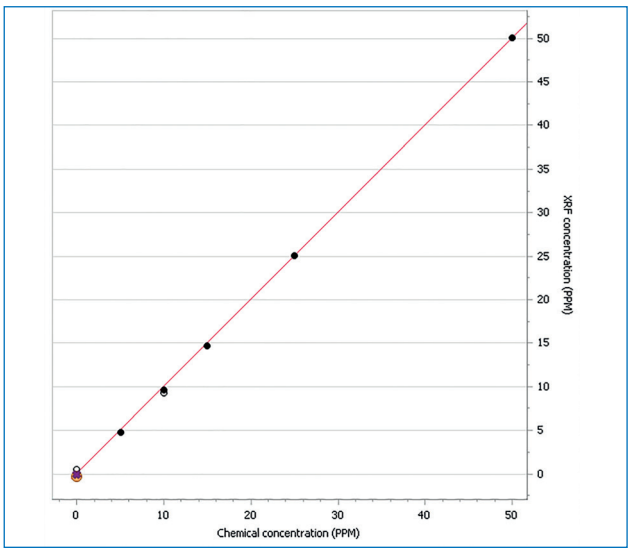

Figure 4: Calibration curve for sulfur in gasoline for the low concentration range between 0 to 50 ppm S

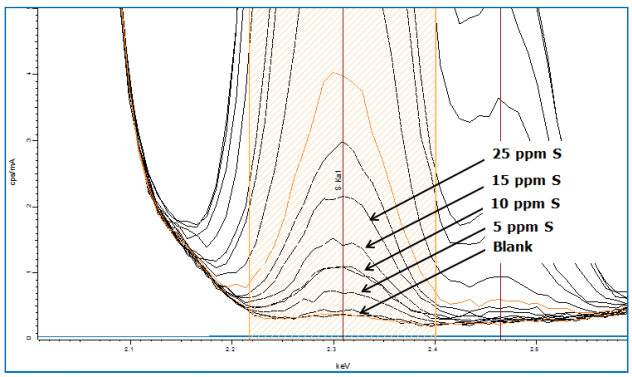

Figure 5: Sulfur signals in gasoline starting with a blank, followed by 5, 10, 15 and 25 ppm S. The integration range is shown in orange.

Even the standard with the lowest S content (5 ppm) shows a clear peak and confirm the analytical performance of the S2 POLAR.

For ease-of-use the ASTM D7220 solution also contains the required quality control (QC) blank sample, two QC samples for the lower concentration range at 10 and 35 ppm S, and one QC sample for the higher concentration range at 200 ppm S as well as a drift correction (DC) sample. There is no need for extensive method set-up and the instrument is immediately available for routine samples.

Results

Repeatability tests proof the excellent performance of the S2 POLAR even for ultra-low sulfur levels (Table 2). The outstanding precision and accuracy of the system for S analyses easily complies with ASTM D7220 and prepares your lab for even more stringent requirements.

Table 2: Repeatability of gasoline analyses

# Measurement	S [ppm]
1	10.1
2	10.0
3	10.2
4	10.9
5	10.4
6	10.4
7	10.3
8	10.4
9	10.1
10	10.2
Mean	10.3
Abs. Std. Dev.	0.2
Rel. Std. Dev. [%]	2.34

In order to determine the Lower Limit of Detection (LLD), 10 measurements of a blank gasoline sample containing no sulfur have been determined (Table 3). The LLD is then defined as three times the standard deviation of these measurements. The measurements were performed with a SampleCare cup.

Table 3: Lower Limit of Detection (LLD) for gasoline

Element	LLD [ppm]	Measurement time [s]
S	0.7	300

Figure 6 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 measurements is for all measurements lower than 1 ppm. The maximum allowed difference is 3.86 ppm S which is easily achieved by the S2 POLAR.

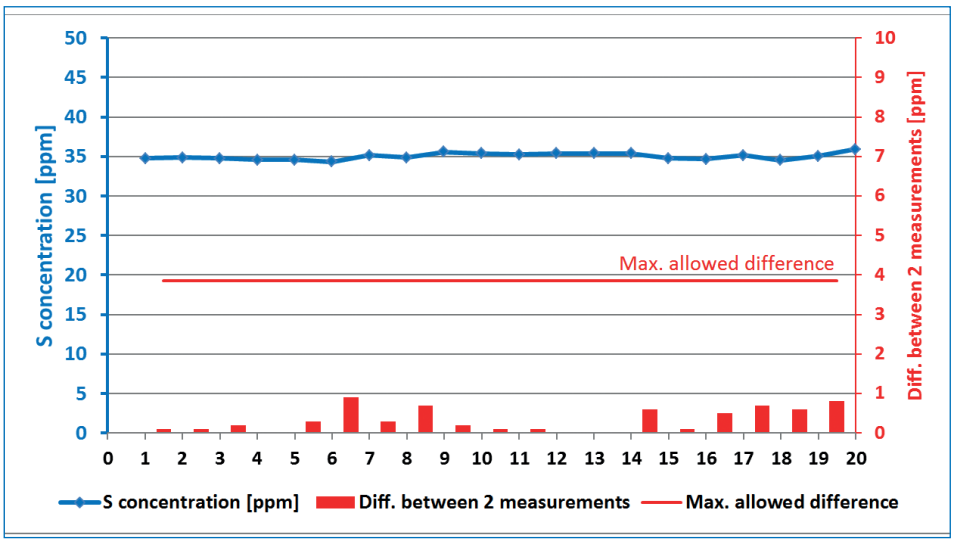

Figure 6: Repeatability test for gasoline samples, according to ASTM D7220

Conclusion

With its optimized HighSense beam path the S2 POLAR allows accurate and precise monitoring of sulfur in automotive fuels, including ultra-low sulfur levels in diesel and gasoline. The instrument is fully norm-compliant with the international accepted norm ASTM D7220-17. With the factory pre-calibrated 'One-Button' Touch-Control solution and the dedicated sample preparation method, routine measurements are easy and straightforward. SampleCare prevents leakages of liquid samples and protects important system components. This guarantees maximum instrument availability.

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