



ASTM D7220: ACCURATE AND PRECISE ANALYSIS OF ULTRA-LOW SULFUR (ULS) IN AUTOMOTIVE, HEATING, AND JET FUELS



Sulfur concentrations are strictly regulated in automotive fuels. The current sulfur limit is at a level of 10 to 15 ppm in many countries around the world and others are to follow. Reducing sulfur in all fractions are causing legal high production costs, especially when it comes to very low sulfur levels. Accurate and precise monitoring of these sulfur levels, often on levels below 10 ppm, leads to cost-effectiveness and pays back immediately.

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 S analysis in automotive, heating, and jet fuels fully norm-compliant to ASTM D7220-17.



S2 POLAR



Figure 1: S2 POLAR - Compact benchtop EDXRF

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 D7220 provide a 'One-Button' Ready-to-analyze solution (Fig. 2). This enables users with minimal training to run routine samples.

Preparation

The preparation accessory kit for fuel samples contains the required parts to prepare liquid cups for fuel samples. This kit contains liquid cups with 40 mm outer diameter, SampleCare™ cups with 51 mm and Mylar® foils with 3.6 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 (Fig. 3). The SampleCare cup itself is also

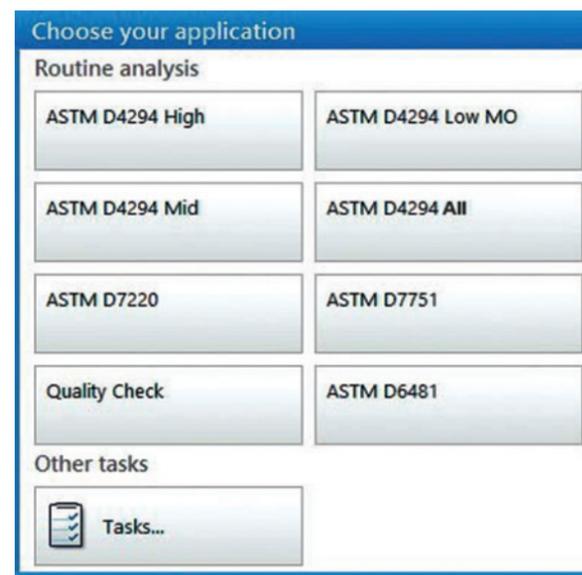


Figure 2: Easy and straightforward to use with factory pre-calibrated 'One-Button' TouchControl™ methods

prepared with a 3.6 μm Mylar® foil. The SampleCare cup prevents

sample leakages and protects important system components. This guarantees maximum instrument availability, even with high throughput of refinery process samples.

Measurement

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

Table 1: Instruments 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. All measurements have been performed with SampleCare cup.



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

The test method 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. The Ready-to-analyze solution ASTM D7220 is a factory calibrated application package and consists of a set of ten validated sulfur standards. The included standards contain 0, 5, 10, 15, 25, 50, 100, 250, 500, 750, and 1000 ppm S. The calibration curve for the lower concentration range is shown in Fig. 4 and overlaid sulfur signals in gasoline are shown in Fig 5.

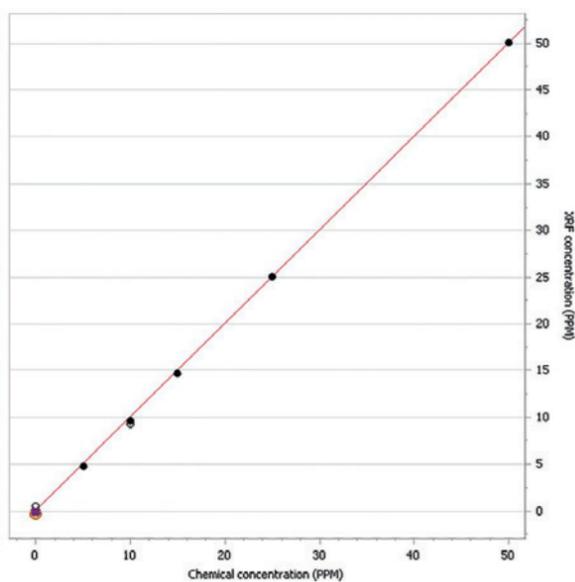


Figure 4: Calibration curve for sulfur in gasoline for the lower concentration range between 0 to 50 ppm S

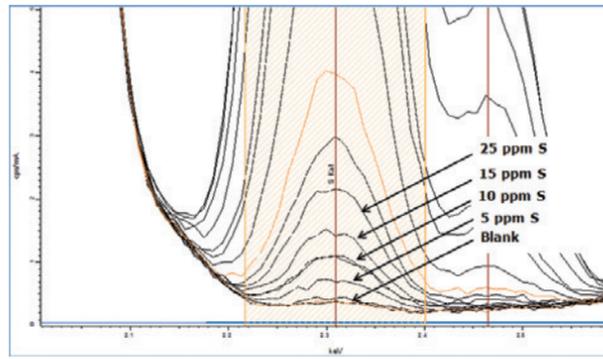


Figure 5: Overlaid sulfur signals in gasoline starting with a blank signal, followed by 5, 10, 15 and 25 ppm S. The integration range is shown in orange.

Already the lowest S standard at 5 ppm shows a decent, from the blank clearly differentiable sulfur signal and confirms the analytical performance of the S2 POLAR. For ease-of-use the ASTM D7220 solution also contains the required QC Blank sample, two QC samples for the lower concentration range at 10 and 35 ppm, and one QC sample for the higher concentration range at 200 ppm 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.

Table 2: Repeatability of gasoline sample

# 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

Results

The S2 POLAR shows excellent repeatability even for ultra-low sulfur levels. Table 2 shows the data of 10 different measurements of the same sample and confirms Bruker 1 the analytical performance of the S2 POLAR.

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

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

Fig. 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.

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 to the international accepted norm ASTM D7220-17. With factory pre-calibrated 'One-Button' TouchControl methods 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.

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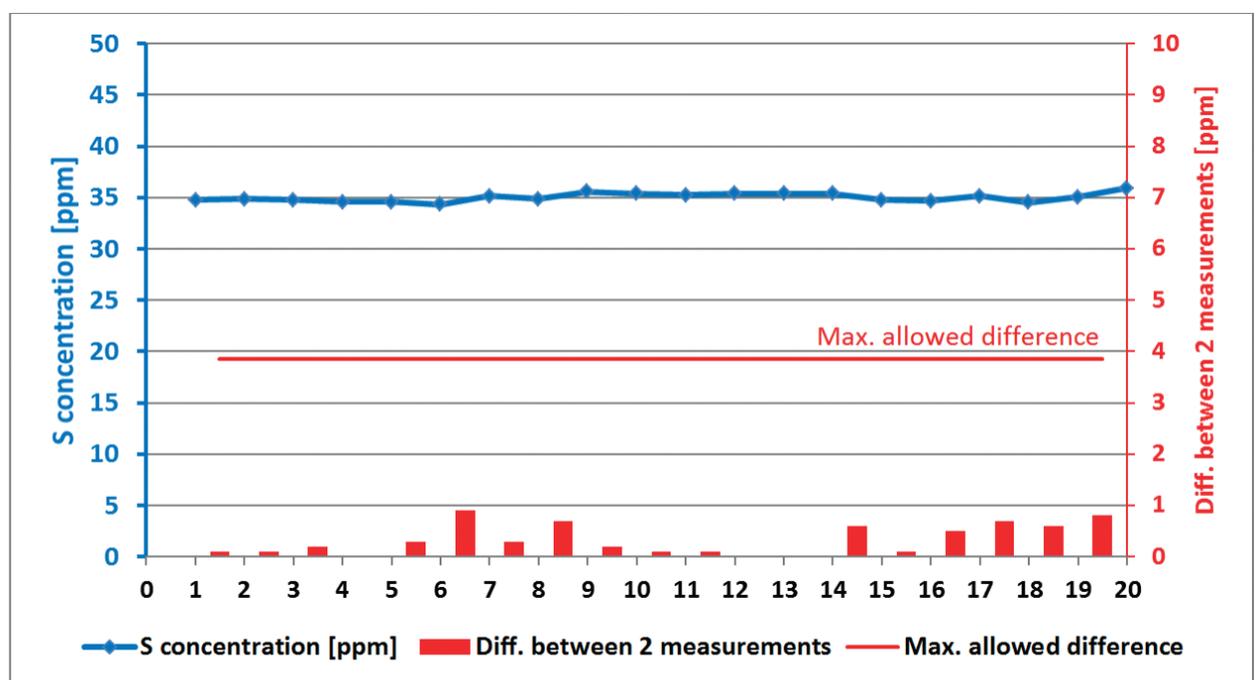


Figure 6: Repeatability of 20 measurements of a gasoline sample, according to ASTM D7220

Author Contact Details

Frank Portala - Product Manager XRF, Bruker AXS GmbH • Oestliche Rheinbrueckenstrasse 49, 76187 Karlsruhe, GERMANY

• Tel: +49 721 50997-5082 • Email: Frank.Portala@bruker.com • Web: www.bruker.com



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