

# Determination of sulfur in petroleum products according ASTM D4294

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## Background

The concentration of sulfur in petroleum products remains an important quality control parameter for oil refineries and distributors. After North America and Europe more and more countries impose the use of ultra-low-sulfur diesel (ULSD). Depending on the country or region the maximum permissible sulfur content can be as low as 10 ppm. XRF and EDXRF in particular is often used as a fast analysis technique for the accurate determination of sulfur in petroleum derivatives. The ASTM D4294 test method covers this type of analysis using the EDXRF technique.

## Instrument

The ARL QUANT'X EDXRF spectrometer used for this application is equipped with a 50 kV, 50 W silver target X-ray tube and a silicon drift detector (SDD) of the latest generation. The ARL QUANT'X employs primary filtered radiation to excite the sample. With a set of nine filters specifically designed to optimize the peak-to-background for elements from F to Am, the ARL QUANT'X can be easily adapted per application or element range. The instrument is equipped with the helium flush option to perform analysis in a helium atmosphere.

## Sample preparation

The petroleum product is measured as such by transferring 3 grams of product into a sample cup of 32 mm outer diameter, sealed with a 4 micron polypropylene film.

## Excitation conditions

Table 1 shows the excitation conditions used to perform the analysis. A thin graphite filter is used to remove the background below the characteristic lines of sulfur while keeping a significant part of the tube's characteristic silver L-lines used to excite sulfur. An excitation voltage of 9 kV is



used while the tube current is automatically adjusted to obtain a dead time of 50%. A helium atmosphere is used to eliminate the absorption of the characteristic sulfur X-rays by air. A total measurement time of 100 seconds (live time) per sample is applied.

**Table 1: Excitation condition used for the analysis of sulfur in petroleum products**

Condition	Filter	Voltage (kV)	Current (mA)	Atmosphere	Live Time (s)	Analyte
Low Za II	Thin Graphite	9	Auto	Helium	100	S

## Calibration

In accordance with ASTM D4294 calibration standards are prepared by mixing Di-n-Butyl Sulfide (DBS) in white mineral oil. ASTM D4294 advises to work with three concentration ranges covering 0-1000 mg/kg, 0.01-1.00 mass % and 1.0-5.0 mass %. For this application note we focus on the concentration range of 0-1000 mg/kg. A set of 10 standards and the blank were prepared to cover the concentration range.

Figure 1 shows the calculated versus given concentrations for the calibration range of 0-1000 mg/kg. The  $R^2$  value equals 0.99999 with a RMSE (root mean square error) of 1.45 ppm. A second order calibration curve was used to relate the net sulfur peak intensity to the sulfur concentration.

## Validation and repeatability

Fresh sample cups were prepared with three of the calibration stock solutions; 10 ppm, 120 ppm and 500 ppm. Each sample was analyzed five times to calculate the repeatability of analysis. Table 2 shows the analysis results. Results indicate that both accuracy and precision are excellent.

## Limit of detection

To determine the limit of detection 10 different sample cups with blank oil were prepared and measured. The limit of detection equivalent to three times the standard deviation of the found concentrations equals 1.05 ppm in 100 s live time.

Figure 1: Calculated versus given concentrations for the 0-1000 mg/kg S in oil calibration

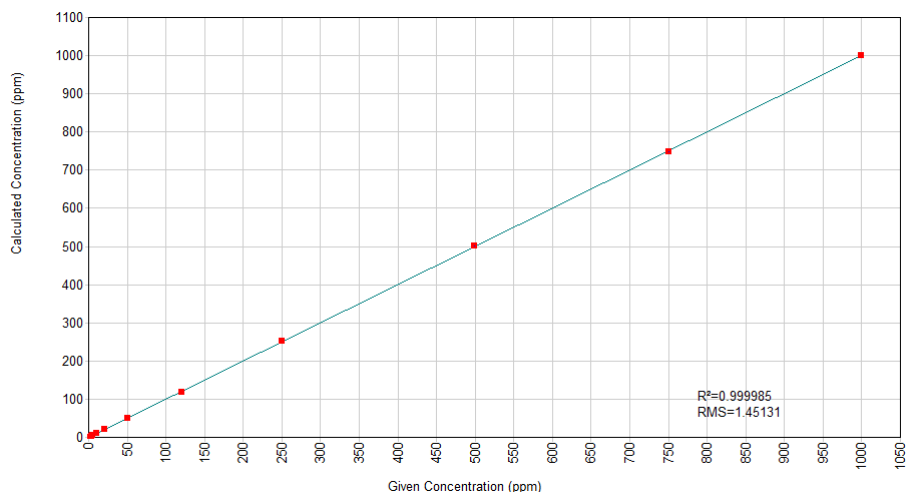


Table 2: Validation and repeatability results for 3 samples over 5 repeats

	S Conc. (ppm)		S Conc. (ppm)		S Conc. (ppm)
<i>Given</i>	10.40	<i>Given</i>	120.00	<i>Given</i>	499.10
Rep 1	10.73	Rep 1	120.28	Rep 1	498.45
Rep 2	10.40	Rep 2	120.75	Rep 2	498.79
Rep 3	11.50	Rep 3	119.63	Rep 3	499.79
Rep 4	10.89	Rep 4	120.72	Rep 4	500.44
Rep 5	10.49	Rep 5	120.88	Rep 5	500.90
<i>Average</i>	10.80	<i>Average</i>	120.45	<i>Average</i>	499.67
<i>StDev</i>	0.44	<i>StDev</i>	0.51	<i>StDev</i>	1.05

If needed this limit of detection can be improved by using a longer counting time. A limit of detection of 0.6 ppm can be achieved with 300 s counting time.

## Conclusion

This application note illustrates the suitability of the ARL QUANT'X EDXRF spectrometer for the fast, accurate and precise analysis of low concentrations of sulfur in petroleum products. The limit of detection is sufficient for reliable quality control of ultra-low-sulfur diesel (Tier 3).

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