



Oil-Trace: Analysis of Sulfur in Fuels, Biofuels and Mixtures Using a Mineral Oil Calibration

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In the United States, the EPA Tier 2 regulations (2002) set an upper limit of 150 ppm sulfur in road fuels, to minimize sulfur dioxide emission. The EU Directive 98/70/EC (2005) has set a maximum sulfur concentration in road fuels of 50 ppm. This concentration will be decreased to only 10 ppm (EU2003/17/EC), starting from the 1st of January 2009. In combination with reduced sulfur contents, there is a trend towards cutting CO₂ emissions from burning fossil fuels by blending with biofuels such as biodiesel and bioethanol. These new fuel–biofuel mixtures pose new challenges to XRF analysis.

Currently XRF is used extensively for the analysis of sulfur in different types of fuels. This is reflected in several norms and standards, like ASTM 2622, ISO 14596 and ISO 20884. Simple sample preparation, high accuracy and precision, and excellent detection limits (0.1–1 ppm) are the main reasons for this choice, and make it an excellent technique for production control.

XRF is a relative technique; therefore unknown fuel samples are best quantified against calibrations comprising standards of similar matrix composition. Traditionally, separate calibrations are needed for every fuel–biofuel combination.

With Oil-Trace, a single calibration based on relatively inexpensive oil standards can be used for quantifying sulfur in a variety of fuels, biofuels and mixtures, such as diesel–biodiesel (for example B20, B50, B80) and gasoline–ethanol (for example E85). Oil-trace achieves this through innovative correction procedures that account for differences in the hydrocarbon and oxygen characteristics of the sample matrix and for differences in sample density and mass.

Instrumentation

Axios-Petro is a fully integrated wavelength dispersive XRF spectrometer, complete with X-Y sample handler and state-of-the-art software. Axios-Petro comes with Oil-Trace (software and standards) and application templates for a successful calibration set-up. Oil-Trace is an innovative new module that enhances SuperQ and provides a powerful solution for fuel analysis.

Preparation of standards and samples

Fifteen grams of each fuel, biofuel and fuel–biofuel mixture was poured into a disposable P2 liquid cell, assembled using a 2.5 μm polyester (Mylar) supporting film.

Analytical conditions

The X-ray tube power setting used for this application was 24 kV - 100mA. To obtain the best sensitivity for sulfur, a curved Ge111 crystal and a 550 μm collimator were used. The measurement program only took two minutes per sample.

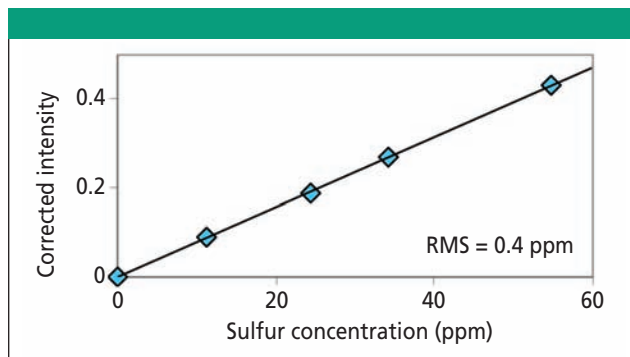


Figure 1: Calibration graph of sulfur in mineral oil.

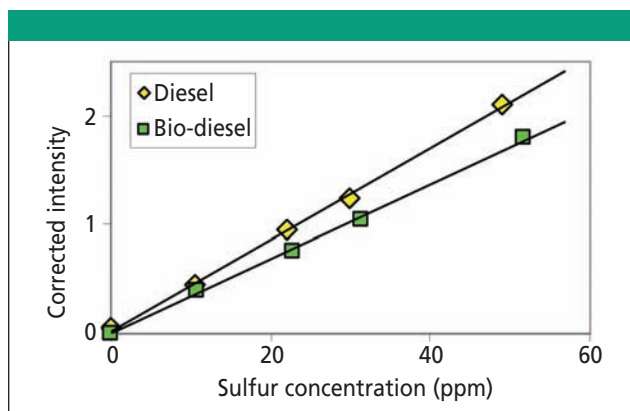


Figure 2: Traditionally, two distinct calibrations curves are required for the analysis of sulfur in diesel and biodiesel.

Calibration accuracy

Sulfur was quantified in pure fuels and biofuels using a single Oil-Trace calibration defined by mineral oil standards (Figure 1). The RMS value (0.4 ppm) indicates the accuracy of this calibration. The RMS is a statistical comparison (1σ) of the certified chemical concentrations of the standards with the concentrations calculated by regression in the calibration procedure.

Accuracy: analysis of pure fuels

The accuracy of Oil-Trace for the analysis of sulfur in fuels using the mineral oil calibration is excellent. Table 1 compares certified and measured concentrations for samples of pure diesel, biodiesel, gasoline and ethanol.

Accuracy: analysis of fuel and bio-fuel mixtures

Table 2 shows the accuracy with which Oil-Trace can analyze fuel–biofuel mixtures by comparing certified and measured concentrations for samples with different mixing ratios.

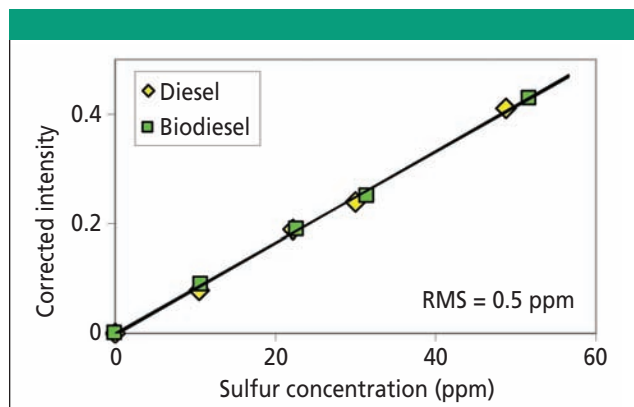


Figure 3: Oil-Trace calibration curve for sulfur in diesel and biodiesel.

Table I: Sulfur concentrations in different fuels determined by Oil-Trace from a mineral oil calibration (Figure 1)

Sample No. (fuel type)	Certified conc. (ppm)	Measured conc. (ppm)	Difference: Ccert - Cmeas (ppm)
1 (Diesel)	10.5	10.8	0.3
2 (Diesel)	29.9	30.6	0.7
3 (Biodiesel)	10.8	11.8	1.0
4 (Biodiesel)	31.4	31.6	0.2
5 (Gasoline)	10.7	12.1	1.4
6 (Gasoline)	30.9	33.8	2.9
7 (Ethanol)	9.8	10.2	0.4
8 (Ethanol)	30.5	29.1	1.4

Matrix characterization with Oil-Trace

The use of biodiesel and mixtures of diesel and biodiesel is becoming increasingly common. However, the required analysis of sulfur in these fuels is made difficult by matrix variations caused by the presence of up to 25 wt% oxygen. Traditionally, separate calibrations are needed for every diesel–biodiesel combination (for example, Figure 2). Now with Oil-Trace, a single calibration is all that is required. This matrix correction is illustrated in Figure 3, which shows a single calibration for sulfur combining both diesel and biodiesel standards. The RMS (accuracy) of this calibration is 0.5 ppm.

Mass and density correction with Oil-trace

The analysis of light-matrix petroleum samples is sensitive to density and mass variations between routine samples and standards. Traditionally, this was partially overcome by analyzing a constant mass. Using an integrated “wedge-effect” correction, Oil-Trace effectively handles variations in both mass and density. Table 3 shows the accuracy of these corrections by comparing certified sulfur concentrations with those determined in 5 g samples of fuel and biofuel mixtures using the 15 g/standard mineral oil calibration (Figure 1).

Table II: Sulfur concentrations in different fuel mixtures determined by Oil-Trace using a mineral oil calibration (Figure 1). B20 = 20:80 biodiesel:diesel; B50 = 50:50 biodiesel:diesel; B80 = 80:20 biodiesel:diesel; E85 = 85:15 ethanol:gasoline.)

Sample No. (fuel type)	Certified conc. (ppm)	Measured conc. (ppm)	Difference: Ccert - Cmeas (ppm)
9 (B20)	10.0	9.7	0.3
10 (B20)	30.3	31.6	1.3
11 (B50)	10.0	10.0	0.0
12 (B50)	30.4	30.6	0.2
13 (B80)	9.6	9.2	0.4
14 (B80)	30.2	31.0	0.8
15 (E85)	11.3	11.2	0.1
16 (E85)	31.7	33.0	1.3

Table III: Sulfur concentrations in 5 g samples, determined by Oil-Trace using the 15 g/standard mineral oil calibration (Figure 1). B20 = 20:80 biodiesel:diesel; B50 = 50:50 biodiesel:diesel; B80 = 80:20 biodiesel:diesel; E85 = 85:15 ethanol:gasoline.

Sample No. (fuel type)	Certified conc. (ppm)	Measured conc. (ppm)	Difference: Ccert - Cmeas (ppm)
17 (B20)	10.0	9.5	0.5
18 (B20)	30.3	31.3	1.0
19 (B50)	10.0	10.3	0.3
20 (B50)	30.4	30.3	0.1
21 (B80)	9.6	9.5	0.1
22 (B80)	30.2	31.4	1.2
23 (E85)	11.3	10.7	0.6
24 (E85)	31.7	33.0	1.3

Conclusions

Axios-Petro in combination with Oil-Trace brings XRF petroleum analysis to the next level. With a simple mineral oil calibration it is possible to accurately and precisely analyze sulfur in diesels, biodiesels, ethanol, gasoline and their mixtures. Moreover, Oil-Trace can correct for differences in sample amount and density. Users benefit from more robust routine analysis and fewer calibrations to maintain.

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