AN APPLICATION BRIEF FROM
SPECTRO ANALYTICAL INSTRUMENTS

When results matter

At-Line Analysis of Sulfur in Fuels According to ASTM D4294 Using ED-XRF Spectroscopy

Introduction

Sulfur content is a key quality determinant for many petroleum products. Knowledge of sulfur content shapes impacts processing and assists in compliance with federal, state, and local agency regulations that seek to control sulfur content for environmental reasons. A number of standards have been developed to guide industry in monitoring sulfur levels. They define acceptable levels that vary widely with the application, ranging from 10 ppm for road fuels up to percent levels in heavy fuel oil.

The need for at-line QC

Analysis of sulfur in fuels using XRF across the full range of concentrations has traditionally been done in the lab, using, for example, Wavelength Dispersive — X-ray Fluorescence (WD-XRF) spectroscopy to test compliance with the ASTM D2622 standard or Energy Dispersive — X-ray Fluorescence spectroscopy (ED-XRF) to test compliance with ASTM D7220 or ASTM D4294.

In such applications, once a sample is collected in the field, it must be transported to the lab, where it would likely be placed in queue. If samples are not found to be in compliance with the target standard, adjustments must be made and test process repeated, further extending time to production. The foot print of ED-XRF technology has been decreasing steadily, so much so that some companies have been using it to detect low levels at the point of production, but this has required an external power source.

New portable ED-XRF instruments such as the SPECTROSCOUT have excellent analytical range and precision, exhibiting very low limits of detection. Using this instrument at-line has been shown to reduce analysis times for substances such as sulfur from hours to minutes.

Now, for the many applications requiring detection not including the ultra-low levels, a new generation of portable ED-XRF technology enables analysis at the production line, shortening time to results from days to minutes. These applications, which are analyzed by methods defined in standard ASTM 4294 include the determination of total sulfur in petroleum and petroleum products that are single-phase and either liquid at ambient conditions, liquefiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosene, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, and similar petroleum products.

Bringing analysis to the line

ED-XRF analysis, on the other hand, is performed directly on a sample, usually with little preparation and with powerful new portable instruments that can be used anywhere in the plant. Once a sample is collected from any process point it can be analyzed rapidly and accurately right at the point of production. ASTM D4294 calls for analysis time of 1 to 5 min per sample and portable ED-XRF accomplishes that easily.

The following analysis was performed using a SPECTROSCOUT portable spectrometer equipped with a transmission target X-ray tube (Rh target), a filter changer, a helium purge system and a high resolution large area SDD. The resolution of the SDD used amounts to <155 eV (Mn Kα) at an input count rate of up to 200,000 cps. The components are packaged in a small cabinet with a footprint of only 31 cm x 31 cm, a transport height of 27 cm and a weight of about 12 kg.

Table 1 shows the measurement parameters. Before measuring each spectrum of an unknown sample, the shutter of the instrument is irradiated to calculate the line energy-channel position function and the line width-line energy relation. This corrects any spectrometer drift.

Minimal sample prep

The only sample preparation involved was pouring approximately 4g of the sample into a plastic cup. The cup had an outer diameter of 32 mm and was closed with a 4 μm thick poly-propylene foil. (Samples with a higher aromatic content might require a different film.)

Calibration

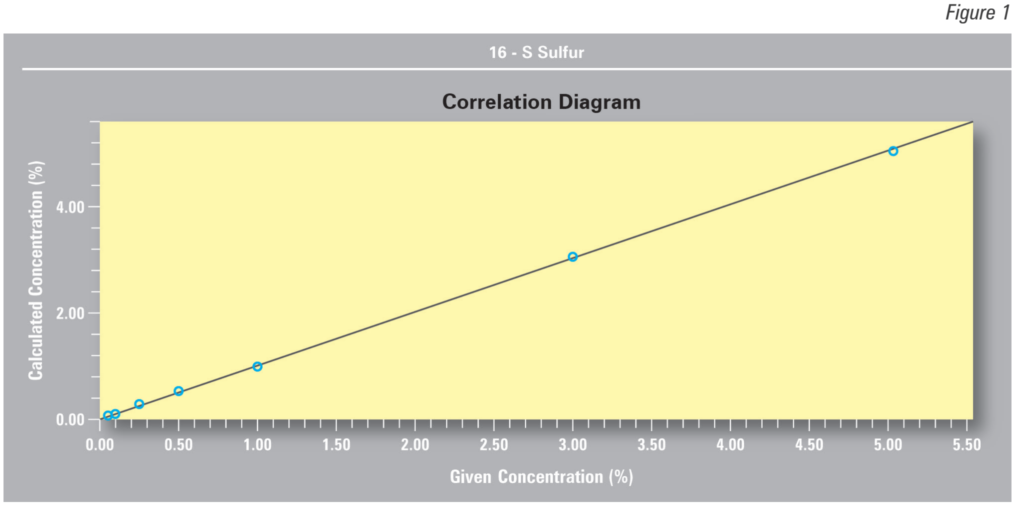
Calibration for all elements was performed by measuring a series of reference samples prepared according to ASTM D4294. Figure 1 illustrates the correlation plot. The correlation coefficient was 0.9999.

Table 1: Measurement conditions

Tube anode	Tube voltage [kV]	Meas. Time [s]
Rh	11	300

(Measurement time = clock time; live time is about half of the given measurement time)

Figure 1



Tables 2 and 3 illustrate high correlation between results obtained on reference samples in the lab and at-line. They show the results of repeatability tests based on analyzis of two samples, on a low concentration sample containing 24.9 mg/kg of sulfur and a high concentration sample with 2.45 % sulfur content. Each sample was prepared freshly for the measurement.

The results from both repeatability tests show compliance with criteria set out in ASTM D4294. Based on the standard deviation of the repeated analysis of the low concentration sample the LOD for sulfur is estimated to be 3 mg/kg, which is also in compliance with the ASTM test method.

With a carefully selected system, at-line analysis using a new generation ED-XRF instrument, can deliver the level of accuracy once found only in the lab, and by doing so, can boost process throughput, reduce costs, and provide your plant with far more flexibility than ever before. And the end result can be more efficient, cleaner petroleum processing.

Table 2: Correlation is high between the reference values for sulfur in fuels and production samples analyzed using laboratory based ICP-OES analysis and values calculated by a SPECTROSCOUT ED-XRF at-line.

Measurement	Unit	Measured
1	mg/kg	25.9
2	mg/kg	26.5
3	mg/kg	24.9
4	mg/kg	25.0
5	mg/kg	25.8
6	mg/kg	23.7
7	mg/kg	24.8
8	mg/kg	26.5
Average	mg/kg	25.4 ±1.0

Table 3: Calculated sulfur values varied by ± 0.01 % from the average value over eight tests of a high concentration sample.

Measurement	Unit	Measured
1	%	2.439
2	%	2.452
3	%	2.456
4	%	2.432
5	%	2.442
6	%	2.449
7	%	2.452
8	%	2.455
Average	%	2.447 ±0.008

Scoping out an at-line ED-XRF system

Although various portable or small ED-XRF spectrometers may implement the same technology, there will be vast differences in their performance, ease of use, and instrument suitability for the at-line application. Here are some of the factors to consider when specifying and comparing ED-XRF spectrometers:

- **Performance.** ED-XRF instruments used for at-line QC applications must have dependable accuracy, repeatability, and sensitivity for the full range of sulfur concentrations.
- **Ease of operation.** Consider who will be using this instrument as ease of use translates into greater productivity and lower training costs. Look for an intuitive interface, simplified software that interacts with a standard PC, and comes with predefined application packages and calibration tools.
- **Portability, compactness, and integral power supply.** Weight, design, and transportability are all key factors in making the most of at-line measurement. If access to a power outlet might be a problem, be sure to specify an instrument that runs on batteries.

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