APPLICATION NOTE

No. AN41706

Analysis of low sulfur in fuels according to ASTM D 2622-08

ARL OPTIM'X Simultaneous-Sequential X-Ray Fluorescence Spectrometer

Key words
ARL OPTIM'X, ASTM D 2622, sulfur regulations, ultra low sulfur diesel, X-ray fluorescence

Introduction

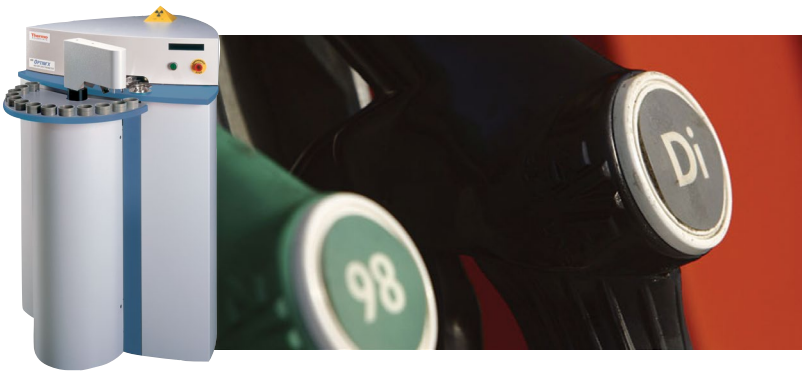
Sulfur reduction in vehicle fuels is a top issue for petroleum refineries and distribution terminals in the downstream petro value chain. The naturally occurring sulfur contaminants from crude oil contribute significantly to air pollution by increasing fine particulate matter (PM) emissions, forming damaging sulfates in vehicle exhaust and sulfur oxides (SOx) in the atmosphere, and furthermore poisoning catalytic converter systems which increases other emissions such as nitrogen oxides (NOx).

Europe and North America lead the world in establishing environmental regulations for ultra-low sulfur diesel (ULSD) and passenger car fuels. U.S. refiners per EPA Tier 3 standards began producing primarily ULSD in 2006 with a maximum of 15 ppm sulfur for on-road fuels; the Euro V fuel standard of 2009 sets a final target of 10 ppm sulfur.

The WDXRF elemental analysis technique is preferred by petroleum analysts for its wide dynamic range including ultra-low to high levels of sulfur. International standard ASTM D 2622, newly updated in 2008, is currently the most stringent WDXRF test method for measuring sulfur in petroleum products. This study demonstrates performance and reliability of the Thermo Scientific ARL OPTIM'X for sulfur analysis in fuels.

Instrumentation

The ARL OPTIM'X is a wavelength dispersive XRF instrument designed for ease of use with minimal running and maintenance costs. The optimized geometry of the ARL OPTIM'X coupled with a low power Rh anode X-ray tube provides the high sensitivity required for this application.



Unlike higher powered WDXRF instruments, the ARL OPTIM'X requires no external or internal water cooling. It also provides 10 times better resolution than EDXRF instruments, as well as superior precision and short- and long- term stability. Ease of operation is obtained though state-of-the-art OXSAS software supporting instrument operation and data handling.

Sulfur analysis in petroleum products

The ASTM D 2622-08 method was followed and a series of standard samples prepared in order to construct calibration curves covering both high and low ranges, from 0 to 1,000 ppm and another from 0.1 % to 5.0 %. The analytical conditions were also set according to ASTM (Table 1).

	Tube volt.	Tube curr.	Detector	Crystal
S Kal,2	30	1.67	SEALED	GE111
S background	30	1.67	SEALED	GE111

Table 1: Instrument settings

The S net intensities were determined with the following formula:

$$S\ net = (S\ K\alpha_{1,2} - S\ background)$$

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Each standard intensity was related to the S content. Figure 1 shows the calibration curve for low levels. The calibration accuracy, as measured by the Standard Error of Estimate (SEE), for the low level calibration range was 3 ppm from 0 to 1,000 ppm. The SEE for the higher range was 0.007 % from 0.1 % to 5.0 %, thus demonstrating excellent accuracy at both low and high concentrations. The limit of detection obtained is 1.2 ppm in 120s counting time (or 0.8 ppm in 300s).

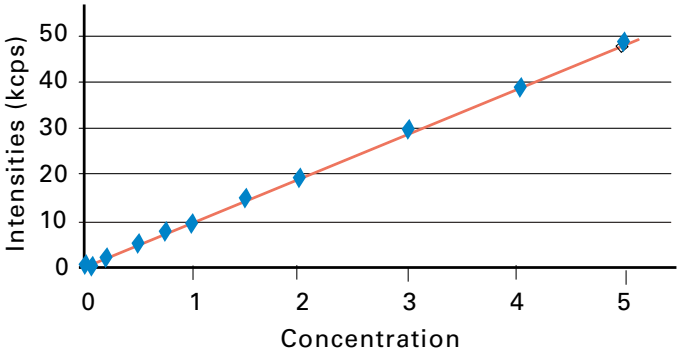

Figure 1: Calibration curve up to 0.1 % S concentration

Precision for sulfur

A sulfur repeatability test was conducted on three fuel samples loaded into seven different liquid cells:

Run #	Sample 1 [PPM]	Sample 2 [PPM]	Sample 3 [%]
Cell 1	25.4	100.6	0.997
Cell 2	25.7	100.7	1.010
Cell 3	26.4	101.8	1.010
Cell 4	26.0	102.3	1.002
Cell 5	25.0	98.4	0.998
Cell 6	25.9	100.5	1.001
Cell 7	26.7	101.5	0.998
Average	25.9	100.8	1.002
St. Dev.	0.58	1.27	0.005

Table 2: Stability test for S analysis on petroleum samples

Examination of these results reveals the excellent repeatability of analysis that can be achieved for S with the ARL OPTIM'X spectrometer at very low concentration levels.

Accuracy of analysis

To further test the accuracy of analysis, five samples of diesel fuel and light oil with varying sulfur levels were prepared and loaded into two different cells. Table 3 shows the concentration results (in ppm) obtained as well as a comparison with the certified sulfur concentrations.

Sample	Certified value [PPM]	1st cell [PPM]	2nd cell [PPM]
Diesel 5	5	4.8	4.9
Oil 25	25	25.4	25.8
Diesel 50	50	50.6	50.2
Oil 400	400	399.7	399.3
Oil 1000	1000	996	999

Table 3: Results obtained for five samples used as unknowns to test the accuracy of sulfur analysis

Conclusion

Excellent calibration curves can be obtained with the ARL OPTIM'X for both low and high sulfur concentrations in vehicle fuels and oils when applying the most stringent international standard test method, ASTM D 2622-08. The limit of detection of less than 1.3 ppm, achieved in only 120 seconds measuring time, ensures a quantification limit of 4 ppm, well under even today's most demanding ULSD specifications of 10-15 ppm sulfur.

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