APPLICATION NOTE

Analysis of ultra-low sulfur in diesel fuels according to ASTM2622-16 with Thermo Scientific ARL PERFORM'X 2500 XRF spectrometer

Introduction

Regulatory vehicle emissions limits for sulfur content of petroleum-based fuels are decreasing in allowable concentration levels around the globe. This trend stems for the environmental concern regarding pollutants such as sulfur oxides (SOX) and fine particulate matter (PM) which is created by the combustion of diesel fuels. The auto industry attempts to reduce these pollutants by installing catalytic converters on vehicle exhausts, however the material used in the converters are depleted over time when high concentrations of sulfur are present in the fuel. To combat the problem, the allowable limits of sulfur in fuel have been reduced to only a few ppm. The term ultra-low sulfur diesel (ULSD) refers to current standards for on-road vehicle diesel fuels from the U.S. EPA and EU authorities limiting sulfur content to 10 ppm. This is a dramatic reduction from previously allowed sulfur levels of 50 ppm or even 350 ppm within recent history. Test standard ASTM D2622 as updated in 2016 is the industry-preferred method for analysis of ultra-low sulfur in diesel and other fuels by wavelength dispersive X-ray fluorescence (WDXRF) spectrometry. Method advantages include ease and speed of sample preparation with excellent precision.

Instrument

The Thermo Scientific™ ARL™ PERFORM'X X-ray fluorescence series spectrometer (Figure 1) used in this analysis was a 2500W system.

Figure 1: ARL PERFORM'X X-ray fluorescence spectrometer

The 2500W version uses only one deionized water circuit linked to an air-water heat exchanger. This spectrometer is configured with 6 primary beam filters, 4 collimators, up to 9 crystals, 2 detectors, helium purge and our 5GN+ Rh X-ray tube for best performance from ultra-light to heaviest elements thanks to its 50 micron Be window. This new X-ray tube fitted with a low current filament ensures an unequalled analytical stability month after month. The ARL PERFORM'X offers the ultimate in performance and sample analysis safety. Its unique LoadSafe design includes a series of features that prevent any trouble during sample flushing and loading. Liquid cassette recognition prevents any liquid sample to be exposed to vacuum by mistake. Over exposure safety automatically ejects a liquid sample if X-ray exposure time is too long. The Secutainer system protects the primary chamber by vacuum collecting any loose powders in a specially designed container, easily removed and cleaned by any operator. For spectral chamber protection, the ARL PERFORM'X uses a helium shutter designed for absolute protection of your goniometer during liquid analysis under helium operation. In the "LoadSafe Ultra" optional configuration, a special X-ray tube shield provides total protection against sample breakage or liquid cell rupture.

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Calibration ranges and results

Analyzing ultra-low sulfur levels requires detecting very low X-ray intensities. For optimal analysis, the conditions and parameters used in this measurement were set to excite the sulfur peak while keeping the background as low as possible. Collimator choice increased peak-to-background signal ratio and power settings were adjusted to further increase peak count rates. The final calibration employed settings of 30 kV-80 mA power, a PET analyzing crystal, flow proportional counter (FPC) and medium collimator (0.4°). In addition to analysis of the sulfur peak we implemented one background measurement point. Because the most challenging function in trace sulfur analysis is at the ultra-low level, a calibration was created for 0 to 20 ppm. A 0.300 % sulfur certified reference material was diluted to concentration of 2.5 ppm, 4 ppm, 14 ppm and 20 ppm using blank oil as the base solvent. A blank oil was analyzed as a blank standard. The conditions of the experiment are presented in the table below.

Name	2 Theta	Crystal	Detector	Collimator	Threshold %	Window %	Counting time, s	kV	mA
S_{Bg}	79,499	PET	FPC	0.4°	40	120	40	30	80
$S_{Ka1,2}$	75,72	PET	FPC	0.4°	40	120	60	30	80

Table 1: Analytical conditions

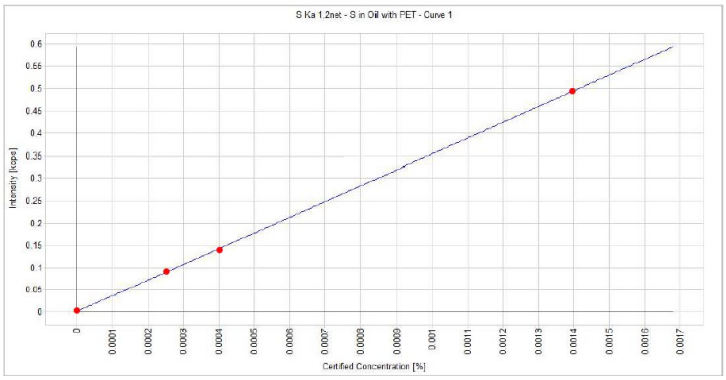

Figure 1: Typical trace sulfur regression calibration curve

From the above calibration, the calculated detection limit is 0.1 ppm at 100 seconds counting time and sensitivity of 351 kcps/% (kilo counts per second per percent). These limits are well inside the regulations for ultra-low sulfur and demonstrate that the ARL PERFORM'X spectrometer is an excellent instrument for this analysis. Below, the repeatability results illustrate the ARL PERFORM'X stability. These results were obtained by preparing up to 15 different liquid cells and pouring equal amounts of the same sample into each. The samples analyzed were gasoline and diesel fuel.

Table 2 on next page shows the repeatability results obtained for S with ARL PERFORM'X 2500W at 7.7 ppm. According to ASTM 2622-16 the maximum permissible difference from one run to the next is set at 0.75 ppm.

Conclusion

These results show that ultra-low sulfur analysis can easily be performed with the ARL PERFORM'X sequential XRF spectrometer. The precision data are shown to be in line with the ASTM 2622-16 limits which work fine in these matrix types for routine or R&D analysis.

Furthermore, operation is made easy through the state-of-the-art Thermo Scientific OXSAS WDXRF software which operates with the latest Microsoft Windows® 10 package.

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Diesel	S Kα peak	S Bg	S net	conc, %	conc, ppm	D	ASTM 2622-16
1	400.74	128.23	282.575	0.00077	7.7		
2	406.78	124.20	282.575	0.00082	8.2	0.5	Ok
3	400.78	127.33	273.449	0.00077	7.7	0.5	Ok
4	397.84	125.10	272.737	0.00077	7.7	0.0	Ok
5	398.21	131.73	266.482	0.00073	7.3	0.4	Ok
6	395.91	130.00	265.907	0.00073	7.3	0.0	Ok
7	396.89	125.63	271.265	0.00076	7.6	0.3	Ok
8	400.16	127.78	272.382	0.00076	7.6	0.0	Ok
9	403.48	124.30	279.175	0.0008	8.0	0.4	Ok
10	399.18	129.53	269.649	0.00075	7.5	0.5	Ok
11	405.64	125.00	280.642	0.00081	8.1	0.6	Ok
12	398.41	128.90	269.507	0.00075	7.5	0.6	Ok
13	400.58	126.05	274.524	0.00078	7.8	0.3	Ok
14	401.03	126.50	274.524	0.00078	7.8	0.0	Ok
15	395.73	123.95	271.774	0.00076	7.6	0.2	Ok
Average	400.09	126.95	273.8111	average	7.7		
SEE	3.3	2.4			R	0.75	
Rel SEE	0.8	1.9					

Table 2: Repeatability obtained for S on a diesel sample

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