

# Analysis of Ultra Low Sulfur in Diesel Fuel

## *Thermo Scientific ARL PERFORM'X Series Advanced X-Ray Fluorescence Spectrometers*

### Key Words

- ARL PERFORM'X 4200 W
- Sulfur
- Diesel fuel
- XRF
- X-ray fluorescence

### Introduction



Regulatory vehicle emissions limits for sulfur content of petroleum-based fuels are decreasing in allowable concentration levels around the globe. This trend stems from 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 15 or 10 ppm, respectively. This is a dramatic reduction from previously allowed sulfur levels of 350 - 500 ppm within recent history. Test standard ASTM D2622 as updated in 2008 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

Thermo Scientific ARL PERFORM'X series spectrometer used in this analysis was a 4200 watt system. This system is configured with 6 primary beam filters, 4 collimators, up to nine crystals, two 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.



### 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-120 mA power, a Ge111 analyzing crystal, flow proportional counter (FPC) and medium collimator. In addition to analysis of the sulfur peak at 0.537 nm wavelength, two background measurement points were implemented.

Because the most challenging function in trace sulfur analysis is at the ultra low levels, a calibration was created for 0 to 3 ppm. A 0.300% sulfur certified reference material was diluted to concentration of 3.2 ppm, 1.6 ppm and 0.35 ppm using xylene as the base solvent. A pure xylene was analyzed as a blank standard.

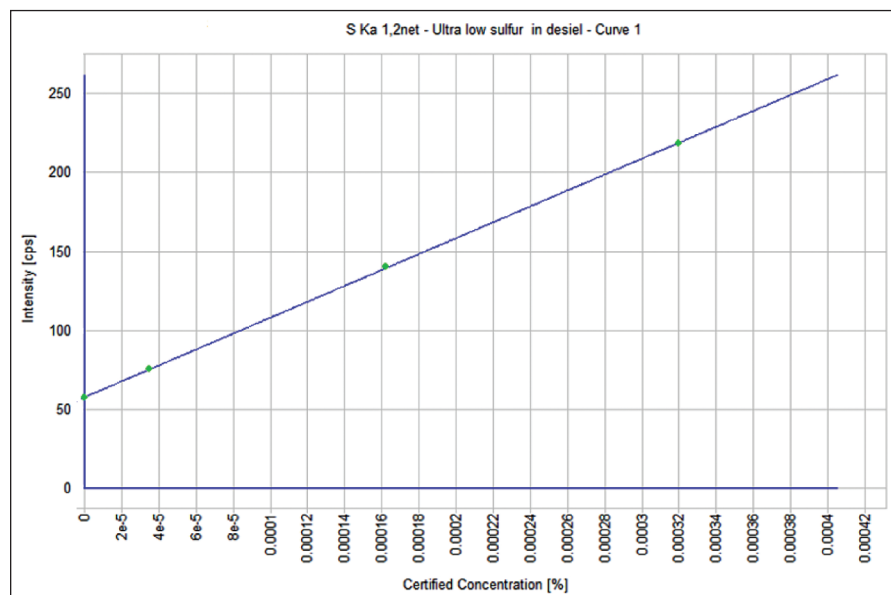


Figure 1: Typical Trace Sulfur Regression Calibration

### Results

From the above calibration, the calculated detection limit is 0.1 ppm at 100 seconds counting time and sensitivity of 504 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 four different liquid cells and pouring equal amounts of the same sample into each. The samples analyzed are independent of the calibration standards.

Sample	S Results (ppm)
Cell 1	1.25
Cell 2	1.29
Cell 3	1.18
Cell 4	1.21
Average	1.23
St.Dev.	0.05

Table 1: Typical Repeatability for Trace Sulfur Analysis

### Conclusion

The results show that ultra low sulfur analysis can easily be performed with the ARL PERFORM'X sequential XRF spectrometer. The precision and accuracy are shown to be excellent 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® 7 package.

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AN41664\_E 02/12C