How Low Can You Go?

Taco van der Maten - Product Manager XRF, PANalytical,
P O Box 13, 7600 AA Almelo, The Netherlands, Tel: +31 (0) 546 534444, www.panalytical.com

Governments worldwide continue to take action to address the major environmental and human health problems caused by sulphur emissions. For the petroleum industry, this has meant the introduction of stringent legislation to limit the allowed levels of sulphur in automotive fuels. As these regulations are set to become even more rigorous from next year onwards, accurate and precise measurement of sulphur in petroleum products has never been more important.

This article presents data obtained from a new Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer, demonstrating its effectiveness for ensuring compliance with the relevant standards for sulphur in automotive fuel.

Ultra-low sulphur diesel

Ultra-low sulphur diesel (ULSD) is a standard term that describes diesel fuel with significantly lowered sulphur content. Petroleum products constitute a significant source of SO_2 in air. As a result, sulphur content has been subject to increasingly challenging controls over the last few decades. Such measures have helped achieve a dramatic reduction in sulphur deposition worldwide - a 71% decrease in SO_2 emissions from 1987 to 2001 has been reported by the World Mineral Exchange. In parallel, car manufacturers have been developing engines with advanced emissions control systems that require the new ULSD fuel.

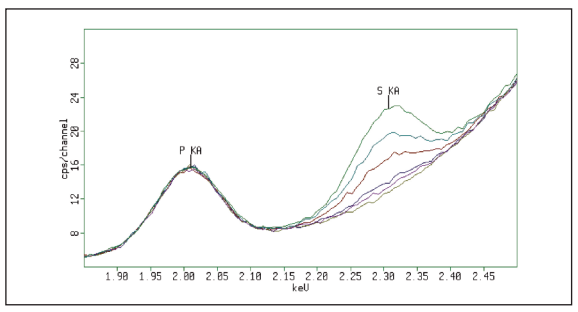

Figure 1. XRF spectra of six gasoline standards. Note: the phosphorous peak is due to impurities in the Mylar supporting foil

Legislation in transition

Today, government regulations impose extremely low limits for sulphur in fuel. For example, in the USA, the EPA (Environmental Protection Agency) has mandated the use of ULSD from model-year 2007. The allowable sulphur content for ULSD in the US is now set at 15 ppm, down from 500 ppm. The EU is in transition - from the current Euro IV standard of 50 ppm to a proposed Euro V regulation (Directive 2003/17/EC) which is due to come into force in January 2009. This will bring the limit down to just 10 ppm. In Asia, many national environmental bodies, those in Taiwan and Singapore for example, have adopted the Euro IV standard.

Improved sensitivity

EDXRF is already well established for the analysis of a broad range of elements in light matrices, such as petroleum products. Importantly, recent technological advances in EDXRF instrumentation have delivered increased detector resolution and sensitivity for this application.

PANalytical's compact MiniPal 4 Sulphur EDXRF spectrometer, has been designed specifically for the non-destructive analysis of petrochemicals. It is ideal for quality control and to ensure compliance with international norms, including ASTM, ISO, DIN and EPA.

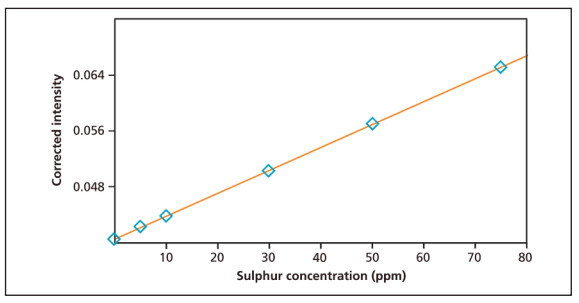

Figure 2. Calibration graph of sulphur in automotive fuels

It is equipped with a new silicon drift detector, which offers the best resolution available in its class, enabling improved sensitivity, high maximum count rates and lower limits of detection.

The data demonstrates the use of the system to analyze low sulphur content in automotive fuels.

Preparation of standards

A series of commercially available oil standards was used to set up the calibration for the determination of sulphur in automotive fuels. Five grams of each standard were put into a 15 ml liquid cell, assembled with a 2.5 µm Mylar supporting foil.

Instrumentation and measurement conditions

Measurements were conducted using a MiniPal 4 Sulphur EDXRF spectrometer, equipped with a silver anode X-ray tube, three tube filters, a helium purge facility and a high-resolution silicon drift detector. Typical detection limit for sulphur in automotive fuel is 1 ppm.

The measurement conditions are listed in *Table 1*. All analyses were performed in a helium atmosphere. The total counting time per sample was ten minutes. The intensities for sulphur were measured with a ROI (region of interest) and a ratio to the Compton peak was used as a matrix correction.

Calibration results

Figure 1 shows the XRF spectra of six gasoline standards with sulphur concentrations of 0, 5, 10, 30, 50 and 75 ppm. Even 5 ppm sulphur in the gasoline standard can be distinguished from the blank.

The calibration curve for determining low sulphur content was set up using the regression model of the MiniPal software. The calibration results are shown in *Table 2* and illustrated graphically in *Figure 2*.

The root mean square (RMS) error, listed in *Table 2*, is an indication of the magnitude of difference between the measured concentration and the certified chemical concentration. The results obtained show good correlation between the certified concentrations and the intensities.

Repeatability

To illustrate the repeatability of the MiniPal 4 Sulphur, a sample with 10 ppm sulphur was measured 15 times. Each measurement used a freshly prepared sample and liquid cell. The average measured concentrations are plotted in *Figure 3*. The results emphasize the excellent analytical precision of the system at these low sulphur levels.

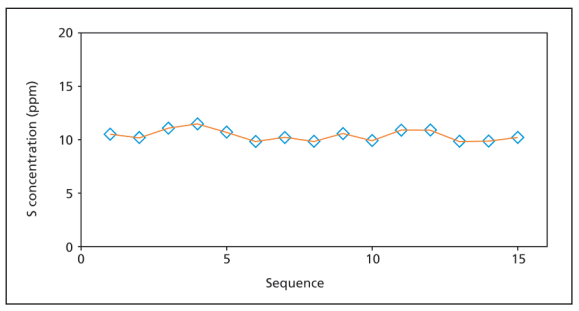

Figure 3. Repeatability results

Ease of use

Standard methods from the ASTM and ISO define three distinct sulphur calibration ranges: 0 – 0.1 wt%, 0.1 – 1.0 wt% and 1.0 – 5.0 wt%. Conventionally, users select one of three calibrations for use when quantifying a particular unknown sample. Now, the latest MiniPal software includes Automatic Program Selection (APS). This automatically selects the best calibration program, without the need for operator interaction, depending on the sulphur concentration of the unknown sample.

Conclusion

Results show that the MiniPal 4 Sulphur EDXRF spectrometer is well suited for the analysis of low sulphur content in automotive fuels. The high resolution and sensitivity of the detector result in a low detection limit of 1 ppm, making the system ideal for current and future regulation. Powerful software matrix correction and automatic program selection features harnesses the power of the detector and contributes to the accurate and precise results presented here.

Element	Voltage (kV)	Current (µA)	Medium	Tube filter	Counting time (s)
S	8	1000	Helium	Ti	600

Table 1. Measurement conditions

Element	Concentration range	Correlation coefficient	RMS (ppm)	LLD (ppm, 600s)
Sulphur	0 - 75 ppm	0.99995	0.3	1.0

Table 2. Calibration details for sulphur in automotive fuels