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X-Supreme @ Work

XSAW-01.v3

Oxford Instrument s X-Supreme8000 for the determination of ultra-low sulfur in automotive fuels and sulfur in petroleum products

Instrument Package: XSP-Sulfur

Complies with ASTM D4294, ISO20847, ISO8754, and ISO13032.

Introduction

Quality control laboratories in refineries and testing houses have long used Energy-Dispersive X-ray fluorescence (EDXRF) spectrometers, e.g. Oxford instruments **Lab-X** and **X-Supreme** to analyse fuels. The excellent performance, versatility, ease of use, speed, and cost-effectiveness of this technique make the EDXRF spectrometer the analytical tool of choice for fuel analysis, from the lower detection limits to high concentration levels.

Environmental and public health issues are forcing continual changes in the use and composition of fuel for transportation or other usage (e.g. burner fuel). For example, the International Maritime Organisation has developed the MARPOL Annex VI regulation to reduce air pollution from ships through regulating emissions such as sulfur oxides (SOx). Since 2005, the global sulfur level in marine fuel is capped at 4.5% and 1.0% in designated SOx emission control areas (such as Baltic and North Sea).

Automotive fuels also follow stringent regulations and many countries already produce ultra-low sulfur (< 10 or 15 $mg.kg^{-1}$ sulfur) automotive fuels. In recent years, policies on renewable energy have encouraged the production of biofuels (such as ethanol and biodiesel blends), which also have to meet fuel specifications. The recently introduced ISO13032 specification (issued April 2012) titled “Determination of low concentration of sulphur in automotive fuels” now gives a recognised test method for the measurement at these ultra low sulphur levels.

Adding to its successful range of benchtop EDXRF spectrometers for fuel analysis, Oxford Instruments now offers a high performance EDXRF spectrometer that successfully performs all sulfur analyses required in the petroleum industry, the **X-Supreme8000**. The **X-Supreme** is the perfect analyser for rapid sulfur determination, from part per million (ppm) to high percent levels, in all fuel types.

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Instrumental

To obtain the best performance for sulfur in fuels, the **X-Supreme** incorporates Oxford Instruments' **Focus *SD*** technology.

Focus-SD has been optimised for fuel analysis, and combines a Silicon Drift detector (SDD) which provides high spectral resolution (see Figure 1), an Oxford Instruments' titanium-target tube providing both excellent elemental excitation and matrix correction, and optimised background filters. This combination gives optimum speed of analysis, low detection limits, and supreme performance for sulfur at all concentrations.

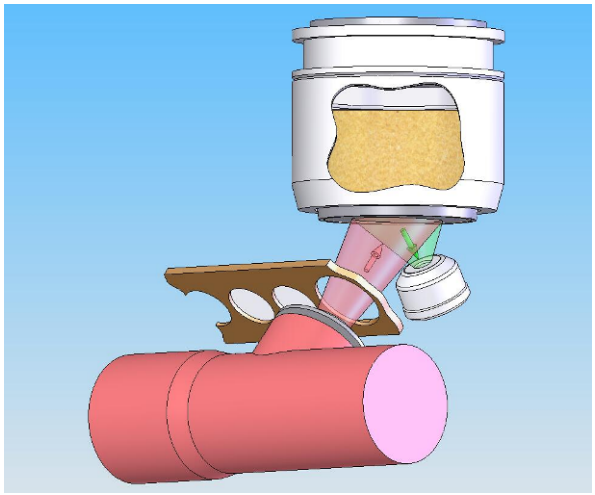

Figure 1: Oxford Instruments Focus SD Technology

All control of the instrument is through the **X-Supreme**'s **integrated PC and software** which provides sophisticated calibration models that handle a wide variability of samples while remaining easy to use. The software features easy data manipulation and storage, a report writing facility and data export.

The **X-Supreme**'s compactness and robustness makes it ideal for location either in laboratories or in production sites for twenty-four-hour operation. The **X-Supreme** includes a **ten-position autosampler** to enable simple and unattended multiple analysis.

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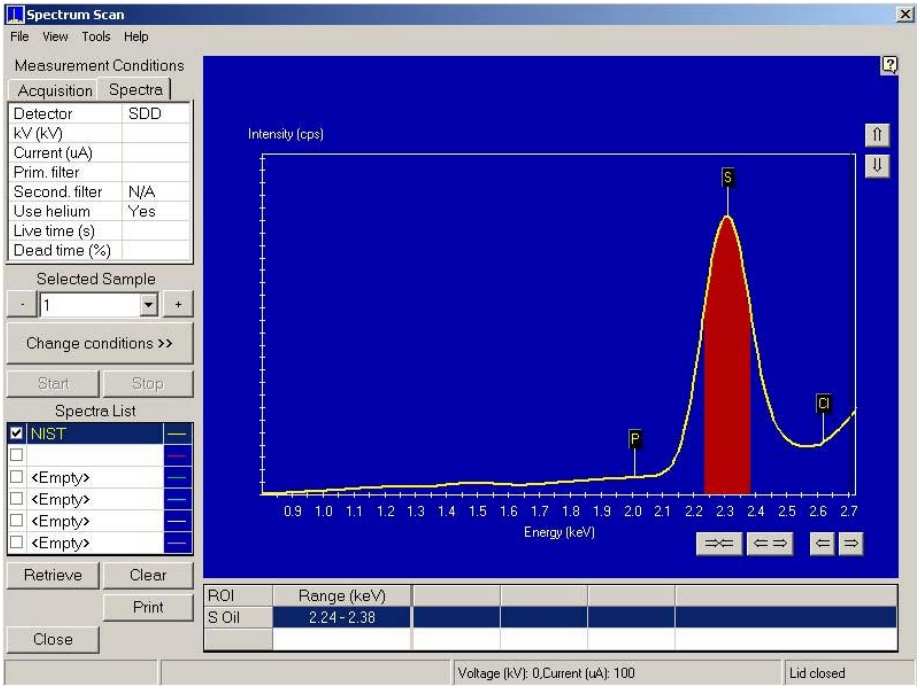

Figure 2: Spectra for sulfur showing good elemental separation from potential interfering elements of phosphorus and chlorine.

Sample preparation and presentation

Sample cups are first simply assembled using Oxford Instruments' Poly-M XRF sample film. For the determination of ultra-low sulfur levels, it is a high-purity window material. This is of consistent quality and giving the minimal background signal necessary for measuring ultra-low, medium and high sulphur levels . It's solvent and chemical resistance properties stand up to all known fuel formulations. Once assembled, (this takes a few seconds), simply pour the sample into the sample cup. There is an internal mark in each sample cup to indicate the filling line at approximately 13ml. Then place the cups on the autosampler using **individual and removable secondary safety windows** which provide instrument protection in case of sample leakage.

After placing the samples on the instrument tray and entering their identification and position at the **integrated keypad**, measurement is then started by pressing the Start button. After the first few seconds of measurements **live results** are displayed, allowing a rapid assessment of product quality to be made. The results are continually updated to the end of the measurement where they can be printed on an attached printer and/or exported to another location.

Calibration

The "**X-Supreme** XSP-Sulfur" application package comes pre-loaded with three optimised method templates, specifying the appropriate operating parameters and correction specifications.
Each of the three methods covers a specific sulfur calibration range: Ultra Low Sulfur (3 -150 $mg.kg^{-1}$), Medium Sulfur (0.015 – 0.5 %m/m), and High Sulfur (0.5 – 5 %m/m).

Simple instructions to setup the **X-Supreme** for these three calibration methods are included in one single Oxford Instruments method sheet, part number XSMS-01.

It is then simply a matter of following the method sheet and running at least six standards with known contents of sulfur that evenly span the ranges of interest for each method.

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For the sulfur applications, official standard test methods (e.g. D4294) permit calibration either with synthetic standards prepared from n-dibutylsulfide and a pure mineral oil, or with standard reference materials. Oxford Instruments can supply sets of standards for these applications.
Note: Optional factory pre-calibration for sulfur in oil over the three concentration ranges is available by quoting part number XSP-Sulfur CAL

Quality control and Instrument correction

The "XSP-Sulfur" package contains three restandardisation setting up samples (SUSs). They are a pure light mineral oil (supplied by user) and SU-S20B or SU-S40D. The pure light mineral oil is the base of the synthetic standards. The others are disks containing a precise amount of sulfur, which act as a long-term reference for the instrument sensitivity for sulfur X-rays.

From time to time, the instrument needs restandardising by measuring the appropriate SUSs. Capitalising on the excellent stability of the **X-Supreme**, the best strategy is regular measurement of a quality control (QC) sample with restandardisation if a result exceeds control limits. This process has been made easy on the **X-Supreme**, as a QC sample can be specified in a tray position with the samples to be measured either by itself, or with production samples. After a series of QC measurements the **QC data** displays the check sample's results over time, in both graphical and numerical format, allowing a rapid assessment to be made. If the results are inside customer specified tolerances then routine analysis can continue, if outside Restandardisation is necessary.

Routine analysis

To ensure, as far as possible, the validity of the measurements, the **X-Supreme** has **SmartCheck** software to apply various tests that confirm the analytical measurement conforms to expected performance.

For example, most official test methods specify the measurement of two portions of the test sample when determining ultra low sulfur levels, and using the average as the final result. SmartCheck can be setup to check for large differences between the two portions, and therefore point out a possible contamination in one of the portions.

Other checks using SmartCheck software can also be specified, such as checking that a sample is in the analysis position, or that the sample is within the calibration range. All these functions can be simply set up thereby ensuring consistency and quality of analysis.

For many official analytical methods e.g. ASTM, there is now a section called "**Helpful Hints**" which is a summary of the various "good ideas" which users of the equipment have found assist them in obtaining good results. For XRF analysis examples include "Do not touch the sample film, ensure no crinkles on the film" etc. However in many cases this information is stored in a file located close to/underneath the desk, or even in the next office. To ensure this information is always at hand, Helpful Hints can be specified by anyone with manager level access for each method. The Hints are displayed clearly in routine analysis. A manager can therefore specify for their laboratory which items could assist the operators to obtain consistent accurate results. It is also a very easy way to ensure that all operators have the required information "at the time of analysis" thereby assisting in overall quality of analysis.

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Performance and results

Figure 3 shows a typical calibration line based on calibration standards prepared with mineral oil and spanning the range 0 to 150 mg.kg^{-1} sulfur.

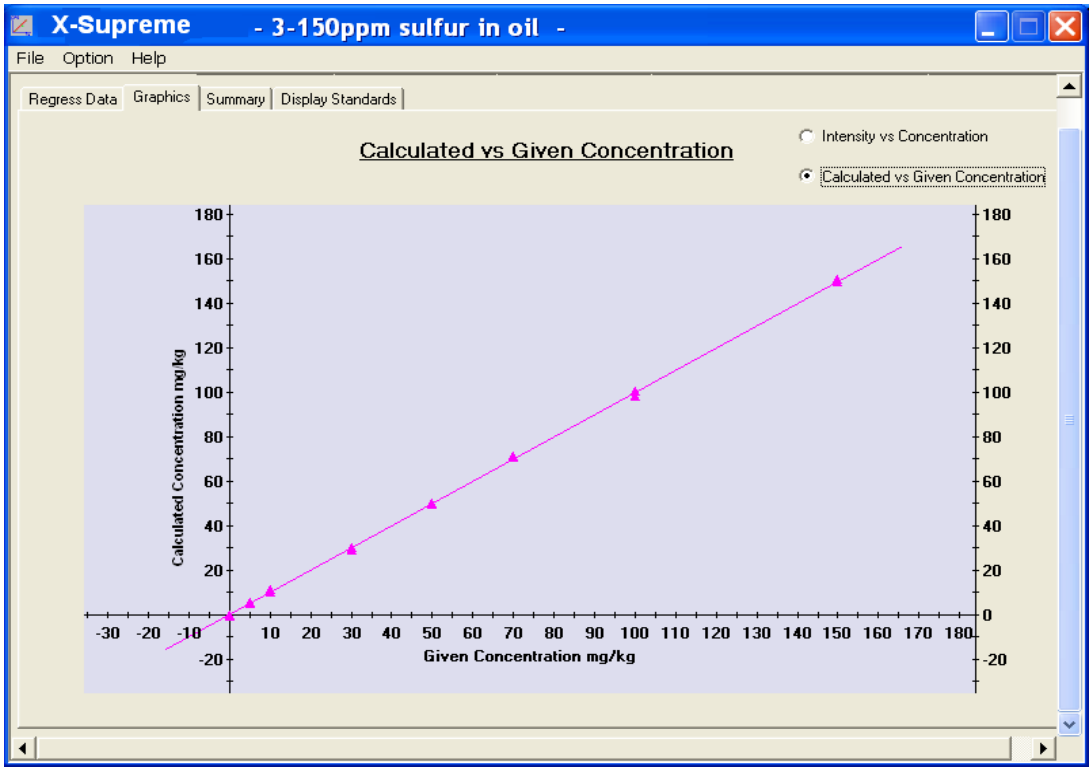

Figure 3: Ultra low sulfur calibration

Table 1: Typical calibration performance for sulfur

Concentration Range	Concentration unit	Counting time* (seconds)	Standard error of calibration	Lowest limit of detection (3σ)	Guaranteed limit of detection (3σ)	Limit of Quantification (10σ)	Precision (95% confidence)
3 – 150	mg.kg^{-1}	2 x 240 *	< 1	< 1	< 1.5	3.3	< 1 at 10 mg.kg^{-1} S
0.015 – 0.5	%m/m	150	0.002	n/a	n/a	n/a	0.001 at 0.1 % m/m S
0.5 – 5	%m/m	50	0.04	n/a	n/a	n/a	0.011 at 1 %m/m S

* This is for the measurements of two aliquots per sample, as per standard test methods ASTM D4294, ISO 20847, and ISO13032.

The ultra-low sulfur method was validated by running certified reference materials as unknown samples on two different **X-Supreme** instruments, using different operators. The results are shown in Table 2.

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Table 2: Validation results for ultra-low sulfur

Sample	Sulfur, $mg.kg^{-1}$		
	Given content	X-Supreme 1	X-Supreme 2
ERML-EF674 (Diesel CRM)	11.0	11.1	11.7
ERML-EF673 (Diesel CRM)	52.4	54.8	54.1

Further validation measurements were carried out to test for matrix correction. The results are in Table 3.
Using Focus ***SD*** technology all validation samples were measured against calibrations done using mineral oil standards i.e. **no matrix-matching** was required giving simplicity for routine operation.

Table 3: Validation results with various matrices for the low-sulfur method

Sample type	Certified reference material number	Certified sulfur content	X-Supreme results
Kerosene	NIST 1616b	8.41 $mg.kg^{-1}$	9.0 $mg.kg^{-1}$
Diesel fuel	NIST 2723a	11.0 $mg.kg^{-1}$	10.5 $mg.kg^{-1}$
Reformulated gasoline	NIST 2299	13.6 $mg.kg^{-1}$	14.8 $mg.kg^{-1}$
Gasoline with 13% MTBE	NIST 2296	40.0 $mg.kg^{-1}$	41.5 $mg.kg^{-1}$
Gasoline with 11% MTBE	NIST 2294	40.9 $mg.kg^{-1}$	41.6 $mg.kg^{-1}$
Diesel fuel	ERM-673a	52.4 $mg.kg^{-1}$	54.1 $mg.kg^{-1}$
Gasoline with 10% Ethanol	NIST 2297	303.7 $mg.kg^{-1}$	304.4 $mg.kg^{-1}$
Diesel	NIST 2724b	0.04265 % m/m	0.04276 % m/m
Crude oil, heavy sweet	NIST 2722	0.21037 % m/m	0.20575 % m/m
Residual Fuel	NIST 1623c	0.3806 % m/m	0.3790 % m/m
Crude oil, light sour	NIST 2721	1.5832 % m/m	1.5893 % m/m
Residual Fuel	NIST 2717a	2.9957 % m/m	2.9298 % m/m

Instrument Specification

The **X-Supreme** instrument package for the analysis of sulfur in road fuels is **XSP-Sulfur.**
This includes the analytical methods, associated method sheet, setting-up samples and other accessories necessary, e.g. sample cups, film…etc required for operation.

Optional factory calibration for sulfur, including provision of calibration standards, is available P/No XSP-Sulfur CAL refers.

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