Hitachi X-Supreme 8000 for the analysis of ultra-low sulfur in fuels, nickel, vanadium, iron in fuel oils, and lead in gasoline

Instrument Package: 10011618

Complies with ASTM D4294, IP 336, ISO 20847 and ISO 13032.

INTRODUCTION

Quality control laboratories in refineries and testing houses have long used Energy-Dispersive X-ray fluorescence (EDXRF) spectrometers, e.g. LAB-X and Twin-X to analyze a wide range of 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 Organization has developed the MARPOL Annex VI regulation to reduce air pollution from ships through regulating emissions such as sulfur oxides (SOx). Since 2020, the global sulfur levels in marine fuel is capped at 0.5%, and 0.1% in designated SOx emission control areas (such as Baltic and North Sea).

Automotive fuels also follow stringent regulations. 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.

Many countries use predominantly unleaded product with a maximum permitted level of lead at 0.013 $g.l^{-1}$. Within the European Union the maximum level for lead is 0.005 $g.l^{-1}$. In unleaded gasoline, lead compounds are in some cases being replaced by other additives such as manganese compounds. In some countries the social and economic advantages of leaded gasoline still justify its use so it will continue in production. Countries with no domestic consumption may produce it for export, so checking of both unleaded and leaded products will continue. There is also the continuing need to monitor the levels of vanadium, iron and nickel in fuel oil.

Hitachi offers a high performance EDXRF spectrometer that successfully performs all elemental analyses required in the petroleum industry, the X-Supreme. The X-Supreme is the perfect analyzer for the rapid determination of part per million (ppm) levels of both low atomic number elements (e.g. sulfur in oil) and higher atomic number elements such as lead (in gasoline), nickel, iron and vanadium (in fuel oil).

INSTRUMENTAL

To obtain the best performance for fuel analysis, the Hitachi X-Supreme uses Hitachi's Focus SD technology.

Focus SD has been optimized for fuel analysis, and combines a Silicon Drift detector (SDD) which provides high spectral resolution, a field-proven titanium-target tube providing both excellent elemental excitation and matrix correct ion, and optimized background filters. This combination allows optimum speed of analysis and low detection limits. This delivers supreme performance for all elements of interest.

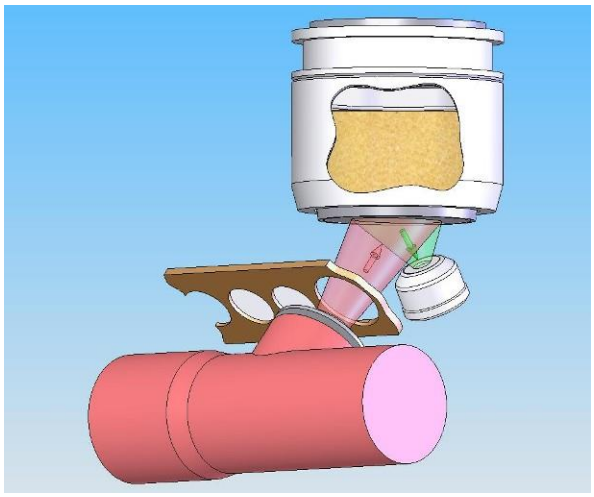

FIGURE 1: HITACHI FOCUS SD TECHNOLOGY

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 make 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.

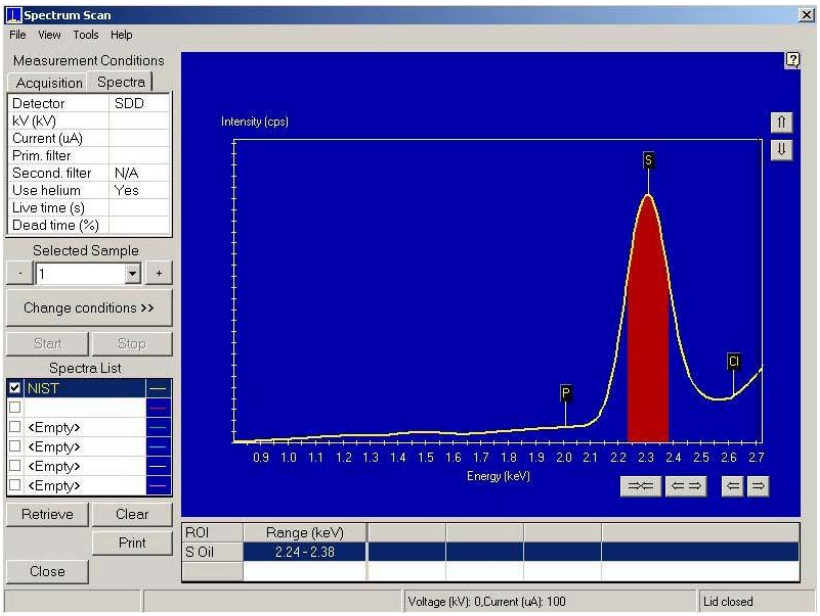

FIGURE 2: SPECTRA FOR SULFUR SHOWING GOOD ELEMENTAL SEPARATION FROM POTENTIAL INTERFERING ELEMENTS OF PHOSPHORUS AND CHLORINE.

SAMPLE PREPARATION AND PRESENTATION

Sample cups are first simply assembled using an XRF sample film. Poly-M is a high-purity window material and is used for ultra-low sulfur fuels (S < 150 $mg.kg^{-1}$). This is of consistent quality and giving the minimal background signal necessary for measuring ultra-low sulfur fuels. For simplicity, it is also used with all other methods included in this package. 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 13 ml. 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, the measurement starts automatically. The results are displayed on the screen using your chosen format, and results can be printed on an external USB printer and/or exported to another location.

CALIBRATION

The “X-Supreme Fuels” application package comes pre-loaded with the following optimized method templates, specifying the appropriate operating parameters and corrections:

- Ultra-Low Sulfur (3-150 $mg.kg^{-1}$).
- Medium Sulfur (0.015-0.5% m/m).
- High Sulfur (0.5-5% m/m).
- Sulfur, Nickel, Vanadium and Iron in fuel oil.
- Lead in unleaded gasoline.
- Lead in leaded gasoline.

Simple instructions to setup the X-Supreme for these calibration methods are included in Hitachi method sheets (one for the sulfur methods, one for the fuel method, and one for the lead methods).

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

Note: Optional factory calibrations for sulfur in oil over the three concentration ranges are available.

QUALITY CONTROL AND INSTRUMENT CORRECTION

The “Fuels” package uses four restandardization setting up samples (SUSs). They are pure light mineral oil (supplied by user), SU-S20B, SU-S40D, and SUGL50D. The pure light mineral oil is the base of the synthetic standards. The others are disks containing precise amounts of the elements of interest, which act as a long-term reference for the sensitivity of the elements’ X-rays.

From time to time, the instrument needs restandardizing by measuring the appropriate SUSs. Capitalizing on the excellent stability of the X-Supreme, the best strategy is regular measurement of a quality control (QC) sample with restandardization 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, that the sample is within the calibration range, or that the correct XRF film is being used. 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 assists 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.

The X-Supreme “Live result update” function displays preliminary results after only a few seconds for each sample. This enables the operator to spot potential production or sample issues very quickly and respond adequately.

TYPICAL PERFORMANCE AND RESULTS

Tables 1 to **7** show typical calibration performance that illustrates how the X-Supreme readily covers the range of fuel specifications for the present and the future. All precision data was obtained from ten repeat measurements of standards and/or certified reference material.

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.

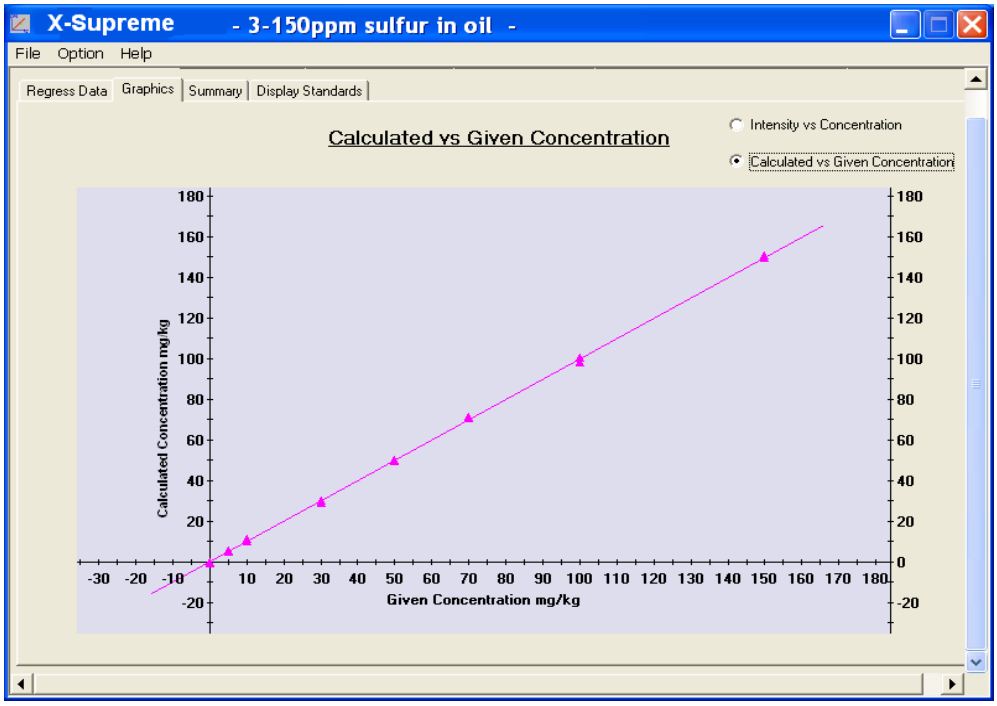

FIGURE 3: ULTRA LOW SULFUR CALIBRATION

TABLE 1: TYPICAL CALIBRATION PERFORMANCE FOR SULFUR METHODS

Concentration Range	Concentration unit	Counting time (seconds)	Standard error of calibration	Lowest limit of detection (3σ)	Guaranteed limit of detection (3σ)	Precision (95% confidence)
3 - 150	$mg.kg^{-1}$	2 x 240 *	< 1	< 1	< 1.5	< 1 at 10 $mg.kg^{-1}$ 1.6 at 15 $mg.kg^{-1}$
0.015 - 0.5	%m/m	150	0.002	n/a	n/a	0.001 at 0.1
0.5 - 5	%m/m	50	0.04	n/a	n/a	0.011 at 1 %m/m

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

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**.

TABLE 2: VALIDATION RESULTS FOR ULTRA-LOW SULFUR

		Sulfur, $mg.kg^{-1}$	
Sample	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 $\%^{m}/_{m}$

TABLE 4: TYPICAL CALIBRATION PERFORMANCE FOR SULFUR, NICKEL, VANADIUM AND IRON IN FUEL OIL

Analyte	Concentration Range	Standard error	Theoretical limit of detection (3σ)	Guaranteed limit of detection (3σ)	Precision (95% confidence)
S	0.5 – 5 $\%^{m}/_{m}$	0.02 $\%^{m}/_{m}$	n/a	n/a	0.05 at 3.45 $\%^{m}/_{m}$
V	0 - 500 $mg.kg^{-1}$	5 $mg.kg^{-1}$	1 $mg.kg^{-1}$	2 $mg.kg^{-1}$	2 at 29 $mg.kg^{-1}$
Fe	0 - 500 $mg.kg^{-1}$	3 $mg.kg^{-1}$	< 1 $mg.kg^{-1}$	1.5 $mg.kg^{-1}$	1 at 7 $mg.kg^{-1}$
Ni	0 - 100 $mg.kg^{-1}$	1 $mg.kg^{-1}$	< 1 $mg.kg^{-1}$	1 $mg.kg^{-1}$	0.7 at 8 $mg.kg^{-1}$

The precision was obtained from ten repeat measurements of a Japanese certified reference material (CRM), JPI SO264.

The method was validated by measuring the same Japanese CRM, and a NIST CRM (NIST 1634c). Sulfur and iron contents were not certified. The results are shown in **Table 5**.

TABLE 5: VALIDATION RESULTS

	JPI SO264		NIST 1634c	
Analyte	**Certified concentration**	**X-Supreme result**	**Certified concentration**	**X-Supreme results**
S	(3.18 $\%^{m}/_{m}$)	3.42 $\%^{m}/_{m}$	(2 $\%^{m}/_{m}$)	2.46 $\%^{m}/_{m}$
V	27 ± 1 $mg.kg^{-1}$	28 $mg.kg^{-1}$	28.2 ± 0.4 $mg.kg^{-1}$	29 $mg.kg^{-1}$
Fe	1 $mg.kg^{-1}$	7 $mg.kg^{-1}$	------	49 $mg.kg^{-1}$
Ni	7.7 ± 0.3 $mg.kg^{-1}$	8 $mg.kg^{-1}$	17.5 ± 0.2 $mg.kg^{-1}$	18 $mg.kg^{-1}$

Values in brackets are not certified.

TABLE 6: TYPICAL CALIBRATION PERFORMANCE FOR LEAD IN UNLEADED GASOLINE

Unit	Concentration Range	Standard error	Theoretical limit of detection (3σ)	Guaranteed limit of detection (3σ)	Mid-range precision (95% confidence)
$g.US\ Gal^{-1}$	0 - 0.3	0.003	0.002	0.003	0.003 @ 0.1
$g.l^{-1}$	0 - 0.08	0.0008	0.0005	0.0008	0.0008 @ 0.03

TABLE 7: TYPICAL CALIBRATION PERFORMANCE FOR LEAD IN LEADED GASOLINE

Unit	Concentration Range	Standard error	Mid-range precision (95% confidence)
$g.US\ Gal^{-1}$	0 - 5	0.017	0.06 at 2
$g.l^{-1}$	0 - 1.3	0.0045	0.016 at 0.5

INSTRUMENT SPECIFICATION

The instrument package for the analysis fuels is 10011618. This includes the analytical methods, associated method sheest, setting-up samples and other accessories necessary, e.g. sample cups, film etc required for operation.

Optional factory calibrations for sulfur, including provision of calibration standards, are available.