Hitachi X-Supreme8000 for the rapid analysis of new and used lubricating oils

Instrument Package: XSP-Lubes

INTRODUCTION

For quality control analysis of new and used lubricating oils, X-ray fluorescence (XRF) spectrometry is one of the simplest, easiest, and most cost-effective elemental analysis techniques. Analysis is non-destructive and simply involves pouring the oil sample into a liquid cell, loading into the instrument, and analysis starts, i.e. no dilution. These simple steps allows the X-Supreme to be operated by production staff on a 24/7 basis giving significant cost and time savings.

Lubricating oil is a blend of various highly refined stock oils and chemical additives that enhance properties to meet specific customer requirements. Additives are oxidation inhibitors, corrosion inhibitors and detergent-dispersive chemicals. Some of these contain one or more of the elements calcium, magnesium, phosphorus, sulfur, zinc and molybdenum. Stock oils also contain sulfur as a natural impurity and certain product specifications also limit chlorine level. Because of all this, it is necessary to closely monitor these elements at the manufacturing location.

Oil should have a long life in protecting valuable machinery but continual changes occur. There is wear from the effects of friction between contacting surfaces and contamination by dirt, water and other fluids. Destructive changes caused by oxygen, combustion gases and high temperatures alter the condition of the oil. Thus lubricating oil becomes a working history of the machinery and measurement of various metals in it can give information about the machine components that are wearing.

Hitachi now offers a new spectrometer the X-Supreme which measures up to nine elements in lubricating oil and up to 18 elements in used oils. In addition following on from the successful use of standard test method ASTM D6481, for phosphorus, sulfur, calcium and zinc in new lubricating oils by energy dispersive X-ray fluorescence (EDXRF), an improved ASTM method with additional elements such as Magnesium, is proposed (work item WK18448) and a round robin is expected in early 2009. This will result in a new ASTM method for additional elements and the X-Supreme will cover this new method.

For the analysis of metals in used oils, a new methodology is used based on a custom set of calibration standards that avoid the limitations imposed by the frequently used serial dilution.

INSTRUMENTAL

To obtain the best performance for measuring a wide range of elements in oils, including Magnesium, the X-Supreme incorporates Hitachi's Focus SD technology.

Focus SD has been optimised for lubricating oil and wear metal analysis and combines a Silicon Drift detector (SDD) which provides high spectral resolution (see **Figure 1**), a field-proven tungsten-target X-ray tube providing excellent elemental excitation, and background filters. This combination gives optimum speed of analysis, low detection limits, and supreme performance for multi-element analysis at all concentrations.

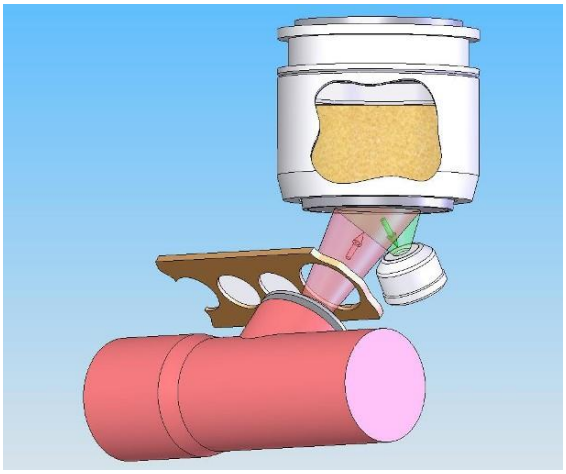

FIGURE 1: HITACHI FOCUS SD TECHNOLOGY

All control of the instrument is through the X-Supreme's integrated PC and software which provides sophisticated calibration models that handle a wide variety 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 a laboratory or on a production site for twenty-four-hour operation. The X-Supreme includes a ten-position autosampler to enable simple and unattended multiple analysis.

The X-Supreme offers producers and users of lubricating oils a cost-effective solution for process control and monitoring of wear metals.

SAMPLE PREPARATION AND PRESENTATION

Sample cups are simply assembled using a high-purity window material, Poly4. This is a very pure film with high X-ray transmission for low atomic number elements. There is an internal mark in each sample cup to indicate the filling line at approximately 13 ml. Secondary stages on the spectrometer's autosampler act as safety windows to retain any liquid in the unlikely event of a leaking sample cup.

After placing the samples on the instrument tray, entering their identification, selecting their tray position and method(s) at the integrated keypad, the measurement starts automatically. The screen shows results in a customised format that can be printed and exported to another location.

CALIBRATION

Each X-Supreme comes pre-programmed with operating parameters that are optimised for each application included in the package. It is then simply a matter of following the relevant Hitachi method sheet and running at least six standards with known analytes contents.

Optional factory calibration is available for both lubricating oil and wear metal analysis; (P/No XSP- Lubes CAL).

QUALITY CONTROL AND INSTRUMENT CORRECTION

Setting-up-samples (SUSs) are measured at the time of calibration. They act as long term reference for the sensitivity of each element's X-rays.

From time to time, the instrument needs restandardising by measuring the setting-up-samples. Capitalising on the excellent stability of the X-Supreme, the best strategy is regular measurement of a quality control (QC) sample and only to restandardise when a result exceeds control limits. This is an easy process on the X-Supreme when using the QC check sample routine. This routine allows a QC sample to be measured at the same time as production sample's, giving total confidence in analytical results for both quality control and assurance purposes.

The QC check sample's results over time can be displayed 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 proceed but if outside then restandardisation is necessary.

TYPICAL PERFORMANCE AND RESULTS

Tables 1 and **2** show typical calibration performance that illustrates how the X-Supreme readily covers the range of specifications in new and used lubricants.

TABLE 1: TYPICAL CALIBRATION PERFORMANCE FOR UNUSED LUBRICATING OIL TO ASTM D7751

Analyte	Calibration range (%$^{m}/_{m}$)	Standard error (%$^{m}/_{m}$)	Guaranteed limit of detection (3σ) (%$^{m}/_{m}$)	Precision (95% confidence) (%$^{m}/_{m}$)	Total analysis time (minutes)
Mg	0-0.4	0.013	0.005	0.012	~ 8
P	0-0.25	0.004	0.004	0.003	
S	0-1.5	0.025	0.003	0.012	
Cl	0-0.4	0.006	0.001	0.002	
Ca	0-1.0	0.008	0.0003	0.0035	
Zn	0-0.25	0.010	0.0001	0.0015	
Mo	0-0.05	0.0008	0.0004	0.0005	

The precision was calculated from the results of ten measurements on a number of the calibration standards that represented suitable mid-range concentrations for the elements.

TABLE 2: TYPICAL CALIBRATION PERFORMANCE FOR USED LUBRICATING OIL

Analyte	Calibration range	Unit	Standard error of calibration	Guaranteed limit of detection (3σ)	Precision (95% confidence)	Total analysis time (minutes)
Mg	0-3500	$mg.kg^{-1}$	60	60	40	12.5
Al	0-400	$mg.kg^{-1}$	47	30	28	
P	0-0.40	% $^{m}/_{m}$	0.006	0.0012	0.0006	
S	0-1.00	% $^{m}/_{m}$	0.014	0.0008	0.0027	
Cl	0-4000	$mg.kg^{-1}$	50	6	4	
Ca	0-0.40	% $^{m}/_{m}$	0.011	0.0008	0.0003	
Sn	0-400	$mg.kg^{-1}$	86	13*	5	
Ti	0-400	$mg.kg^{-1}$	4	2	4	
V	0-400	$mg.kg^{-1}$	4	1	3	
Cr	0-400	$mg.kg^{-1}$	13	1	2	
Mn	0-400	$mg.kg^{-1}$	4	1	2	
Fe	0-400	$mg.kg^{-1}$	6	1	2	
Co	0-400	$mg.kg^{-1}$	10	1	1	
Ni	0-400	$mg.kg^{-1}$	8	1	2	
Cu	0-400	$mg.kg^{-1}$	12	2	1	
Zn	0-0.40	% m/m	0.003	0.0002	0.0002	
Pb	0-400	$mg.kg^{-1}$	9	1	4	
Mo	0-400	$mg.kg^{-1}$	7	8	6	

* Limit of detection for Sn with no spectral interference.

The precision was calculated from the results of ten measurements of a cup containing CONOSTAN S21-300.

INSTRUMENT SPECIFICATION

The X-Supreme instrument package for the analysis of lubricating oil additives and wear metals is XSP-Lubes 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 lubricating oil and wear metal analysis is available P/No XSP-Lubes CAL.