APPLICATION NOTE

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X-SUPREME8000

Figure 1: X-Supreme8000 Field proven benchtop EDXRF analyser for quality control/assurance

Figure 2: Simply pour the oil sample into the sample cell – no weighing or volumetric measurements required

Determination of Ultra Low Chlorine (and Sulfur) in Oil

ANALYSIS USING ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF)

Within the Petroleum industry, routine 24/7 quality control analysis for sulfur in a range of petroleum products, e.g. diesel fuel, kerosene, jet fuel, naptha, crude oil, biodiesel etc. is often carried out using simple to use benchtop Energy Dispersive X-ray Fluorescence (EDXRF) analysis such as the LAB-X3500 and X-Supreme8000 instrument.

This application can now be extended to include Chlorine determination in crude oils offering the same benefits of analysis by EDXRF including:

- No sample preparation, i.e. the liquid sample is poured directly into the sample cell with no weighing or volumetric measurements required.
- Non-destructive analysis so that the sample can be retained for any future investigation.
- Rapid analysis with provisional results available five seconds after measurement starts and continuously updated until the end of the measurement period allowing a rapid sample assessment to be made.

The X-Supreme8000 is the latest benchtop EDXRF analyser from Hitachi offering field proven reliability with simple methods to deliver trusted, reliable accurate analysis. 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.

Key Benefits

The X-Supreme8000 can be used as part of a quality control procedure to ensure petroleum products are manufactured to customer specifications, allowing optimisation of the production process with resultant cost savings.

Recently the possible presence of chlorine in crude oils has become a concern in the industry as chlorine in the oil can potentially cause corrosion damage in the refining process. The request was to develop an additional rapid, simple to use, analytical method on the X-Supreme to detect and quantify Chlorine.

The resultant calibration demonstrates good performance to detect Chlorine from ppm's to high % concentrations levels even when the oil contains high % levels of sulfur. This allows verification of the Chlorine concentration to confirm product specification and optimisation of the refining process.

1. SAMPLE PREPARATION AND CALIBRATION STANDARDS

The oil samples were poured directly into Hitachi sample cells (P/No L242) fitted with Poly-M sample film. The quantity of sample is not critical providing its depth is at least two millimetres. However it is advisable to be consistent and fill the sample cup to the internal line (approximately 13 ml). A secondary safety window is also fitted with Poly-M film so in the unlikely event of sample leakage the secondary safety window will retain the oil and prevent possible instrument contamination with any associated downtime.

Note: Before filling the cup ensure it is free or any hair (hair contains approx. 5% sulfur) and if present in the cup or on the film, will increase the sulfur result on samples.

Two optimised calibrations were derived, one covering the ultra low concentration of Chlorine (0-200 ppm) and the other for higher levels of chlorine (0-1%) with details shown in Table 1.

Table 1: Calibration standards details.

Calibration/Method template	XSMET-07A	XSMET-07B	XSMET-07C
Chlorine concentration	0-50 ppm	0-200 ppm	0-1%
Sulfur concentration	0-150 ppm	0-1%	0-1%
Standard set P/No	54-CS0032	54-CS0031	54-CM0003
Number of standards	10	10	10
Measurement Time (sec)	240	240	50

Key Benefit

For highest level of accuracy and traceability, an empirical calibration was derived using a series of commercially available oil standards containing Chlorine and Sulfur.

Table 2: Details of calibration standards for ultra low Cl and S methods and for Cl and S method.

	Ultra low Cl and S method XSMET-07A (Standards P/No 54-CS0032)		Ultra low Cl and S method XSMET-07B (Standards P/No 54-CS0031)		Cl and S method XSMET-07C (Standards P/No 54-CS0003)	
Standard	**Cl ppm**	**S ppm**	**Cl ppm**	**Sulfur Wt%**	**Cl Wt%**	**Sulfur Wt%**
#1	0	0	0	0	0	0
#2	5	150	125	0.1	0.8	0.1
#3	10	75	10	0.602	0.5	0.6
#4	15	25	150	0.201	0.3	0.2
#5	20	15	175	0.7	0.2	0.7
#6	25	5	25	0.3	0.6	0.3
#7	30	50	200	0.4	0.1	0.4
#8	35	10	100	0.5	0.4	0.5
#9	40	100	50	0.801	1	0.8
#10	50	125	75	1	0	1

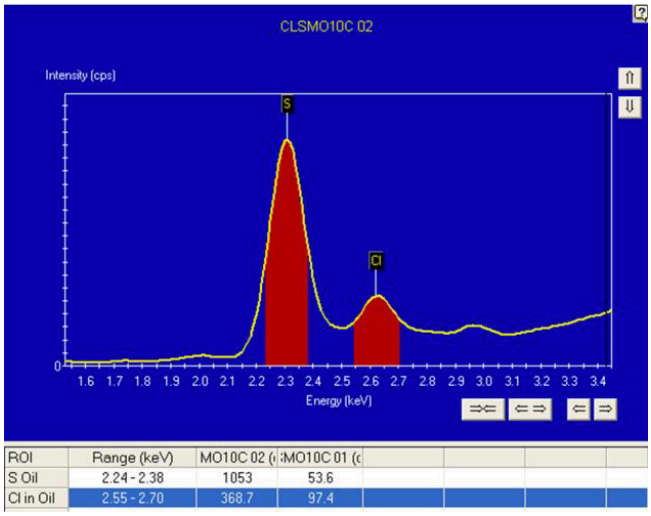

Figure 3: Spectrum scan of S: 0.100% and Cl: 125 ppm in mineral oil sample.

2. CALIBRATION DETAILS

Measuring the oil calibration standards shown in Table 2, a regression was obtained as shown in Figures 4 and 5.

Key Benefit

Excellent correlation demonstrates high accuracy of analysis for both low and high Cl concentrations in crude oil. Routine measurements gives accurate Cl values so any potential corrosion issues can be quickly quantified and minimised/prevented.

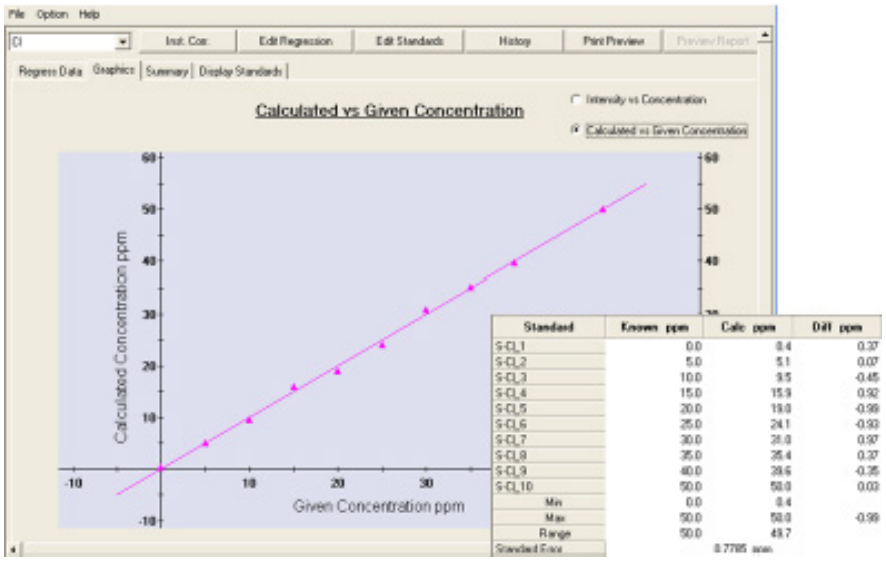

Figure 4: X-ray calibration (regression line) of Chlorine (0 to 50 ppm) showing given versus calculated concentration.

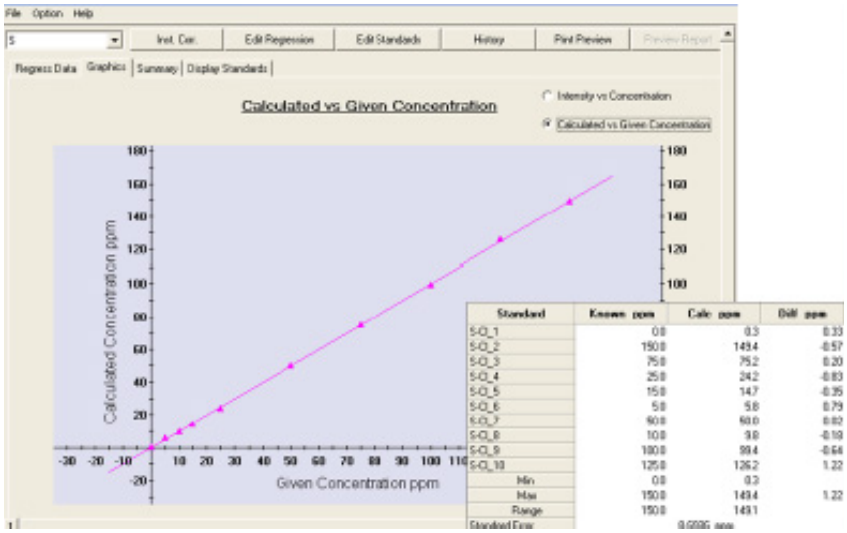

Figure 5: X-ray calibration (regression line) of Sulfur (0 to 150 ppm) showing given versus calculated concentration.

3. RESULTS

For the low Chlorine and sulfur method -ppm levels, calibration standard number 3 (set CS0032) was measured ten times (one measurement is the average of the aliquots) to demonstrate instrument repeatability (see results in Table 3).

For the low Chlorine and high sulfur method, the calibration standards number 3 and 10 (set CS0031) were measured ten times to demonstrate instrument repeatability (stability) and results are shown in Table 4.

Table 3: Standard 3 repeat measurement results measuring two aliquots with an analysis time of 2x 240 seconds.

	Standard Number 3	
Measurement	**Chlorine ppm**	**Sulfur ppm**
#1	10	74
#2	10	73
#3	11	75
#4	12	73
#5	11	75
#6	11	76
#7	11	75
#8	11	75
#9	11	75
#10	11	75
Average	11	75
Certified concentration	10	75
Standard Deviation (1σ)	0.6	0.9
Precision (2σ)	1.2	1.8

Table 4: Standard 3 and 10 repeat measurement results using 240 second measurement time each.

	Standard Number 3		Standard Number 10	
Measurement	**Chlorine ppm**	**Sulfur Wt%**	**Chlorine ppm**	**Sulfur Wt%**
#1	11	0.587	71	1.007
#2	11	0.588	73	1.007
#3	9	0.588	71	1.009
#4	9	0.588	74	1.007
#5	9	0.587	72	1.008
#6	11	0.588	72	1.007
#7	10	0.587	73	1.008
#8	10	0.586	73	1.007
#9	11	0.586	73	1.007
#10	11	0.587	72	1.006
Average	10	0.587	72	1.007
Certified concentration	10	0.602	75	1
Standard Deviation (1σ)	0.7	0.001	0.8	0.001
Precision (2σ)	1.4	0.002	1.6	0.002

Typical calibration performance for ultra low chlorine and ultra low sulfur in oil method is listed in Table 4.

Table 5: Typical calibration performance for ultra low sulfur and ultra low chlorine in oil method XSMET-07A (S 0-150 ppm, Cl 0-200 ppm).

Analyte	Calibration range	Standard error of calibration	Theoretical limit of detection* (3σ)	Guaranteed limit of detection*	Precision (95% confidence-2σ)	Total analysis time (seconds)
Cl	0-50 ppm	0.8 ppm	<1 ppm	<1.5 ppm	1.2 ppm	240 x 2
S	0-150 ppm	0.7 ppm	1 ppm	<1.5 ppm	1.8 ppm	

Table 6: Typical calibration performance for sulfur and ultra low chlorine in oil method XSMET-07B (S 0-1.0 wt%; Cl 0-200 ppm), n/a = not applicable due to high concentration.

Analyte	Calibration range	Standard error of calibration	Theoretical limit of detection* (3σ)	Guaranteed limit of detection*	Precision (95% confidence-2σ)	Total analysis time (seconds)
Cl	0-200 ppm	1.5 ppm	<1 ppm	<1.5 ppm	1.3 ppm	240
S	0-1.0 wt%	<0.01 wt%	N/A*	N/A*	0.002 wt%	

Table 7: Typical calibration performance for sulfur and chlorine in oil method XSMET-07C (S and Cl 0-1.0 wt%); n/a = not applicable due to high concentration.

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.

Analyte	Calibration range	Standard error of calibration	Guaranteed limit of detection* (3σ)	Precision (95% confidence-2σ)	Total analysis time (seconds)
Cl	0-1.0 wt%	<0.01 wt%	N/A*	0.002 wt%	50
S	0-1.0 wt%	<0.01 wt%	N/A*	0.003 wt%	

Conclusion

The X-Supreme8000 can determine sulfur and chlorine in oil samples with ease and typical calibration performance shown in Tables 5, 6 and 7.

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.

INSTRUMENT CONFIGURATION

These methods (P/No XSMET-07A, XSMET-07B, XSMET-07C) are specific to an X-Supreme fitted with a Titanium target X-ray tube. The instrument plus accessories required to measure Cl and S in oil are listed below.

Item	Description	P/No
1	X-Supreme fitted with Ti tube and SDD	54-B-ZX0008
2	Helium Gas Purge	ZX08
3	Liquid sample accessories pack	54-TXPAK1
4	Poly-M sample film	54-L77
5	Method templates	XSMET-07A , XSMET-07B, XSMET-07C
6	High setting-up sample (SUS) for S and Cl	54-SU-S40D
7	Low SUS for S and Cl, light mineral oil	54-CM0038

Note 1: The X-Supreme XSP-Fuels application package includes method templates XSMET-07A, B and C.

Note 2: calibrations standards are not included. They must be provided by the user, or they can be ordered from Hitachi High-Tech Analytical Science. See part numbers in Table 1.

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