Fast and Accurate Simultaneous Determination of Sulphur and Chlorine Using Modern Energy Dispersive X-Ray Fluorescence (EDXRF)

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Featuring simple operation and world-class EDXRF analytical performance, the HORIBA MESA-6000 delivers the rapid, precise and reliable Sulphur and Chlorine measurement capability needed for today's demanding petroleum based process control and product quality assurance applications. These applications range from the need to characterise crude oil and controlling contaminations in the refining process to ensuring regulatory compliance of finished products. Consequently, the determination of sulphur and chlorine content in a wide variety of petroleum based matrices is essential. The following is an introductory overview of the HORIBA MESA-6000, with data that demonstrates the power and flexibility made possible by this unique polarised mono-chromatic X-ray beam technology.

Background

Energy Dispersive X-Ray Fluorescence (EDXRF) is a well established technique and is widely utilised due to its ease of operation. However, standard direct radiation EDXRF is not able to achieve ultra low sensitivity requirements without susceptibity to matrix effects.

To meet new tough requirements for low sulphur measurement in automotive fuels and other petroleum products, the MESA-6000 was developed.

Instrumentation

The MESA-6000 is a compact (33W x 52D x 41H cm) and lightweight (22kg) analyser that can readily measure sulphur and chlorine content in petroleum products to part per million levels, in just 180 seconds. The optical path is under vacuum – no helium or other inert gas purges are required.

The instrumentation requires only a stable power source (100/250 VAC); with no other utilities required for this non-destructive and non-combustion technique.

The apparatus features a large and responsive touch screen display that is easy to use and sample analysis can be initiated with a minimum of user inputs.

Sample preparation and handling are simplified with the use of Mylar® film sealed disposable plastic cups, allowing instrument use by non laboratory trained technicians.

MESA-6000

A powerful on-board computer allows a full line-up of data handling, printing, and processing features that are needed for data transfer and compliance with good laboratory practice requirements.

For safe operation the instrument has an automatic control that de-powers the X-Ray tube anytime that the sample compartment is opened. Optimum X-Ray tube operating status is also ensured by an integrated, self-testing scheme that is initiated each time the instrument is started.

Of particular interest, MESA 6000 users can also simultaneously measure chlorine and sulphur content from weight percent down to part per million levels.

The NEW Technology

The MESA-6000 is based on the latest advances in Energy Dispersive X-ray Fluorescence (EDXRF) technology. It utilises a proprietary X-ray optical technology that produces a **Polarised, Mono-chromatic X-ray** energy beam. This approach is critical to achieve an ultra low noise background needed for the best limits of detection for both sulphur and chlorine. Also incorporated are; excellent performance at high concentration (multiple wt.% levels), simultaneous multi-element analysis and applicability over a wide range of sample types.

Interferences produced by matrix differences or other elements are also minimised. The MESA-6000 performance is well established, as it is compliant with ASTM and ISO International Sulphur Determination Norms:

• ASTM D7220	• ASTM D4294
• IP 532	• EN ISO 8754
• EN ISO 20847	• PrEN ISO 13032

Principle

The MESA-6000 features a unique, patented design with a close-coupled, doubly curved HOPG X-ray optic. It simultaneously polarises, focuses, and mono-chromates the X-ray beam.

This yields the ideal X-ray source for measuring chlorine, sulphur and lower atomic number elements at low concentrations. This technique creates an environment with ultra-low background similar to other optics-based X-ray analysers, but retains the EDXRF benefit of allowing for simultaneous analysis of multiple elements.
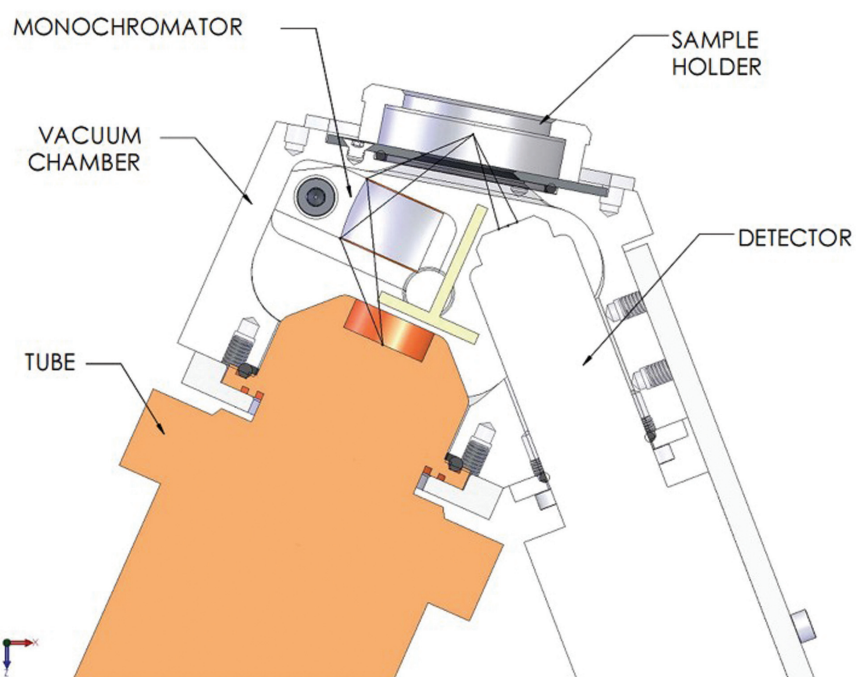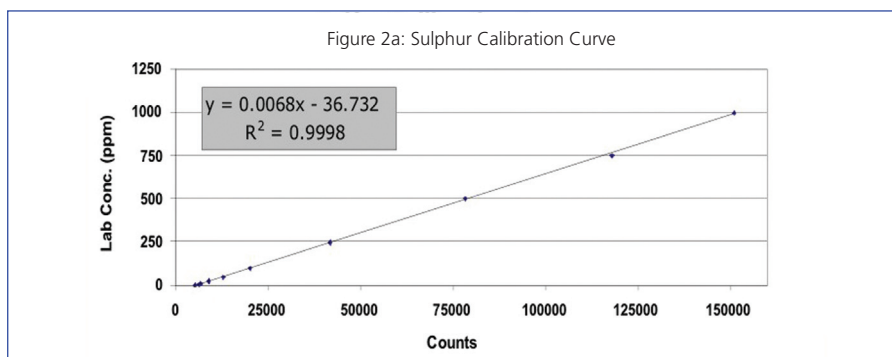

Figure 1: MESA-6000 principle, polarised Mono-chromatic EDXRF

Calibration and Linearity

Figure 2a depicts the typical near perfect calibration linearity exhibited by the MESA-6000.

The sulphur in mineral oil range of concentration standards used is - 0, 50, 100, 250, 500, 750 and 1000 mg/kg sulphur.

Figure 2a: Sulphur Calibration Curve

$$y = 0.0068x - 36.732$$
$$R^2 = 0.9998$$

Operators can calibrate the MESA-6000 with their own standards to generate and store up to 50 different calibration curves.

The same high quality calibration curve can be obtained on the MESA-6000 for chlorine as can be seen in figure 2b. The chlorine in mineral oil range of concentration standards used is - 0, 5, 25, 50, 150, 500, 300 and 500 mg/kg chlorine.

Figure 2b: Typical Chlorine Calibration Curve

$$y = 0.005x - 2.4405$$
$$R^2 = 0.9999$$
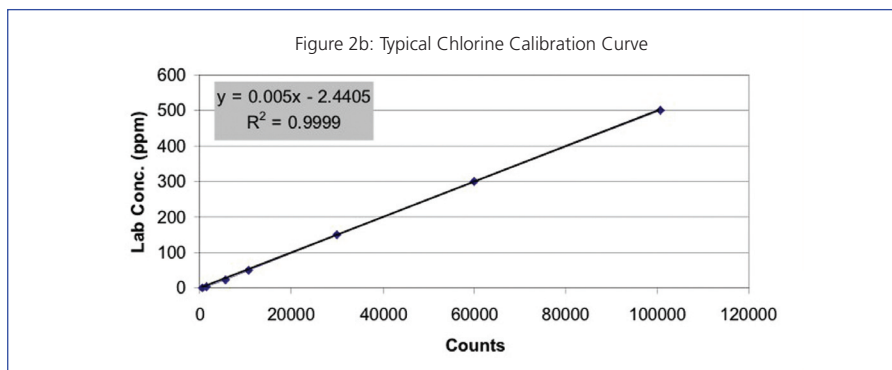
Precision and Estimation of Level of Detection

To determine precision, an 11mg/kg sulphur in diesel sample was used. The data was derived from the average of two consecutive 180 second analyses of 5ml of the diesel run consecutively 14 times. This data is illustrated in Figure 3a.

Figure 3a: Sulphur Precision Data

**LOD/LOQ Estimate Using 11 mg/kg S in Diesel**
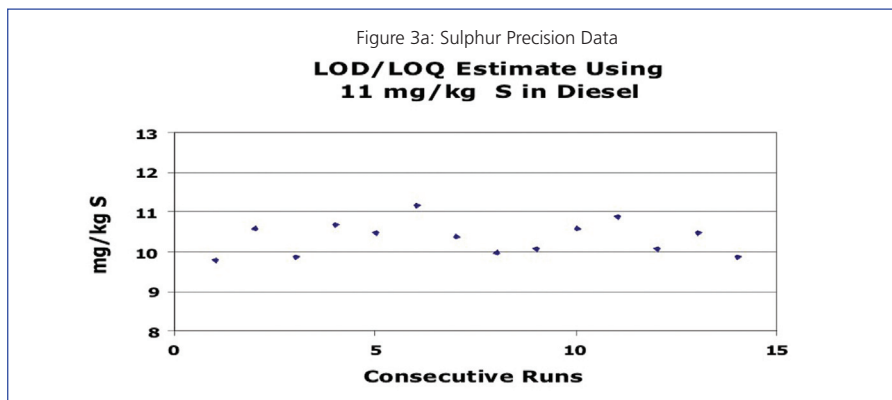
The repeatability data was then analysed using a modified EPA method detection limit (MDL) technique to estimate level of detection (LOD) and level of quantification (LOQ) and MDL at the 95 percent confidence level. These estimates are shown in Table 1a. It should be noted that the elevated signal to noise (S/N) ratio of 24.8 indicates that a lower concentration can be analysed and that detection limits are likely to be lower than indicated here.

MESA-6000 Sulphur	
STDEV	0.42 mg/kg
LOD	**1.25 mg/kg**
MSDL, 95%	**0.72 mg/kg**
S/N Ratio	24.8

Table 1a: Sulfur Limit of Detection

As with previous testing, a-certified 40 mg/kg Chlorine performance check sample was used to determine the precision for chlorine. The data was derived from the average of two consecutive 180 second analyses of 5 ml of transformer oil run consecutively 21 times. This data is illustrated in Figure 3a.

Figure 3b: Chlorine Precision Data

LOD/LOQ Estimate Using 40 mg/kg Cl
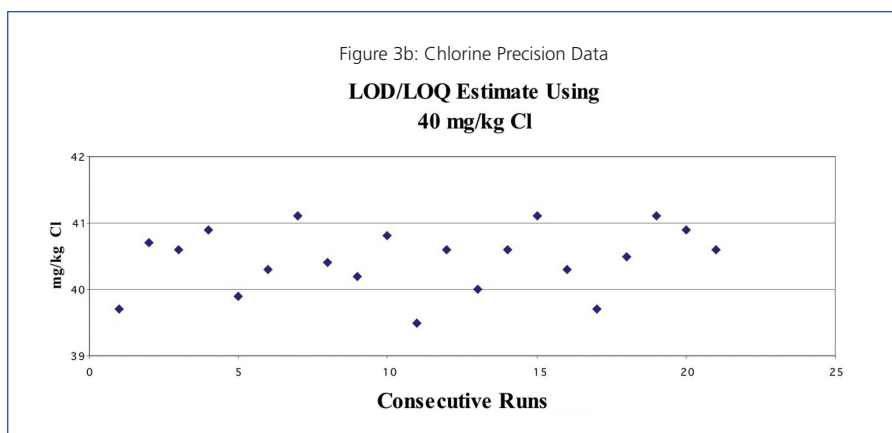
Using the same modified EPA method, described above, the chlorine repeatability data was analysed for LOD, LOQ and MDL at the 95% confidence level. These estimates are shown in Table 1b. It should be noted the elevated signal to noise (S/N) ratio of 84.4 indicates that a much lower concentration can be analysed and that detection limits are likely to be lower than indicated.

MESA-6000 Chlorine	
STDEV	0.48 mg/kg
LOD	**1.44 mg/kg**
MSDL, 95%	**0.88 mg/kg**
S/N Ratio	84.4

Table 1b: Chlorine Limit of Detection

Equivalency

In order to determine how the MESA-6000 methodology performance might compare to established sulphur measurement technologies, a similar set of calibration standards and sample sets were prepared and measured by the following technologies:

- Energy Dispersive X-Ray Fluorescence Instrumentation (EDXRF) MESA-6000
- Combustion UV Fluorescence analyser Method ASTM D-5453
- Energy Dispersive X-Ray Fluorescence Method ASTM D-4294

Following instrument calibration with sulphur in mineral oil standards, 11 samples were analysed. Analysis demonstrates that for the 9 lower concentration materials the MESA-6000 and D5453 results readily compare. For the 2 higher concentration samples, which are outside the scope of D5453, the MESA-6000 and D4294 results are found to be equivalent to each other.

Sample Type	ASTM D5453	MESA-6000
Gasoline	39.2	35
Diesel	7.3	8.8
Kerosene	226	231
E85	6.4	5.0
RFG	33.1	34
Jet A	437	437
ULSD	7.97	8.0
Transformer Oil	38	35
B100	1.5	2.2
Sample Type	**ASTM D2494**	**MESA-6000**
Crude Sweet *	3600	3603
Crude Sour*	1.03%	1.23%

Table 2: ASTM D-5453 and ASTM D-4294 to MESA-6000

Case Study: Sulphur in Automotive and Transportation Fluids

Five laboratories participated in a modified round robin ruggedness study. The MESA-6000 instruments utilised were all calibrated in the 0-50 mg/kg sulphur in mineral oil and 50-1000 mg/Kg sulphur in mineral oil calibration ranges.

All lab sites measured the sulphur content, in 11 various petroleum products. Each days result was derived from the average of two consecutive 180 second analyses of 5 ml of sample in the same sample analysis cup. The day one and day two results were then averaged to yield a final result for each sample from all five labs. The test was designed to permit evaluation of between instrument agreement and short term calibration stability. The results are displayed in Table 3 below.

Sample Typre	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
Diesel Low S	5	6	6	6	6
B- 11 (Diesel)	9	10	8	8	12
Gasoline E10	35	35	35	36	37
Diesel Low S	3	4	3	3	5
B20 (Diesel)	5	7	6	6	9
Transformer Oil	34	33	32	31	34
Kersosene	234	233	236	237	240
Jet A	446	441	440	435	449
HFO	941	938	936	921	953
Jet B5	433	429	429	425	437
Hydraulic Fluid	508	508	500	498	510

Table 3: Results of Automotive and Transportation Fluids

Case Study: Chlorine recovery in the presence of high Sulphur in Crude Oil

Seven mineral oil samples were analysed in the laboratory for simultaneous determination of low chlorine and sulphur. These samples contained 50ppm chlorine and varying values of sulphur 0ppm – 1.5wt%. High levels of sulphur will have an adverse effect on the ability to accurately measure

chlorine on typical EDXRF systems. This is due to the fact that as sulphur levels increase the kb emission line for sulphur will interfere with the chlorine emission, resulting in higher chlorine numbers. The data shows that above 2000 ppm sulphur, the integrated area for chlorine will start to include the shouldering peak from the high sulphur. A spectral representation of this interference is depicted in figure 4.

Figure 4: Sulphur and Chlorine Spectra
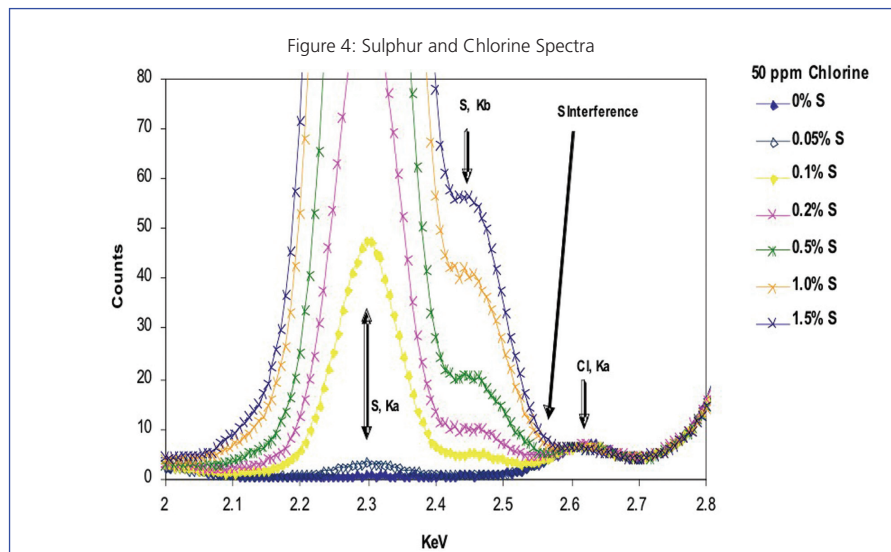
The samples were analysed on two calibration curves. Curve A was a chlorine only calibration curve, 0-100ppm chlorine in mineral oil. Curve B was a chlorine (0-100ppm) and sulphur (0.1 – 2wt%) calibration curve in mineral oil. Curve A displays chlorine data and the effects from sulphur interference, Curve B demonstrates how the results for chlorine were automatically corrected by software for the increasing sulphur concentrations. The results are displayed in Table 4.

The MESA-6000 clearly demonstrates its ability to not only correct for the presence of sulphur, but

Sample ID		Curve A No S Correction		Curve B S Correction	
		Cl, ppm	S, wt%	Cl, ppm	S, wt%
0 Cl	0S	0.0	NA	0.0	*0.0
50Cl	0S	50.7	NA	50.0	*0.0
50Cl	0.005%S	49.7	NA	49.9	*0.004
50Cl	0.099%S	49.0	NA	48.2	0.098
50Cl	0.21%S	49.9	NA	49.3	0.21
50Cl	0.50%S	55.0	NA	49.8	0.49
50Cl	1.00%S	62.1	NA	49.5	1.01
50Cl	1.43%S	62.5	NA	49.8	1.43

Table 4: Analytical results for Sulphur and Chlorine (* Sulphur values reported outside the calibration range)

to simultaneously measure sulphur and chlorine accurately.

The following data depicted in table 5 below are typical gas oil samples analysed on the MESA-6000.

Sample ID	Cl, ppm	S, wt%
Gas Oil #1	4.6	3.10
Gas Oil #2	4.1	2.97
Gas Oil #3	3.8	3.2
Gas Oil #4	10.4	1.2

Table 5: Analytical results for Sulphur and Chlorine in Gas Oil

Conclusion

Innovative diffractive optics coupled with the simplicity of EDXRF technology define the MESA-6000 as an extremely simple instrument to operate for multiple element analysis in a wide variety of samples. The instrument's versatility and flexibility make the MESA-6000 the instrument of choice in the petroleum and fuel industry.