HORIBA Scientific

Application Note

Petrochemistry

X-Ray Fluorescence

MESA 40

Fast and Accurate Simultaneous Determination of Sulfur 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 Sulfur 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 characterize crude oil and controlling contaminations in the refining process to ensuring regulatory compliance of finished products. Consequently, the determination of sulfur 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 polarized mono-chromatic X-ray beam technology.

Background

Energy Dispersive X-Ray Fluorescence (EDXRF) is a well established technique and is widely utilized 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 sulfur 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) analyzer that can readily measure sulfur 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. A powerful onboard computer allows a full lineup 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 depowers 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 sulfur content from weight percent down to part per million levels.

MESA-6000

The NEW Technology

The MESA-6000 is based on the latest advances in Energy Dispersive X-ray Fluorescence (EDXRF) technology. It utilizes a proprietary X-ray optical technology that produces a **Polarized, 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 sulfur 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 minimized. The MESA-6000 performance is well established, as it is compliant with ASTM and ISO International Sulfur Determination Norms:

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

Principle

The MESA-6000 features a unique, patented design with a close-coupled, doubly curved HOPG X-ray optic. It simultaneously polarizes, focuses, and mono-chromates the X-ray beam.
This yields the ideal X-ray source for measuring chlorine, sulfur and lower atomic number elements at low concentrations. This technique creates an environment with ultra-low background similar to other optics-based X-ray analyzers, but retains the EDXRF benefit of allowing for simultaneous analysis of multiple elements.

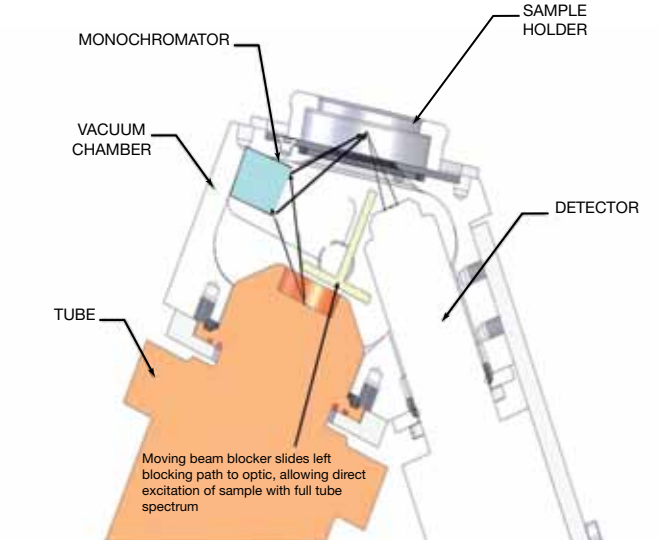

Figure 1: MESA-6000 principle
Polarized Mono-chromatic EDXRF

Calibration and Linearity

Figure 2a depicts the typical near perfect calibration linearity exhibited by the MESA-6000.
The sulfur in mineral oil range of concentration standards used is - 0, 50, 100, 250, 500, 750 and 1000 mg/kg sulfur.

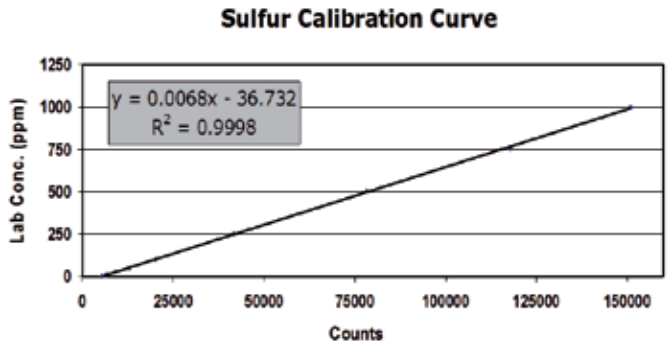

Figure 2a: Sulfur Calibration Curve

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.

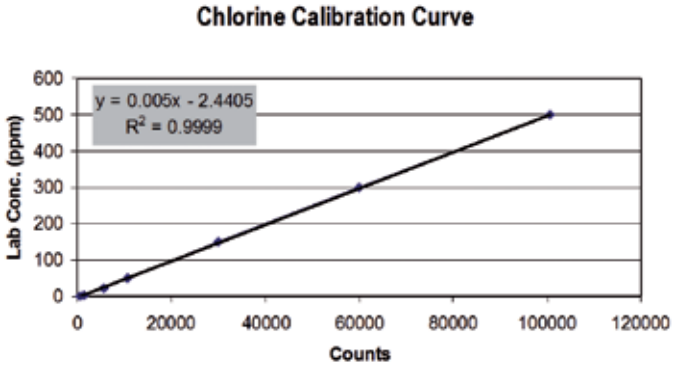

Figure 2b: Typical Chlorine Calibration Curve

Precision and Estimation of Level of Detection

To determine precision, an 11mg/kg sulfur 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.

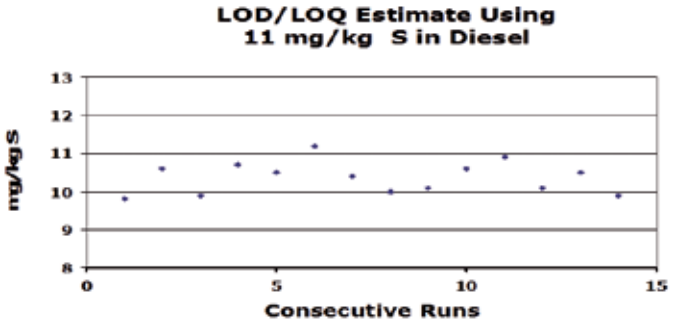

Figure 3a: Sulfur Precision Data

The repeatability data was then analyzed 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 analyzed and that detection limits are likely to be lower than indicated here.

MESA-6000 Sulfur	
STDEV	0.42 mg/kg
LOD	**1.25 mg/kg**
MDL, 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 3b.

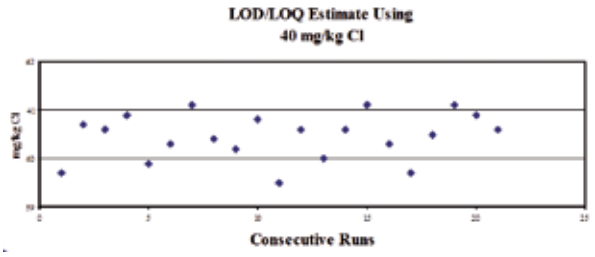

Figure 3b: Chlorine Precision Data

Using the same modified EPA method, described above, the chlorine repeatability data was analyzed 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 analyzed and that detection limits are likely to be lower than indicated.

MESA-6000 Chlorine	
STDEV	0.48 mg/kg
LOD	**1.44 mg/kg**
MDL, 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 sulfur 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 analyzer Method ASTM D-5453
- Energy Dispersive X-Ray Fluorescence Method ASTM D-4294

Following instrument calibration with sulfur in mineral oil standards, 11 samples were analyzed. 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 D4294	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: Sulfur in Automotive and Transportation Fluids

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

All lab sites measured the sulfur 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 Type	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
B-20 (Diesel)	5	7	6	6	9
Transformer Oil	34	33	32	31	34
Kerosene	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 Sulfur in Crude Oil

Seven mineral oil samples were analyzed in the laboratory for simultaneous determination of low chlorine and sulfur. These samples contained 50ppm chlorine and varying values of sulfur 0ppm – 1.5wt%. High levels of sulfur will have an adverse effect on the ability to accurately measure chlorine on typical EDXRF systems. This is due to the fact that as sulfur levels increase the kb emission line for sulfur will interfere with the chlorine emission, resulting in higher chlorine numbers. The data shows that above 2000 ppm sulfur, the integrated area for chlorine will start to include the shouldering peak from the high sulfur. A spectral representation of this interference is depicted in figure 4.

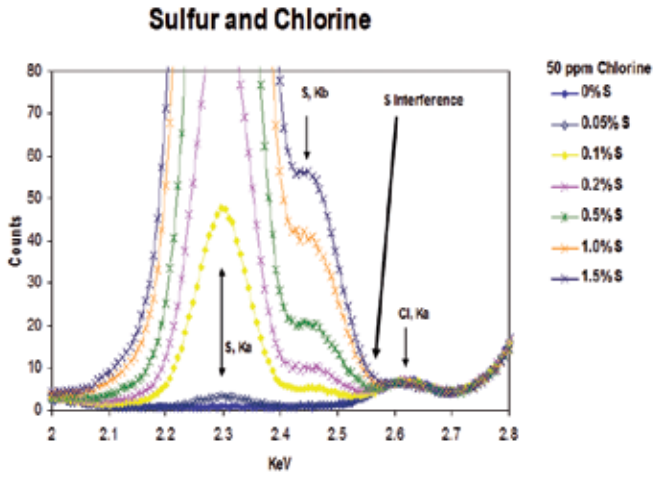

Figure 4: Sulfur and Chlorine Spectra

The samples were analyzed 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 sulfur (0.1 – 2wt%) calibration curve in mineral oil. Curve A displays chlorine data and the effects from sulfur interference. Curve B demonstrates how the results for chlorine were automatically corrected by software for the increasing sulfur concentrations. The results are displayed in Table 4 below.

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
50 Cl 0S	50.7	NA	50.0	*0.0
50 Cl 0.005% S	49.7	NA	49.9	*0.004
50 Cl 0.099% S	49.0	NA	48.2	0.098
50 Cl 0.21% S	49.9	NA	49.3	0.21
50 Cl 0.50% S	55.0	NA	49.8	0.49
50 Cl 1.00% S	62.1	NA	49.5	1.01
50 Cl 1.43% S	62.5	NA	49.8	1.43

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

The MESA-6000 clearly demonstrates its ability to not only correct for the presence of sulfur, but to simultaneously measure Sulfur and Chlorine accurately.

The following data depicted in table 5 below are typical gas oil samples analyzed 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 Sulfur 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.

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