Automotive and Transportation Fuels

With federal and international regulations becoming increasingly stringent, the need to determine the sulfur content as a part of the characterization of petroleum oils and fuels is a critical component. In crude oil, sulfur can be present in concentrations up to 5% by weight. The petroleum products distilled from these crude oils will, therefore, contain varying concentrations of sulfur from wt. % levels in lubricating oils down to trace ppm levels in automotive fuels. Hazardous air pollution caused by sulfur oxides and the harmful effects of sulfur on machine engines are driving forces behind these regulations. It is essential that sulfur concentrations be closely monitored and controlled in all petroleum products.

Introduction

Energy Dispersive X-Ray Fluorescence (EDXRF) is a well established technique for the analysis of sulfur in petroleum products. The analysis methodologies are regulated through international standards such as ASTM 4294, ASTM 7220, and prEN ISO 13032. To meet these tough requirements for the measurement of sulfur in automotive fuels and other petroleum products, Innov-X Systems has developed the MESA 6000. This report will demonstrate the analytical performance of the MESA 6000 for the determination of sulfur in these products.

Instrumentation

The MESA 6000 is a compact (330mmW x 508mmD x 41mmH) and lightweight (21kg) analyzer that can readily measure sulfur content in petroleum products to part per million levels, in just 180 seconds. The optical path is under vacuum – no helium or nitrogen purges are required.

The instrumentation requires only a reliable electrical power source (100/250 VAC), no other utilities are required for the non-destructive and non-combustion mono-chromatic EDXRF technique.

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

Sample preparation and handling are simplified by the use of Mylar® film sealed disposable plastic cups. This allows the instrument to be used by laboratory trained technicians, rather than scientists.

MESA 6000

A powerful onboard computer enables 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. The optimum X-Ray tube operating status is also ensured by an integrated, self -

testing scheme that is initiated each time the instrument is started.

When desired, users can simultaneously measure chlorine and sulfur content from weight percent down to part per million levels with the MESA 6000.

Calibration and Linearity

Figure 1 depicts the typical near perfect linearity exhibited by the MESA 6000. The sulfur in mineral oil range of concentration standards used - 0, 50, 100, 250, 500, 750 and 1000 ppm S.

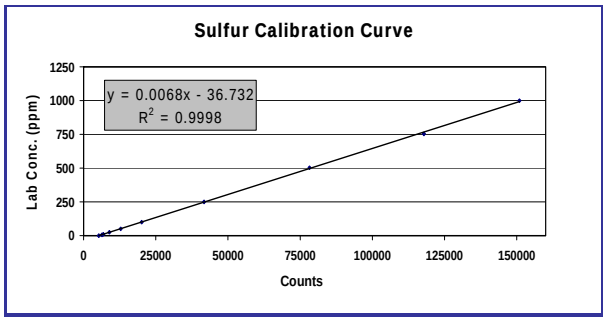

Figure 1:
Sulfur Calibration Curve

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

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 sec analyses of 5mls of the diesel run consecutively 14 times. This data is illustrated in Figure 2.

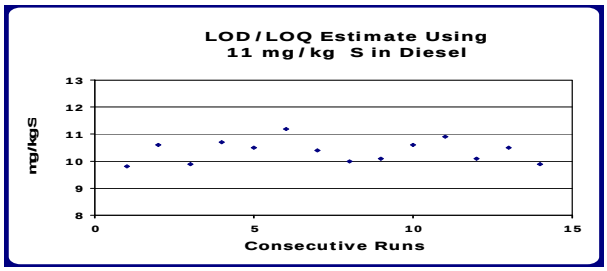

Figure 2:
Precision Data

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 1. 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 those indicated here.

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

Table 1:
Limit of Detection

Equivalency

In order to determine how the MESA 6000 performance might compare to established sulfur measurement technologies; a set of calibration standards and sample sets were prepared and measured by the following two technologies:

- Polarized, mono-chromatic energy dispersive X-Ray fluorescence instrumentation (EDXRF) MESA 6000
- Combustion ultra-violet fluoresence instrumentation D5453

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Following instrument calibration with sulfur in mineral oil standards, 11 samples were analyzed by both techniques. An analysis of this data demonstrates that the MESA 6000 and UV results were very comparable.

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
Crude Sweet	3600	3603
Crude Sour	1.03%	1.23%

Table 2:
Comparison D5453 to MESA 6000

Case Study of Sulfur in Automotive and Transportation Fluids

Five instruments were utilized and all demonstrated excellent linearity throughout the 0-50 mg/kg S in mineral oil and 50-1000 mg/Kg S in mineral oil calibration ranges.

Five sites measured the sulfur content in various automotive and transportation fuel samples. Each days result was derived from the average of two consecutive 180 second analyses of 5 mLs 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 instruments. The final averaged results are illustrated in Figure 3. The test demonstrated excellent instrument-to-instrument reproducibility and good short term calibration stability.

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
B20 (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

Conclusion

The final results from the sulfur case study clearly demonstrate that the MESA 6000 exceeds the existing international standards for sulfur analysis by EDXRF. The MESA 6000 by virtue of the Olympus/Innov-X NDT diffractive optics technology, can analyze very low concentrations of sulfur to meet the stringent requirements.

The instrument's flexibility for other analytical measurements, such as chlorine, along with its ease of use makes the MESA 6000 the instrument of choice in the petroleum and fuels industry.

For more information on **MESA 6000**, please visit: www.horiba.com/us/oil.

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