



Monochromatic EDXRF Analysis of Home Heating and Stationary Source Fuels

After over a decade of vigorous transportation fuel sulfur reduction regulations, government mandates for reducing the sulfur (S) content in home heating oils are being enacted worldwide. Of vital importance to producers and distributors of this new category of low sulfur distillate; is a fast, easy-to-operate and reliable method for determining less than 15 mg/kg sulfur.

Introduction

In the U.S., EPA-based haze reduction state implementation plans or (SIP)s have led to new sulfur regulatory standards for home heating oil (HHO) and other stationary source fuels. These new state laws require, interim fuels with less than 500 part per million (mg/kg) and then ultimately a less than 15 mg/kg sulfur (S) content. Primarily impacted, for now, is the U.S. northeastern region. However, these new fuel regulations have already created a new ultra low sulfur heating oil commodity class that must be stored and distributed in a marketplace that still provides more traditional HHO that has much higher (>500 mg/kg) S content.

Also, some countries (Canada) and individual states (Connecticut) require that biodiesel (derived from vegetable oils and animal fats) be included in the content of these types of fuel. Accordingly, suppliers of HHO have been compelled to drastically reduce S levels and install downstream biodiesel blending capability.

This application note details the performance of the HORIBA MESA-7220 energy dispersive X-ray fluorescence (EDXRF) analyzer.

Sample Preparation

Shake the room temperature sample gently and allow any entrained air (bubbles) to dissipate. To ensure consistent sample depth of at least 5 mm, transfer a 5 mL aliquot to an X-ray sample cup. Mylar film (2-6 um) is typically used to provide the sample cup seal. Carefully avoid contamination of the X-ray cup film testing surface and when analyzing very low (< 15 mg/kg S) start the sulfur analysis immediately after sealing the sample cup. Provide a small X-ray cup vent hole whenever volatile sample materials are analyzed.

ASTM and International Normatives

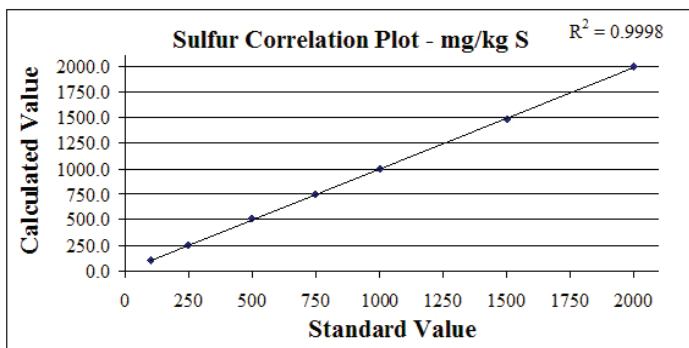
The HORIBA MESA-7220 monochromatic EDXRF analyzer complies with all major international standard test methods for the determination of sulfur in home heating fuels and ultra low sulfur distillate / biodiesel blends using EDXRF based technology.

Standard Test Method	Sulfur Range
ASTM D7220	3 - 950 mg/kg
ASTM 4294	16 mg/kg - 5 wt%
EN ISO 8754	300 mg/kg - 5 wt%

Calibration for Traditional High Sulfur HHO

Construct a calibration curve that will include (bracket) the range of sulfur to be measured. For traditional heating oil analysis, a 100 - 2000 mg/kg S calibration curve can be employed. The following is an empirical calibration that was built using seven certified calibration standards.

Element S	Units: mg/kg Correlation: 0.9998	
Sample ID	Standard Value	Calculated Value
1	100	106
2	250	255
3	500	515
4	750	747
5	1000	995
6	1500	1475
7	2000	1994



Precision and Accuracy (Traditional HHO)

The above calibration curve was used to establish HORIBA MESA-7220 repeatability and accuracy. Two traditional (HHO High) and one interim HHO and a NIST diesel standard reference material (SRM) were measured seven times and evaluated as shown in the table below. A single result is achieved by analyzing the sample directly (no sample preparation required) and is derived by the automatic (user controlled) reporting of the average of two consecutive 180 sec determinations. Analysis was then repeated with a new sample cup containing a fresh test specimen.

High Sulfur HHO and a NIST SRM Sample

Heating Oil Sample	Average Value mg/kg	Std. Deviation mg/kg	% Relative
NIST 2724b 426.5 mg/kg	430	6.3	1%
HHO Interim	348	7.5	2%
HHO High	949	6.6	1%
HHO High	1812	17.0	1%

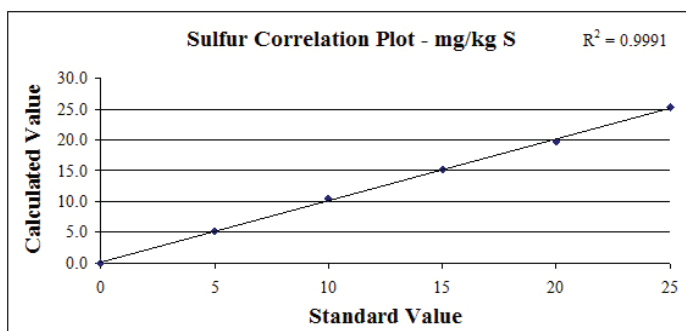
Calibration for Ultra Low Sulfur HHO

As described above, construct a calibration curve that will include (bracket) the range of sulfur to be measured. For ultra low sulfur HHO analysis and quality control purposes, a 0 - 25 mg/kg calibration curve can be employed. The following is a calibration that was built using six certified standards.

Calibration Curve Information

Gravimetrically prepared: Sulfur source; N-dibutyl Sulfide. Matrix; Light mineral oil

Element S	Units: mg/kg Correlation: 0.9991	
Sample ID	Standard Value	Calculated Value
1	Zero (Blank)	0
2	5	5.2
3	10	10.5
4	15	15.1
5	20	19.7
6	25	25.4



Precision and Accuracy (Ultra Low Sulfur HHO)

By evaluating seven repeated analyses of each of the ultra low sulfur HHO, HHO / biodiesel blends and NIST - SRM samples, shown in the following table, MESA-7220 repeatability and accuracy can be demonstrated. Results are again derived by reporting the average of two consecutive 180 sec determinations.

Ultra Low Sulfur HHO and SRM Sample

Heating Oil Sample	Average Value mg/kg	Standard Deviation	% Relative
NIST 2723a 11.0 mg/kg S	10.7	0.88	8%
HHO Low	5.1	0.77	15%
ULSD / 2% Biodiesel (B-10)	12.1	0.80	7%
ULSD / 10% Biodiesel (B-10)	9.3	0.39	4%
ULSD / 20% Biodiesel (B-20)	6.3	0.54	9%

No Oxygen Interference

Biodiesel Fuels – Biodiesel formulations can be derived from a wide variety of renewable biomass

resources and can contain varying levels of oxygen that range from low (< 2 %) to more elevated (> 10 %) levels. Therefore, an HHO blended to contain 20% biodiesel that has 10% oxygen content could easily produce a final biodiesel blend containing 2% oxygen. The table below demonstrates the lack of oxygen interference with HORIBA MESA-7220 sulfur determination capability when oxygen is present at levels up to 5%. The lack of oxygen interference is demonstrated because all values meet ASTM D7220 repeatability requirements (agree within 2.1 mg/kg) at the 10 mg/kg sulfur concentration range.

D7220 Repeatability Requirement at 10 mg/kg equals 2.1 mg/kg		
Standard Value Sulfur mg/kg	Volume % oxygen added	Sulfur Determined
10.0	1%	10.2
10.0	2%	9.4
10.0	3%	10.8
10.0	4%	9.9
10.0	5%	9.6

Conclusion

Results shown in this application note indicate that the HORIBA MESA-7220 provides exceptional performance for the determination of sulfur in contemporary and future HHO, particularly in the less than 10 mg/kg S range.

An ability to analyze HHO/biodiesel blends with no need for special calibration is also demonstrated. The large sulfur operating range, conforms to ASTM testing methods. Easy sample preparation and instrument use, plus economical bench-top form factor provide additional value.



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