



### Monochromatic EDXRF Analysis of ULSD

Measuring and controlling sulfur concentrations has been and will remain important to the petroleum industry because sulfur contamination affects everything from crude oil prices to refinery operations to final product quality. A fast, easy-to-operate and reliable method of determining and monitoring sulfur concentrations throughout the petroleum industry is of vital importance.

#### Introduction

For years, various governmental regulations have limited the amount of allowable sulfur in all forms of transportation fuels. For example, #2 road or highway diesels have been limited to a maximum sulfur concentration of 10-15 mg/kg depending on country or region for over a decade. Presently this ULSD requirement is expanding to almost all non-road compression-ignition engine fuel applications including mobile sources found in farm, construction, marine and recreational use diesel engines. Additionally, stationary diesel engines, such as those used to generate electricity and operate compressors and pumps at power and manufacturing plants are also affected. The need to measure and control ultra-low sulfur contamination affects all segments of the petroleum industry downstream product distribution system.

This application note details performance for the determination of sulfur in ultra-low sulfur diesel (ULSD) using the HORIBA MESA-7220 energy dispersive X-ray fluorescence (EDXRF) analyzer.

#### Sample Preparation

Ensure each sample is stable and homogeneous. 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  $\mu\text{m}$ ) is typically used to provide the sample cup seal. Carefully avoid contamination of the X-ray cup film testing surface and start the sulfur analysis immediately after sealing the sample cup. Provide a small X-ray cup vent hole whenever reactive or volatile sample materials are analyzed.

Calibration: Construct a calibration curve that will include (bracket) the range of sulfur to be measured. For routine ULSD screening and quality

control purposes a 0 - 25 mg/kg calibration curve is often employed. Below an empirical calibration was built using six certified calibration standards.

#### ASTM and International Normatives

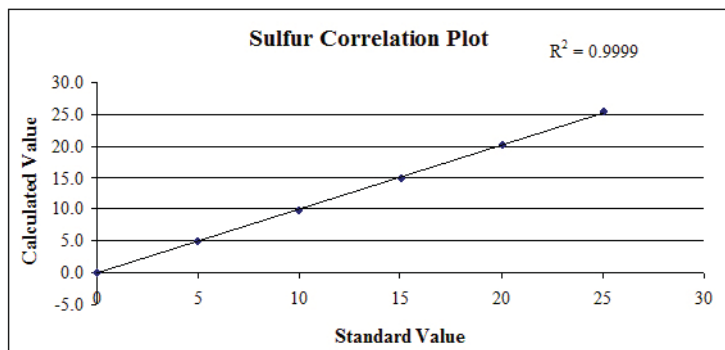
The HORIBA MESA-7220 monochromatic EDXRF analyzer complies with several international standard test methods for the determination of sulfur in petroleum oils, fuels and ULSD using EDXRF based technology.

| Standard Test Method | Sulfur Range      |
|----------------------|-------------------|
| ASTM D7220           | 3 - 950 mg/kg     |
| ASTM 4294            | 16 mg/kg - 5 wt%  |
| EN ISO 20847         | 30-500 mg/kg      |
| EN ISO 8754          | 300 mg/kg - 5 wt% |
| Pr EN ISO 13032      | 8mg - 50 mg/kg    |

#### Calibration

Construct a calibration curve that will include (bracket) the range of sulfur to be measured.

| Element   | Units: MG/kg<br>Correlation: 0.9999 |                  |
|-----------|-------------------------------------|------------------|
| S         | Standard Value                      | Calculated Value |
| Sample ID |                                     |                  |
| 1         | Zero (Blank)                        | 0                |
| 2         | 5                                   | 5.1              |
| 3         | 10                                  | 9.9              |
| 4         | 15                                  | 15               |
| 5         | 20                                  | 20.2             |
| 6         | 25                                  | 25.3             |



## Precision

The above calibration curve was used to establish MESA-7220 repeatability by evaluating 9 repeated analyses of each calibration check sample shown below. A single result is derived by the automatic (user controlled) reporting of the average of two consecutive 180 s determinations taken on the same test specimen placed in the analysis position. Analyses are then repeated with a new sample cup containing a fresh test specimen.

| ULSD Sample #                  | Assigned Value mg/kg | Avg. Value mg/kg | Std. Deviation | % Relative |
|--------------------------------|----------------------|------------------|----------------|------------|
| Certified Ref. Sample (Diesel) | 8                    | 7.9              | 0.5            | 6%         |
| NIST 2723a                     | 11                   | 10.6             | 0.5            | 5%         |
| Certified Ref. Sample (Diesel) | 4                    | 3.8              | 0.3            | 8%         |

## Unique One Analysis - Two Results Capability

| Sulfur and Chlorine Detection Limits: |           |               |
|---------------------------------------|-----------|---------------|
| Element                               | LOD mg/kg | Analysis Time |
| Sulfur                                | 0.53      | 180 s x 2     |
| Chlorine                              | 0.41      | 180 s x 2     |

## Discussion

Sample handling, sample preparation and measurement protocols are very important for the analysis of ULSD and low (< 10 mg/kg) levels of chlorine. Calibrations for sulfur only, chlorine only and simultaneous sulfur and chlorine determinations

can be readily constructed and maintained by the user. Simultaneously measurement of chlorine and sulfur content from weight percent down to part per million levels with the MESA-7220.

## ULSD Biodiesel Blend Capability

Biodiesel Fuels – Biodiesel fatty acid methyl ester (FAME) formulations can be derived from a wide variety of renewable resources and can contain varying levels of oxygen. Therefore, oxygen contents in biodiesel can range widely from very low (< 1 %) to more elevated 10 % levels. This means that a B-20 diesel fuel (20 % biodiesel in regular petroleum diesel) could contain 2 or 3 % oxygen. The table below demonstrates no oxygen interference with MESA-7220 sulfur determination capability when oxygen is present at levels up to 5% as ASTM D7220 repeatability requirements are easily met.

| D7220 Repeatability Requirement at 10 mg/kg Sulfur = 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 here in this application note indicate that the HORIBA MESA-7220 provides exceptional performance for the determination of sulfur in ULSD and diesel/biodiesel blends in the 10-15 mg/kg commercial range as well as down to the very low mg/kg sulfur levels of control that are needed in refinery and distribution operations.

The wide range of material types, large sulfur concentration range and chlorine determination capabilities also makes the HORIBA-7220 an ideal tool for the measurement of many petroleum-based matrices, such as crude oils, lube oils and used/waste oils found throughout the petroleum industry.

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