

## ASOMA® PHOENIX II

### Analysis of Sulfur Content in Ethanol and Methanol Blends for Use as Automotive Spark Ignition Engine Fuel



#### Summary

The PHOENIX II XRF spectrometer provides a fast, precise, accurate and economic solution for the analysis of the sulfur content in ethanol and methanol blends.

#### Introduction

Recently, there have been major advancements in the development of biofuel diesel and gasoline.

The use of sugars and other plant materials to manufacture alcohols as 100% fuels or as extenders to produce bio-gasoline has been around and actively applied in countries like Brazil, and more recently Sweden, for many years. In other countries, regionalized programs were started to make bio-gasoline available. This has resulted in a large number of investments in bio-ethanol plant production.

Elemental analysis is required to control fuel quality and show compliance with actual specifications.

For ethanol and methanol fuel, ASTM, amongst others, has published specifications:

**ASTM D 5797**, "Standard Specification for Fuel Methanol (M70-M85) for Automotive Spark Ignition Engines," ASTM International

**ASTM D 5798**, "Standard Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark Ignition Engines," ASTM International.

**ASTM D 4806**, "Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark Ignition Engine Fuel," ASTM International.

Although energy dispersive X-ray Fluorescence spectrometry (EDXRF) is currently not listed as one of the standard test methods for the elemental analysis of biofuels, the technique can be used to monitor the elemental concentration limits in ethanol, methanol, and their blends when they are used as spark emission engine fuel. Test methods, which describe EDXRF for the analysis of sulfur content in petroleum products, include:

**ASTM D 4294**, "Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-Ray Fluorescence Spectrometry," ASTM International.



For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

## Instrumentation

### **PHOENIX II**

The samples were excited by a forced air cooled low power Pd end window X-ray tube combined with a curved HOPG crystal for polarization of the primary tube spectrum. A gas-filled proportional counter (prop counter) was used to collect the fluorescence radiation from the sample. All radiation paths were flushed with helium. The components are packaged in a compact benchtop design with a small footprint. All measurement parameters are controlled by the onboard computer using a touch screen user interface.

## Calibration Standards

To cover the full range of various products synthetic standards for ethanol, methanol and white mineral oil were created to cover a full range of the pure material and their blends. Commercially available standards may be used as well.

First a calibration for sulfur in white mineral oil was created. To study matrix effects from the oxygen content in ethanol/methanol, calibrations for these materials were repeated with a reduced number of standard samples.

## Sample Preparation

Five ml of each oil standard were poured into a 24 mm inner diameter liquid cell, assembled using a 4µm polypropylene supporting foil. This type of cup was equipped with a second polypropylene foil as a safety window. For blends with a higher gasoline content (>50 %) a polycarbonate film might be suitable as the gasoline will attack the polypropylene film.

## Measurement

All measurements were performed using the following conditions:

- || Polarized indirect excitation
- || Tube settings: 20 kV, 1950 µA
- || Prop Counter detection system
- || He flush
- || 300 s measuring time
- || K-Lines of S

Units: 1mg/kg = 1 ppm

The Limit of Detection (LOD) for an element is determined as three times the standard deviation of ten analyses of the blank sample containing no sulfur.

The achievable LOD is listed in the following table, derived using this empirical method based on mineral oil. Comparable detection limits are achievable for ethanol and methanol matrices.

### **LOD for Sulfur in Mineral Oil**

| Element | LOD       |
|---------|-----------|
| S       | 1.5 mg/kg |

## Calibration Techniques

Calibration was performed by measuring assayed calibration standards with known concentrations. Intercept, slope and curvature were determined by the least square fit based on Given Assay vs. X-ray Intensity.

Because of the matrix influence from the different C-H-O ratios in the samples, the measured intensities vary when different matrices are analyzed, such as E85, E15, M85, etc.

The effects from the different matrices can be corrected with three different approaches:

### **Approach 1: Matrix-matched Calibration**

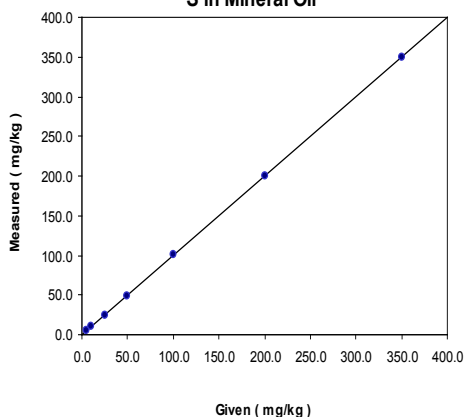
Setting up calibration curves for each type of sample with matrix matching calibration standards.

The following shows an example of an empirical calibration for sulfur in mineral oil. Comparable results are achieved calibrating for sulfur in pure ethanol or pure methanol, or for separate matrix-matched using E85, E15 or M85.

**Calibration for S in Mineral Oil**

| <b>Element: S</b>                                       |       |          |
|---|-------|----------|
| <b>Units: mg/kg     Std. Error of Estimate: 0.32176</b> |       |          |
| Sample  | Given | Measured |
| 1   | 5.0   | 5.3      |
| 2   | 10.0  | 9.8      |
| 3   | 25.0  | 25.2     |
| 4   | 50.0  | 49.5     |
| 5   | 100.0 | 100.2    |
| 6   | 200.2 | 200.2    |
| 7   | 350.3 | 350.3    |

**Correlation Plot  
S in Mineral Oil**



**Approach 2: User Corrections**

Calibration of one matrix using mineral oil, and employing User Corrections.

User Corrections are determined by calibrating using mineral oil (as per ASTM methods), then obtaining three known standards of the particular matrix (E15, E85, E100, M85, or M100) and analyzing them against the mineral oil calibration. Plot of the Given assay values for the particular matrix vs. the Measured values of the particular matrix analyzed against the mineral oil calibration. The slope of that plot is the Factor and the offset is the Term. The Factor and Term are then applied to the Measured value to give a Corrected value.

The Factor and Term to use for each matrix are dependent on detector response and must be determined for each individual XRF system.

The table below shows examples of User Corrections:

| Matrix  | Given (mg/kg) | Measured (mg/kg) | Factor    | Term    | Corrected (mg/kg) |
|---------|---------------|------------------|-----------|---------|-------------------|
| (mg/kg) | Factor        | Term             | Corrected | 2.3515  | 51.7              |
| (mg/kg) | 100           | 74.7             | 1.2758    | 2.3515  | 97.7              |
| E100    | 225           | 175              | 1.2758    | 2.3515  | 225.6             |
| E85     | 50            | 42.9             | 1.3194    | -6.8294 | 49.8              |
| E85     | 100           | 81.2             | 1.3194    | -6.8294 | 100.3             |
| E85     | 250           | 194.6            | 1.3194    | -6.8294 | 249.9             |
| E15     | 50            | 86.6             | 1.1555    | -50.283 | 49.8              |
| E15     | 100           | 130.3            | 1.1555    | -50.283 | 100.3             |
| E15     | 250           | 259.8            | 1.1555    | -50.283 | 250.0             |
| M100    | 50            | 38.8             | 1.3987    | -2.2895 | 52.0              |
| M100    | 100           | 71.3             | 1.3987    | -2.2895 | 97.4              |
| M100    | 250           | 180.8            | 1.3987    | -2.2895 | 250.6             |
| M85     | 50            | 47.8             | 1.4620    | -21.488 | 48.4              |
| M85     | 100           | 84.6             | 1.4620    | -21.488 | 102.2             |
| M85     | 250           | 185.3            | 1.4620    | -21.488 | 249.4             |

## Approach 3: Correction Factor

Calibration of one matrix using mineral oil and correcting the analysis results with a factor depending on the Ethanol or Methanol material or blend.

The following correction factors for typical base material and blends were determined, based on analysis against a mineral oil calibration. These factors were derived as an average across the concentration range 50-250 mg/kg. This method may not be as accurate as the User Correction method.

### **Correction factors for ethanol, methanol and blends for the analysis of sulfur**

| Matrix            | Correction Factor |
|-------------------|-------------------|
| Mineral white oil | 1.00              |
| Ethanol (E100)    | 1.31              |
| Ethanol (E85)     | 1.23              |
| Ethanol (E15)     | 0.77              |
| Methanol (M100)   | 1.36              |
| Methanol (M85)    | 1.19              |

## Conclusion

The high analytical performance of the PHOENIX II analyzer is demonstrated for the analysis of sulfur content in ethanol, methanol and their blends, which are used as fuel for spark ignition engines. Results are rapid, precise and analysis is easily carried out, even by non-laboratory personnel. Because no consumable chemicals are used, the relative "cost of ownership" is much lower than other analytical techniques.



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