

## S4 EXPLORER: ASTM D2622 Analysis of Sulfur in Petroleum Products

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Fig. 1: Bruker AXS S4 EXPLORER WDS.

### Introduction

On October 1, 1993, the U.S. Environmental Protection Agency's Clean Air Act Amendment of 1990 took effect and required that all highway diesel fuels have a maximum sulfur concentration of 500 ppm by weight. Proposed amendments to this regulation could reduce the maximum sulfur concentration to 30 ppm or lower by 2009, and many European countries are also making rapid moves to reduce sulfur in fuels. The European Union's recently adopted "Auto Oil Package" sets a maximum of 350 ppm for sulfur in diesel fuel, with a reduction to 50 ppm by 2005. Some European countries provide tax incentives for low-sulfur diesel fuel (<50 ppm in the United Kingdom and Finland, <10 ppm in Sweden).

The standard method by which the EPA regulates the maximum sulfur concentration is based on the ASTM D2622 designation [1]. This designation outlines the standard test method for determining sulfur in petroleum products using a wavelength-dispersive X-ray spectrometer (WDS) as the recommended analytical instrument.

Until now, appropriate WDS systems for this test were limited to either high-cost, high-performance systems with 3 - 4 kW X-ray generators or low-cost, low-performance systems with 0.2 - 0.4 kW sources. Here we present a low-cost, high-performance WDS system with an optimal configuration for the analysis of petroleum products. The level of precision and lower limit of detection (LLD) of sulfur in diesel fuels is also discussed.

### Instrument Configuration

The S4 EXPLORER (Fig. 1) is an ideal solution for analyzing petroleum products. This system is capable of matching the analytical performance of a high-power system, at a fraction of the cost, and includes some unique features that make it better suited than most high-power systems for analyzing petroleum products. The S4 EXPLORER is a compact unit with very small footprint and is mounted on casters. Thus, the instrument requires only a small niche in the lab and can be easily rolled out for better access whenever service is required. The cost of operating the S4 EXPLORER has also been reduced; it does not require an external water supply, compressed air, or P10 gas for the detector. The only connections required by the S4 EXPLORER are an electrical power outlet and a helium gas supply for analyzing liquids.

The S4 EXPLORER uses a specially designed 1-kW ceramic X-ray tube with an ultra-thin 75- $\mu$ m beryllium end-window. This X-ray tube is positioned below the sample to optimize liquid sample presentation to the X-ray beam. A closely coupled optical path provides high intensities and low detection limits for all elements. The low operating power minimizes adverse effects of sample heating by the X-ray



Fig. 2: S4 EXPLORER automatic sample loader.

beam, i.e., degassing of the sample, deformation of the sample cell window, and evaporation. Automatic computer control of the X-ray generator provides maximum sensitivity for all elements.

The S4 EXPLORER has the same features found in expensive systems: a 10-position primary beam filter changer, up to 4 primary collimators, and up to 8 analyzer crystals. It uses two detectors mounted side-by-side in the vacuum chamber. One is a scintillation detector, which is used to measure the higher energy lines, and the other is a newly developed Pro4 sealed proportional detector for measuring the lower energy lines. This detector provides the same performance as a traditional gas-flow detector without its added expense.

Traditional liquid sample analysis requires the entire optical path in the X-ray spectrometer to be flushed with helium gas. Bruker AXS has developed a unique vacuum seal that utilizes a thin window between the spectrometer chamber and the sample chamber. This allows the spectrometer chamber to remain under vacuum at all times, and only the sample chamber needs to be flushed with helium when measuring liquids. This arrangement minimizes the time required to switch between the conventional vacuum and helium-flush modes of operation. The vacuum seal also provides a safety interlock between the sample and spectrometer chambers, preventing liquids from contaminating the optical path in the event of sample spills or cup leakage.

The Bruker AXS S4 EXPLORER features an automatic sample loader (Fig. 2) which is designed to handle a mix of liquid and solid samples with random access capabilities. Priority levels can be set for individual samples, thereby controlling the sample sequence during measurement. New samples can be added during a run and given a high priority (e.g. "next" sample) without interruption of the current analysis. Alternatively, an "immediate" mode is also available which allows the interruption of the current measurement (without loss of the data collected up to that point) so that rush samples can be analyzed immediately. These features allow a wide variety of samples to be handled routinely without any modifications to the system.

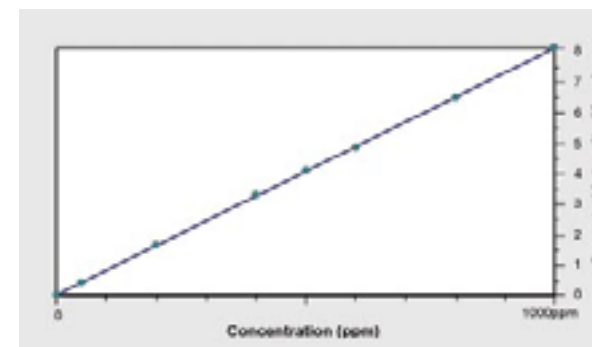


Fig. 3: Calibration curve for sulfur in 8 petroleum reference samples.

### Instrument Calibration

Ten liquid calibration standards with concentrations ranging from 0 to 1000 ppm sulfur by weight were obtained from a commercial laboratory [2]. These standards were prepared in accordance to ASTM method D2622 and are NIST traceable. Individual specimens were prepared by pouring the liquid samples into 40-mm diameter plastic cells fitted with 6- $\mu$ m polypropylene windows. Each cell was vented to prevent the polypropylene window from bulging during analysis. These liquid cells were then placed into sample holders with stainless steel masks with 28-mm diam. openings. The intensities at the peak and off-peak background angles were measured from the liquid samples using the S4 EXPLORER. A calibration curve (Fig. 3) was calculated from eight of the ten standards by multiple regression of the measured net intensities on the known concentrations of the standards. Two of the calibration standards (25 ppm and 100 ppm) were held back for use as test samples. The calibration data had a standard deviation of 4 ppm with a sensitivity of 82000 cps/% for sulfur. The Lower Limit of Detection (LLD) for sulfur in diesel fuel was calculated to be 0.5 ppm at a counting time of 100 s.

### Precision Test

A precision test for sulfur was performed on twenty individual samples prepared from the 25- and 100-ppm sulfur standards, which were not used to define the calibration curve. The results summarized in Table 1 show that the measured mean  $\pm$  std. dev. values were  $25 \pm 0.4$  and  $99 \pm 0.9$  ppm, respectively. The ASTM D2622 test method allows a range of 7 ppm sulfur for successive measurements with a 25-ppm sample, and a range of 4 ppm for a

100-ppm sample. The maximum sulfur ranges measured with the S4 EXPLORER were 2 and 4 ppm, respectively.

Table 1. Precision test ( $n = 20$ ) for measurement of sulfur standards with the S4 EXPLORER.

Sulfur Sample	25 ppm	100 ppm
Maximum value	26	102
Minimum value	24	98
Range of values	2	4
Average value	25	99
Abs. Std. Dev. ( $1\sigma$ )	0.4	0.9
Rel. Std. Dev. ( $1\sigma$ )	1.7%	0.9%

### Summary

The S4 EXPLORER easily met the EPA requirements for the accurate determination of sulfur in diesel fuels, and it is certainly capable of meeting the proposed future requirements of the EPA and European countries. The S4 EXPLORER is ideally suited for the wide range of process control applications in the petroleum industry.

### References

- [1] D2622 Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry, American Society for Testing and Materials, West Conshohocken, PA, (1999).
- [2] Analytical Services, Inc, Woodlands, Texas 77387, (409) 273-1780.