



## Set It and Forget it Long-term Stability of Sulphur Analysis by XRF

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Precision over time is a must-have in petrochemical analysis, and PANalytical's high-throughput wavelength dispersive X-ray fluorescence (XRF) spectrometry solution can deliver the certainty that the oil industry needs. Industry methods, such as ISO 20884:04 and ASTM D2622-08, are utilized to monitor sulphur in road fuels within strict limits. Importantly, these methods also set the standard for analytical repeatability and reproducibility. In this article, we take a look at the performance of PANalytical's Axios-Petro high-throughput XRF spectrometer for sulphur analysis – at the '20 consecutive measurement' specification set out in ISO and ASTM norms. New data, assessing precision out to 122 days is also presented.



Figure 1: PANalytical's Axios-Petro wavelength dispersive X-ray fluorescence spectrometer

While sulphur occurs naturally in crude oil, research has shown that its presence in finished road fuel products makes a major contribution to greenhouse gas emissions and smog formation. Sulphur dioxide and sulfate particulate emissions contribute directly to pollution load, but the main driver for reducing sulphur levels in road fuels is to maximise the CO<sub>2</sub> reduction capabilities of new engine technology, for fuel efficiency and emission control. The industry is now locked in to strictly regulated sulphur levels and oil refineries have come to rely on elemental analysis to ensure they remain within these tight confines.

To maintain optimum productivity, oil processors demand certainty from the analytical data upon which they base their operational decisions. Non compliance with industry standards can result in fines being applied downstream. XRF is recognised as a fast, relatively straightforward analytical technique that provides elemental and trace element analysis of catalysts, metals and hazardous ingredients in crude oil, oil derivatives and fuels throughout the refining process.

Axios-Petro (Figure 1) is a sequential wavelength dispersive XRF spectrometer configured specifically with integrated software packages – SuperQ and Oil-Trace – to meet the needs of the petrochemical industry. Oil-Trace exemplifies this by enabling analysis of sulphur in different blends of diesel-biodiesel with one calibration. The Axios-Petro is designed to perform all relevant XRF applications including, for example, the analysis of sulphur, catalysts and wear metals. Compact enough to be integrated into any laboratory setting, it has been designed to withstand the more demanding environment within a processing plant. The availability of specific standard sets and a performance testing program (see Box 1) complete the PANalytical solution for petrochemical analysis.

### BOX 1:

PANalytical's performance testing program enables independent, third party inter-laboratory analysis of performance and proficiency

This online service enhances the use of PANalytical's petrochemical standard sets for X-ray fluorescence (XRF). It provides users with the opportunity to check and verify their analysis data against certified reference material data. Simply entering analysis data gives immediate feedback on performance and proficiency.

Offering flexible and convenient integration into internal QC schemes, the performance testing program provides a robust, traceable verification process. Validation documentation can feed directly into QC accreditations such as ISO 17025:2003.

Available standard sets:

- Wear metal calibration set
- Lube oils
- Sulphur in diesel fuel
- Sulphur in oil
- Sulphur in iso-octane

### Analysis of sulphur in petroleum products

In the US, the EPA Tier 2 regulations (2002) set an upper limit of 150 mg/kg sulphur within road fuels while the EU Directive 98/70/EC requires a maximum level of 50 mg/kg from 2005 onwards (Emission Standard Euro IV). The EU limit will be further reduced this year (2009) by the introduction of Euro V, which will enforce a maximum of 10 mg/kg of sulphur in petroleum emissions.

International standard test methods for the analysis of sulphur in petroleum products include ASTM 2622, ISO 14596 and ISO 20884. While ASTM 2622 and ISO 20884 methods both employ mathematical matrix corrections, ISO 14596 employs a Zr internal ratio correction method. Of all three methods, it is the latest 2008 version of ASTM D2622 that demands the highest levels of repeatability and reproducibility.

In the following study, setup and calibrations following the ASTM D2622-08 standard methodology are used to analyze low-level sulphur in fuels.

### Simple sample prep – push-button analysis

Sample preparation is the key to precision analysis. For XRF spectroscopy, oil samples must first be loaded in liquid cells. Careful assembly of these liquid cells can eliminate a significant source of error in the final data (Figure 2).

To make this process reliable and to assist the operator, PANalytical includes a specific tool as part of the Axios-Petro package. To generate the data presented in this article, this simple but effective tool was used to prepare 38 mm diameter disposable cups constructed using Mylar film. Commercially available synthetic standard material (15 ml) was analysed. Placing the prepared samples on the Axios spectrometer in the priority position triggers the QuickStart setting, enabling virtually 'hands-free' analysis (Figure 3).

Both ISO 20884 and ASTM 2622 methods recommend the use of a Ge-111 analyzing crystal for the analysis of the sulphur K $\alpha$  line. By using a laterally curved Ge-111 crystal in place of the traditional flat version, significant improvements in sensitivity and resolution are achieved.

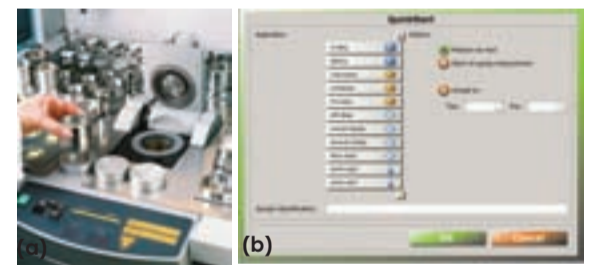


Figure 3: (a) Samples being placed onto the priority position of an Axios-Petro WDXRF spectrometer (b) Push-button XRF analysis from the Axios-Petro QuickStart screen

### Repeatability using ASTM criteria

The repeatability requirements of the ASTM D2622-08 test methods demand that not more than one in every twenty successive test results should exceed given limits. These limits are calculated using the following formulae for samples with less than 60 mg/kg sulphur:

- ASTM method =  $0.1462 \cdot \text{mean}(\text{mg/kg}) \cdot 0.8015$

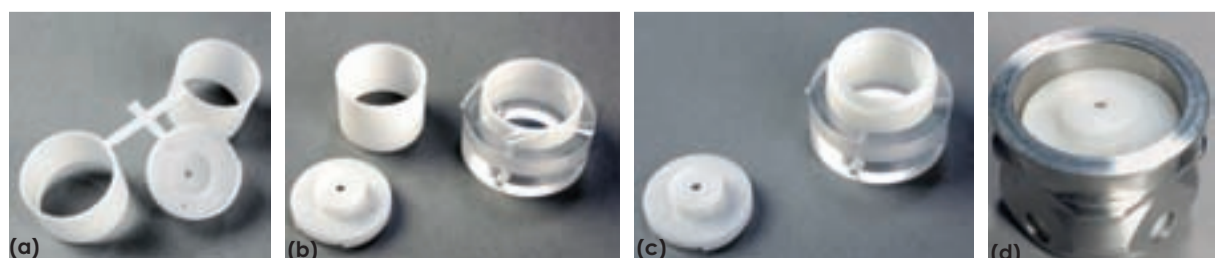


Figure 2: Simple and reproducible assembly of the liquid cells is made easy by the PANalytical tool supplied (pictures b and c)

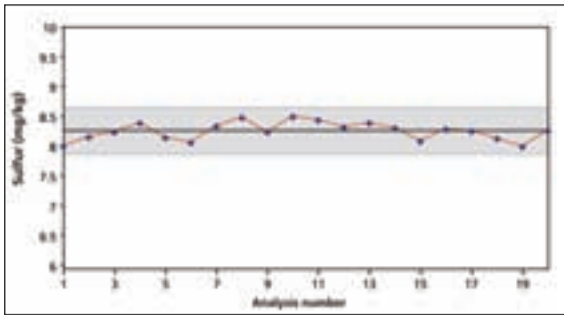


Figure 4: Repeatability of sulphur measurements in oil with respect to ASTM D2622-08 precision limits (shaded area)

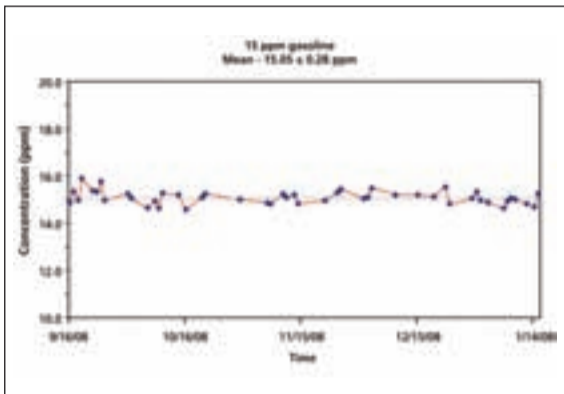


Figure 5: Repeatability of sulphur measurements in oil with respect to ASTM D2622-08

Matrix	20 Consecutive Measurements		4 Months Reproducibility	
	Mean	Stdev	Mean	Stdev
Biodiesel	5.08	0.2	5.03	0.2
Diesel	10.79	0.15	10.78	0.24
Gasoline	4.23	0.19	4.04	0.32

Figure 6: Comparison of 20 consecutive measurements and 122 days reproducibility

Data resulting from twenty consecutive measurements using Axios-Petro sit comfortably within the above criteria (Figure 4). All samples tested under ASTM method conditions contain 8.2 mg/kg of sulphur.

#### Long-term repeatability

The results of an extended study on gasoline are shown in Figure 5. Performance over 122 days is stable, well within the specifications of the ASTM method. Furthermore, comparing the 20 consecutive measurements and 122 days data (Figure 6), confirms that the system maintains performance over this extended period.

#### Conclusion

From the perspective of reproducibility, the Axios-Petro spectrometer provides exactly what oil refineries need. Compliance with short-term repeatability called for in the mandatory ASTM D2622-08 method is assured; and long-term data, reported here up to 122 days, is excellent. Importantly, working with PANalytical offers much more than just instrumentation. The company's package of relevant standards, a performance testing program and sample preparation expertise delivers a powerful solution that meets the needs of the industry today and into the future.