Analysis of Low-Level Sulfur in Petroleum Products in Accordance with ISO 20884:04 and ASTM D2622-10

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Sulfur occurs naturally in crude oil, in concentrations typically ranging from 0.5 – 5.0 wt%. However, research has shown that the presence of sulfur in road fuels, at just a few hundred mg/kg, makes automobile pollution a major contributor to greenhouse gas emission and smog formation. Exhaust emissions of sulfur as sulfur dioxide and sulfate particulates directly contribute to the pollution load. However, the main drive for reducing the sulfur level of fuel is to maximize the CO_2 reduction potential of new fuel-efficient engine technology and to improve the efficiency of emission control devices, such as catalytic converters, reducing emissions of NOx and particulates.

In the United States the EPA Tier 2 regulations (2002) set an upper limit of 150 mg/kg for the sulfur content of road fuels. However, in the European Union even more stringent regulations are being set. The EU Directive 98/70/EC requires that, from 2005 onwards, the sulfur level in road fuels does not exceed 50 mg/kg (Emission Standard Euro IV). This is to be followed by Euro V, which requires a reduction of sulfur in fuel to a maximum of 10 mg/kg in 2009.

X-ray fluorescence spectrometry is used extensively for the analysis of sulfur in petroleum products. Simple sample preparation, high accuracy and precision, and good to excellent detection limits (0.2 – 1 mg/kg) are the principal reasons for this choice, and make it an excellent technique for production control.

International Standard Test Methods

Both ASTM 2622 and ISO 20884 methods are broadly analogous, employing mathematical matrix corrections, and are distinct from ISO 14596, which employs a Zr internal ratio correction method.

The latest 2010 version of ASTM D2622 is the most stringent test method in terms of repeatability and reproducibility.

In this study we have set up and made separate calibrations in accordance with the methods stipulated in both ASTM D2622-10 and ISO 20884:04 norms.

Preparation of Standards and Samples

Commercially available synthetic standards, prepared according to the test methods, were used for this study NIST Diesel SRM 2723a was used as purchased. Fifteen milliliters (15 ml) of sample material (standard or routine) were poured into 38 mm diameter disposable liquid cells, constructed using Mylar X-ray film.

Axios^{mAX}-Petro

The Axios^{mAX}-Petro is especially configured to meet the needs of XRF analysis in the petrochemical industry – today and in the future.

Offering the highest levels of reliability in this demanding environment, the Axios^{mAX}-Petro is a sequential XRF system for all XRF applications, from sulfur through catalysts to wear metals. It is simple to operate, and the compact design is easily integrated into today's laboratories.

Precision and instrument stability

The precision and repeatability of the Axios^{mAX}-Petro is excellent. For comparison, the counting statistical error (CSE) calculated in mg/kg is also shown in Table 1.

	Sample 1	Sample 2	Sample 3
Test method	ISO 20884:04		ASTM D2622-10
Peak + bkg time (s)	30 + 14	30 + 14	80 + 40
Mylar Film (µm)	3.6	3.6	6
REPEATABILITY			
Mean	10.0	32.9	8.2
RMS	0.41	0.63	0.15
RMS (rel%)	4.10	1.90	1.78
Petroleum product	Diesel		Oil
COUNTING STATISTICAL ERROR			
CSE (mg/kg)	0.22	0.26	0.26
CSE (rel%)	2.20	0.80	5.65
STATISTICAL COMPARISON ACCORDING TO TEST METHOD			
This study	1.51	1.89	0.5
Norm repeatability requirements	1.95	2.52	0.8

Table 1. Analytical precision for sulfur analysis; repeatability of 20 consecutive measurements. Differences in the RMS and CSE values for the ISO and ASTM data in Table 1 can be attributed to different measurement times and different X-ray fi lm thickness.

For the ISO method, 20 consecutive measurements of a sample demonstrate standard deviations better than 2 % relative at the 33 mg/kg level, e.g. 32.9 ± 0.6 mg/kg S, and this includes the error associated with preparing twenty different liquid cells.

The repeatability requirements of both test methods require that successive test results should not exceed certain limits more than one case in twenty. For samples with less than 60 mg/kg sulfur these limits are according to the equations below:

- ISO 20884:04 =

  1.7 + (0.0248*mean(mg/kg))
- ASTM D2622-10 =

0.1462* mean(mg/kg)0.8015

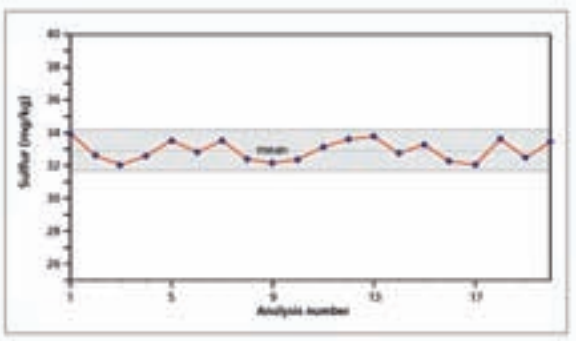


Figure 1. Repeatability of sulfur measurements in diesel according to ISO 20884:04. Shaded area represents the precision limits set in the method.

The repeatability of measurements for samples containing 33 mg/kg and 8.3 mg/kg sulfur, together with the repeatability limits for the ISO and ASTM methods are illustrated in Figures 1 and 2, respectively.

Sample preparation: The key to analytical precision

Assembly of the liquid cells is critical to the precision of the method. Without careful attention it can easily become a significant source of error in the analysis.
Therefore, a special assembling tool is included in the Axios^{mAX}-Petro package.

Repeated measurements on NIST diesel SRM 2723a for over 120 days have a maximum difference between two successive measurements of 0.5 mg/kg*.

The results demonstrate excellent longterm stability for the Axios^{mAX}-Petro.

Accuracy

The accuracy of the calibrations is illustrated in Figure 4. In this plot the calibration RMS value (0.23 mg/kg) is a statistical comparison (1 sigma) of the certified chemical concentrations of the standards with the

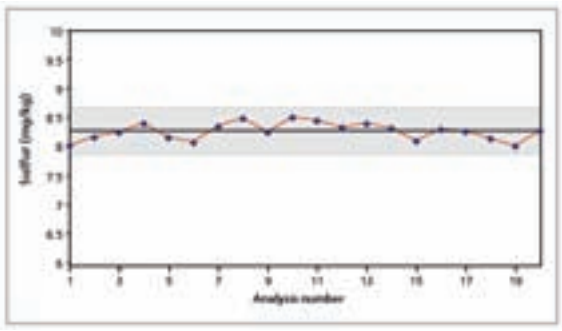


Figure 2. Repeatability of sulfur measurements in oil according to ASTM D2622-10. Shaded area represents the precision limits set in the method

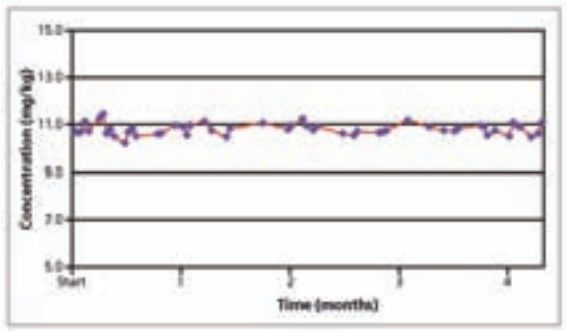


Figure 3. Repeatability measurements of sulfur in NIST diesel SRM 2723a for over 120 days.
**data obtained on Axios^{mAX}-Petro 4.0 kW*

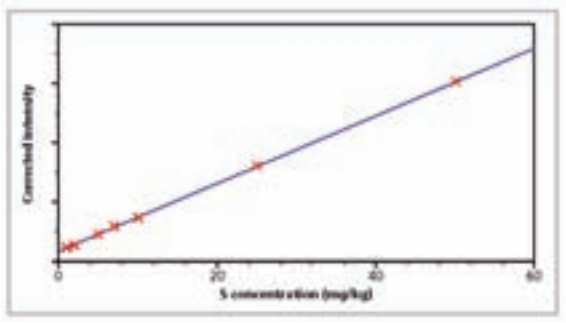


Figure 4. Calibration plot for sulfur in oil analyzed according to ASTM D2622-10

Table 2. Detection limits for sulfur in petroleum products

Detection limit (mg/kg)	ISO 20884 (Diesel, 3.6 µm Mylar)	ASTM 2622 (Oil, 6.0 µm Mylar)
LLD (application)	0.50	0.57
LLD (100 s)	0.19	0.26

concentrations calculated by regression in the calibration procedure.

Detection Limits

The detection limits for sulfur in diesel and oil are given in Table 2. Sub-mg/kg detection limits are possible for comparatively short measurement times and show that the analytical method is easily capable of satisfying the more stringent regulations governing sulfur in road fuels from 2009 and beyond.

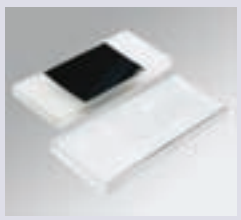
Summary and Conclusions

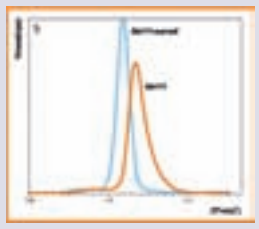
The analysis of sulfur in road fuels by XRF is a fast, relatively simple analytical technique. As demonstrated, the Axios^{mAX}-Petro is capable of accurate and precise analysis of sulfur in petroleum products, easily fulfi lling the requirements of the internationally certifi ed ISO and ASTM test methods.

Sub-mg/kg detection limits ensure that Axios^{mAX}-Petro will be able to meet the requirements of industry, even as more stringent government regulations come into force.

Curved Ge-111

ISO 20884 and ASTM 2622 require the use of a Ge-111 analyzing crystal for the analysis of the sulfur Kµ line. A laterally curved Ge-111 crystal is an option for Axios^{mAX}-Petro.
The benefits of curved crystal technology are significant improvements in sensitivity and resolution compared to traditional flat crystals.
These characteristics enhance the precision and detection capabilities of the instrument.





QuickStart

Samples placed on the Axios' priority position trigger QuickStart.

QuickStart can make routine analysis as simple as placing a sample on the spectrometer.

Advanced X-Ray Transmission (XRT) Gauge for Crude Oil, Marine Bunker Fuel and Blending Operations

Rigaku's (USA) NEX XT is the next generation process gauge for high-level sulphur measurement (0.02% to 6% S) of crude, bunker fuel, fuel oils, and other highly viscous hydrocarbons, including residuums. This versatile, compact and robust X-Ray Transmission (XRT) process gauge is specifically optimised for the sulphur analysis needs of refineries, pipelines, blending operations, bunkering terminals and other storage facilities. Applications include bunker fuel blending to meet MARPOL Annex VI sulphur restrictions, interface detection of different grade fuels delivered via pipelines, refinery feedstock blending and monitoring, and the quality monitoring of crude at remote collection and storage facilities. XRT can measure sulphur (S) from 200 ppm to 6 wt% at up to 1480 psig and 200°C and offers a data update every 30 seconds. This user-friendly system has reduced standards requirements, no routine maintenance, sample condition, recovery system or radioisotopes Among its other key features are a simplified user interface, automatic density compensation, automatic water compensation, password protection, and standard platform for communicating sulfur, density, and water content to a plant-wide DCS. Click the button to request more information on this new process gauge .

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Super X-ray Detector

The Super SDD is the newest X-ray detector technological advancement at **Amptek** (USA). The Super SDD is a 25 mm2 x 500 µm super silicon drift detector (SDD), with unsurpassed performance of 127 eV FWHM resolution; 11.2 µs peaking time; and a peak to background ratio of 8,000. The super silicon drift detector (SDD) enables extremely high count rate applications with excellent energy resolution. The detector is housed inside the same TO-8 package as Amptek's other detectors, so its form-factor is a direct replacement for current systems and is compatible with all Amptek accessories and options. The Super SDD's low price, high performance and small size make it the ideal detector for OEM hand-held applications to bench-top analysers. The X-ray detector, reamplifier, and cooler system is thermoelectrically cooled. Also mounted on the 2-stage cooler are the input FET and a novel feedback circuit. These components are kept at approximately -55 °C, and are monitored by an internal temperature sensor. The hermetic TO-8 package of the detector has a light tight, vacuum tight thin Beryllium window to enable soft X-ray detection. Amptek Inc. is a world leader in supplying low cost thermoelectrically cooled X-Ray Fluorescence (XRF) Detectors and Electronics for the OEM. The Super SDD, Si-PIN, and CdTe detectors, Preamplifiers and Digital Pulse Processors (DPP), are ideal for OEMs developing table-top or hand-held XRF analysers. Applications include RoHS/WEEE, Process Control and Alloy/Lead analysis. For their high reliability and performance, AMPTEK detectors were selected to perform XRF on the surface of Mars.

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New Breed of Handheld XRF Analysers

Innov-X Systems (USA) introduces their new family of handheld XRF analysers - the Delta Line. The result of Innov-X's extensive field portable instrumentation experience and innovation leadership, the Delta Line satisfies an urgent demand in the analytical industry. That is, a handheld XRF fully ruggedised to industrial standards - including no PDA or movable display - to withstand harsh environments while at the same time providing peerless analytical performance.

Innov-X founder and CEO Don Sackett remarked, "I am really proud of the accomplishments of our development teams. They've redesigned our analyzers from the ground up to create a true inspection tool that is both analytically superior and rugged enough for virtually any environment - no compromises. The Delta analysers feature the latest technology to optimize analysis throughput and uptime."

Exclusive to Innov-X's Delta line of analysers is their auto-calibrating, auto-charging docking station. With the unique, first of its kind Delta docking station, operators never have to power their analyser off -the station charges the analyser battery and a spare, and periodically performs a calibration check. Users can then remove the analyser anytime for immediate testing.

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