



## Bench-top WDXRF Sulphur Analyser for Ultra Low Sulphur Fuel

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Recent developments in ultra low sulphur diesel (ULSD) fuel has improved fuel efficiency and created cleaner exhaust gas. Refiners in USA are required to produce 80% of their annual output as ultra low sulphur diesel (ULSD) fuel oil, with a maximum of 15 ppm of sulphur from 2006. In addition, the regulations of ultra low sulphur fuel for the sulphur content are moving ahead in all other nations. The sulphur content in the regulations will be less than 10 ppm from 2007 in Japan and from 2009 in the EU, and so on.

Thus, there is a strong possibility that these regulations will become even more severe in the near future and it is forecasted that levels will be lowered to 5 ppm.

For compliance verification, X-ray fluorescence (XRF) spectrometry is the definitive analysis tool for use at distribution terminals, refineries, as well as mobile or stationary testing laboratories.

### Introduction to the equipment



Fig1. Rigaku/Mini-Z Sulphur Analyser

The Mini-Z Sulphur Analyser is the bench-top type, wavelength dispersive X-ray fluorescence analyser dedicated to sulphur analysis. To make the equipment operational, a standard AC power electric outlet and a helium gas container are the only requirements.

It differs from both the combustion ultraviolet fluorescence method and the oxidative microcoulometry method. The analyser can analyze infinitesimal amounts of sulphur, and measurements are not just limited to either organic or inorganic sulphur compounds. The total sulphur content in all sulphur compounds are detected during analysis.

Obtaining measurements does not require any special sample preparation for analysis - the sample oil is poured into the container which is then placed onto the turntable. The user then simply pushes the 'start' button and the measurement begins automatically. Also, stable measurements of highly volatile oils, such as gasoline, can be achieved with low power X-ray irradiation of samples with Mini-Z Sulphur Analyser compared to general purpose large XRF instruments.

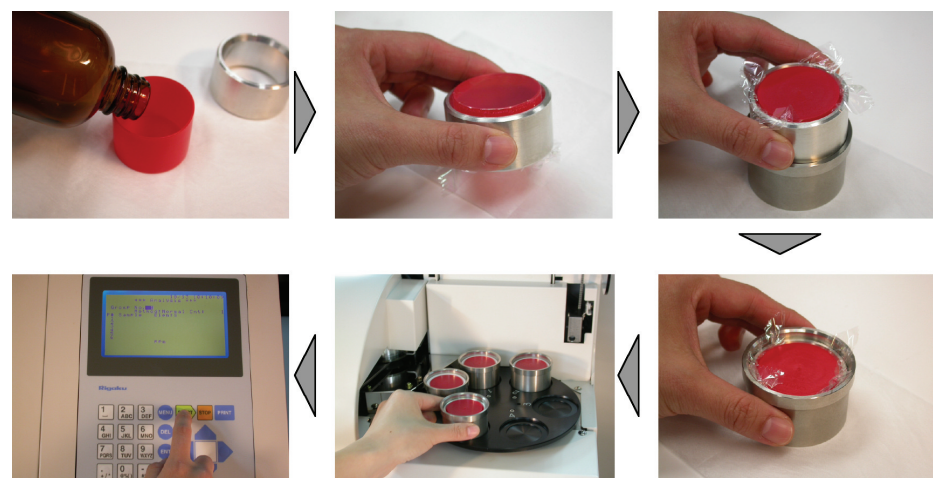


Fig. 2 Operation from the sample loading to starting measurement

### Features

The Mini-Z Sulphur Analyser is a spectrometer especially sensitive to sulphur. Despite having a relatively low X-ray power of 40 W, analysis from infinitesimal to high concentration levels can be performed with high degree of sensitivity and repeatability. The quantitative range is from 1 ppm to 4 mass% and it is possible to measure a wide range of oil samples.

Also, the special sensitive spectrometer for sulphur has a mechanism for measuring both S-K $\alpha$  peak intensity and the background intensity which complies to ASTM-D2622, ISO

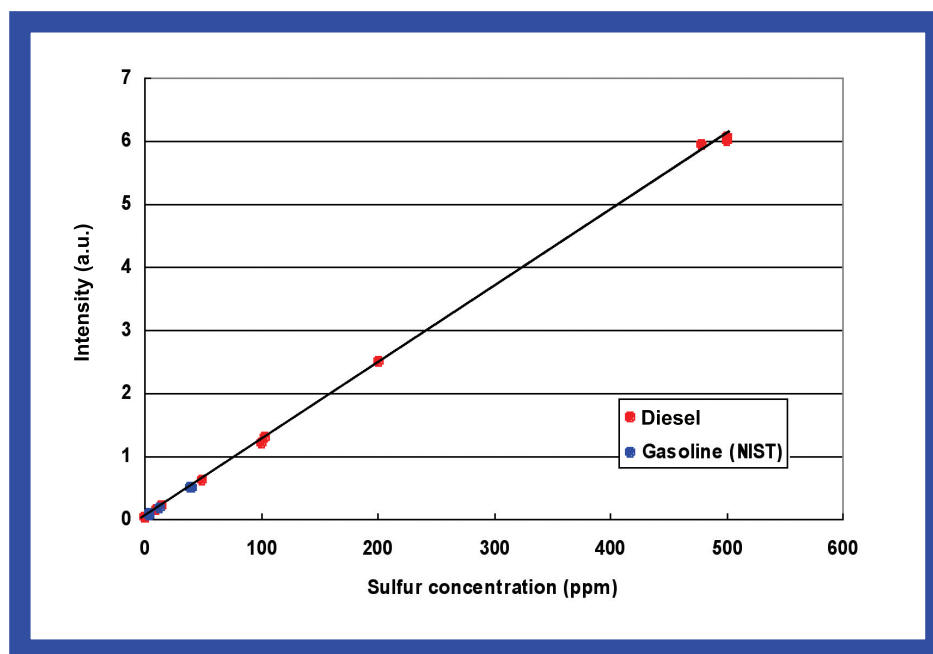


Fig 3. Calibration curve of gasoline and diesel

20884 and JIS K2541-7.

Since the background is low and the performance with signal to background ratio is excellent, a single calibration curve covers for the analysis of different kinds of oils.

### Precision data

Stability tests of short-term repeatability and long-term reproducibility for 20 days were carried out according to the ISO 20884 testing method.

Repeatability, demonstrated by successive measurements (Table 1), was shown to be  $\leq 0.25$  ppm irrespective of sampling technique. Illustrated in fig.4, results demonstrated better than 1 ppm precision for the 5 ppm standard at the 95 % confidence interval. Performance was shown to exceed ISO 20884 and ASTM D-2622 specifications and, thus, be ideal for ULSD validation measurements.

Table 1. Result of long-term reproducibility for ultra-low sulphur diesel standards

	Short-term Repeatability (1 $\sigma$ ppm)	Short-term Repeatability (1 $\sigma$ ppm)	Long-term Repeatability (1 $\sigma$ ppm)
Sulphur (ppm)	10 successive measurements (back-to-back)	10 successive measurements (resampled)	10 successive measurements (back-to-back) per day for 20 days
1	0.12	0.15	0.24
5	0.18	0.19	0.23
10	0.24	0.25	0.25
15	0.26	0.36	0.3
50	0.38	0.5	0.56
100	0.85	0.56	0.77
500	1.88	2.64	1.25

### Comparison with the related products

Rigaku spectrometer lineup has general purpose X-ray fluorescence spectrometers with the tube below optics which are suitable for oil analysis in addition to the Mini-Z Sulphur Analyser.

The typical spectrometers are the Primini, a bench-top system, and the large-sized, highly efficient general purpose machine ZSX Primus.

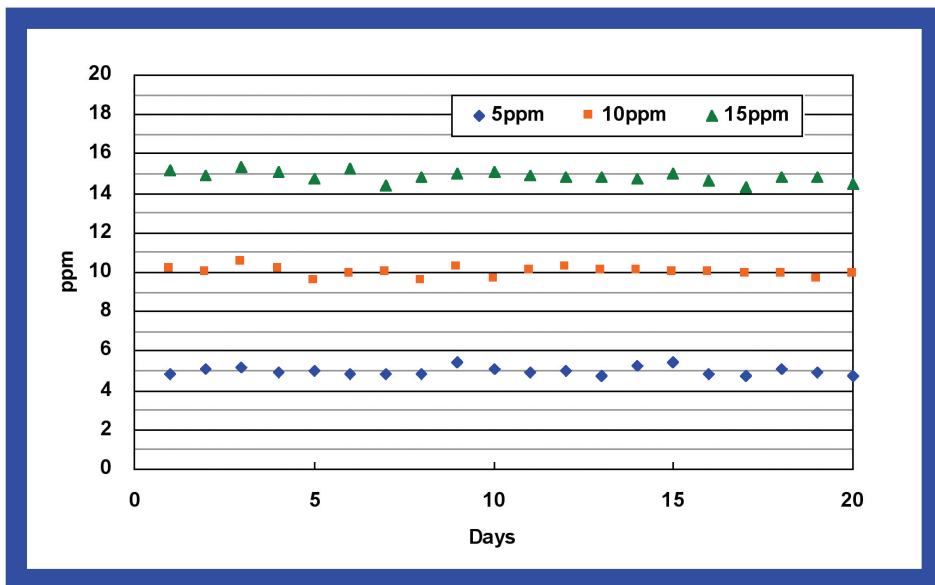


Fig.4. Plot of long-term reproducibility for 5 ppm, 10 ppm, and 15 ppm ultra-low sulphur diesel standards.

Table 2. Typical use and performance of X-ray analyser

	Mini-Z Sulphur Analyser	Primini (Sequential Type)	ZSX Primus (Sequential Type)
Analysis Element	$^{16}\text{S}$	$^9\text{F} - ^{92}\text{U}$	$^4\text{Be} - ^{92}\text{U}$
Sample	Fuel Oil	Fuel Oil, Catalyst	Fuel Oil, Catalyst
L.L.D.(Sulphur)	< 0.3 ppm	1.5 ppm	0.3 ppm
Power(X-Ray)	40 W	50 W	Max 4k W

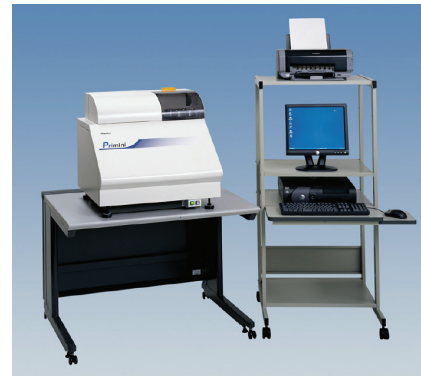


Fig.5 Rigaku/Primini

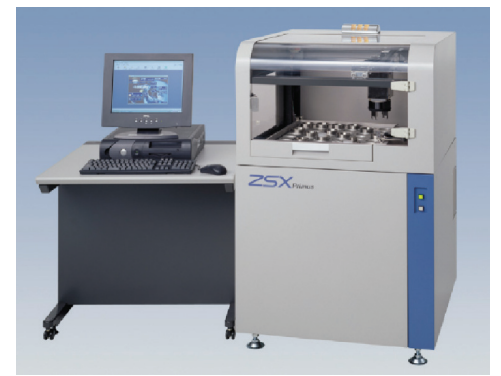


Fig.6 Rigaku/ZSX Primus

Since the general purpose spectrometers can analyze elements other than sulphur, they can be applied to the analysis of impurity elements in oils and the analysis of catalyst.

### Conclusion

Mini-Z Sulphur Analyser is a dedicated sulphur in oil analyser and is in compliance with ASTM-D2622, ISO 20884 and JIS K 2541-7. L.L.D. performance is less than 0.3 ppm and therefore the 5 ppm regulation level can be more than adequately measured. The day to day reliability of measurements is very high and sample preparation only involves pouring of the sample oil into the container. Measurements are obtained by placing the sample container on the turntable and simply pushing the start button, making this analytical tool ideally suited for routine-analysis.

## XRF and XRD Spectrometers Address Environmental Applications Needs



**Thermo Fisher Scientific** (USA) announces that its innovative series of X-ray Fluorescence (XRF) and X-ray powder Diffraction (XRD) spectrometers is ideally suited for a diverse range of environmental applications.

Designed for accurate and reliable analysis of drinking water, waste water, soils, sludge, air monitoring and spent materials such as paints, plastics and tires, these novel spectrometers are designed for use in manufacturing plants and contract laboratories as well as in the water, energy, waste disposal and recycling industries. Thermo has published several application notes to demonstrate the unique analytical capabilities of its XRF and XRD spectrometers including Thermo's ARL QUANT'X, ARL X'TRA and ARL ADVANT'X which are all specifically suited to the environmental market. These application notes are available to download free-of-charge from the Thermo Fisher website.

Thermo's comprehensive suite of WDXRF (Wavelength Dispersive X-ray Fluorescence), EDXRF (Energy Dispersive X-ray Fluorescence) and XRD spectrometers employs fast multi-element techniques. Achieving precise and repeatable results covering all elements and respective ranges, they also provide detection limits in the ppm range.

Additionally, the instruments are particularly easy to install and use while requiring very little or no sample preparation and offer flexible sample handling. The WDXRF and the EDXRF techniques, designed for use with Thermo's ARL ADVANT'X and ARL QUANT'X, are ideally suited to the analysis of waste oils, plastics, paints and contaminated soils whereas the ARL X'TRA spectrometers used with XRD are mainly used for analyzing particulates in air such as asbestos and quartz. Both XRF and XRD techniques are capable of handling totally unknown samples thanks to the powerful "standard-less" analysis packages such as UniQuant® and SiroQuant®.

This series of spectrometers has also been designed to help scientists comply with strict European and US regulations, including the RoHS/WEEE directives. These RoHS/WEEE regulations have been introduced to reduce the damage to both the environment in terms of pollution as well as to human health from occupational exposure and exposure following disposal.

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### New Low-Cost Benchtop Analyser Offers Improved Resolution and Detection Limits

**Jordan Valley's** (USA) new low-cost EX-Cite will replace the EX-310, the previous base model energy dispersive x-ray fluorescence (EDXRF) benchtop analyser. The EX-Cite EDXRF benchtop spectrometer has many improved features over the EX-310, including an integrated computer system, a smaller footprint, vastly improved resolution and corresponding improved detection limits.

With newly developed improvements to proven PIN diode technology, the 35kV, 9 watt EX-Cite produces superior sensitivity with improved peak-to-background ratios, high count throughputs and superior resolution as compared to earlier PIN diode instruments. At the same time, the high-voltage, high-powered x-ray source delivers traditional laboratory instrument performance in a compact, self-contained package that fits conveniently on a traditional laboratory bench. The side window x-ray tube and advanced optical design permit extremely close

coupling to the sample. The EX-Cite provides non-destructive qualitative and quantitative determination of Sodium through Uranium. It can be easily customized for several different industries and applications.

Laura Oelofse, Vice President of Sales and Marketing at Jordan Valley said, "The EX-Cite is a natural evolution in Jordan Valley's quest to provide low-priced XRF analysis at the best possible price-performance ratio."

The integrated computer system combined with the robust design make the instrument ideal for a mobile laboratory. It meets MIL-810E specifications for shock testing.

For more powerful performance, Jordan Valley's new 50kV, 50 watt EX-Calibur includes a fully integrated computer system and provides full qualitative, semi-quantitative and quantitative analytical capabilities. This liquid nitrogen free EDXRF spectrometer achieves similar resolution to a traditional LN2 cooled Si(Li) detector, while eliminating the cost and inconvenience associated with liquid nitrogen.

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## Screening of Ultra-low Sulphur Diesel



The determination of sulphur in fuels is one of the most important analytical applications in the petroleum oil industry. As one of the worldwide leading manufacturers of analytical instruments for energy dispersive X-ray

fluorescence analysis (EDXRF), **Spectro** (Germany) has prepared a new application for the SPECTRO PHOENIX II EDXRF analyser for this analytical task. This inexpensive compact instrument has been designed for utilisation in refineries, pipelines, terminals, tank farms and distribution centres and is especially easy to operate. In production control and sorting control of sulphur petroleum oils, the instrument enables sulphur determination in accordance with ASTM D4294, IP 336, IP 496, ISO 8754 and ISO 20847.

Spectro has prepared an application report about the new application with detailed information as to the analytical procedure and measurement results. The PHOENIX II design is ideal for the screening, identification and verification of ULSD (ultra-low sulphur diesel) at peripheral test points. The report can be requested at [www.spectro.com](http://www.spectro.com).

As documented in the report, the new application is thoroughly tailored to simple use. This begins with the simple sample preparation. Due to its polarised excitation source and rugged proportional counter detector, the Spectro Phoenix II achieves a very low detection limit for sulphur while maintaining high precision for the measurement. In addition to ULSD the Phoenix II also measures sulphur at the higher levels in off-road diesel, aviation gasoline, kerosene, bunker fuel and crude oil, as well as the low sulphur in gasolines and road diesels. Several elements can be measured in residual oils, lube oils, waste oils and cutting fluids. This enables the application to deal with many analytical tasks in production control in the petrochemical industry.

The Phoenix II does not require an external mouse or keyboard and offers USB, VGA and Ethernet connections for networking and connecting to external devices. As a useful tool in the petroleum industry, the Phoenix II XRF system gives the operator a unique combination of simplicity, high powered X-rays, a rugged detector system and a high sample throughput, all at a very affordable price.

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