

Benchtop WDXRF ultra-low sulfur analyzer for fuel oil

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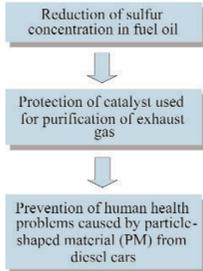
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Introduction

Regulations concerning the sulfur content in fuel oil, such as diesel fuel and gasoline, have been tightened. In one regulation, the sulfur content is limited up to 10 ppm in diesel fuel. In addition, the regulated value of the sulfur content is supposed to be lower. Therefore, analysis methods in which such low sulfur concentrations can be quantified are required. ASTM-D2622 and ISO-20884 are the analytical standards that comply with the regulations. These standards specify that wavelength dispersive X-ray spectrometers shall be used and also that measurement of the peak and background of the S- α line are required.

Two large effects caused by sulfur-free fuel oil



Effect 1. Reduction of the amount of CO₂ discharge in order to improve mileage of cars

When sulfur-free gasoline (with <10 ppm sulfur) becomes popular, a new type of vehicle with a better mileage engine will be developed since it will be possible to use a new type of catalyst.

Effect 2. Reduction of exhaust gas (NO_x and PM)

Generally speaking, sulfur is poison for catalysts. Sulfur-free fuel is effective for improving the life of catalysts and reducing the exhaust gas.

Table I. Regulations for sulfur level in ULSF

Market	Target year	Fuels and sulfur level	Remarks
USA	2004	Gasoline 30 ppm	10 ppm may have been introduced in 2005
	2006	Diesel 15 ppm	
Europe	2009	Diesel 10 ppm	
		Gasoline 10 ppm	
Japan	2007	Diesel 10 ppm	Oil refineries began to supply 10 ppm in 2005
	2008	Gasoline 10 ppm	

Table II. Major analytical method of sulfur determination in fuel oil

Analytical method	ASTM (Sulfur concentration)	ISO (Sulfur concentration)	JIS (Sulfur concentration)
Oxidative micro-coulometry	ASTM-D3120 (3–100 ppm)	ISO/DIS16591 (1–1000 ppm)	JISK2541-2 (1–1000 ppm)
Ultraviolet fluorescence (UVF)	ASTM-D5453 (1–8000 ppm)	ISO/DIS20846 (3–500 ppm)	JISK2541-6 (3–500 ppm)
WDXRF	ASTM-D2622 (3 ppm–5 mass%)	ISO20884 (5–500 ppm)	K2541-7 (5–500 ppm)
Monochromatic WDXRF (MWDXRF from XOS)	ASTM-D7039-04 (2–500 ppm)	n/a	n/a
EDXRF	ASTM-D4294 (0.015–5 mass%)	ISO8754 (0.03–5 mass%)	K2541-4 (0.01–5 mass%)

ASTM-D2622

Apparatus

Wavelength dispersive X-ray fluorescence spectrometer, capable of measuring the count rates of S- α X-ray fluorescence radiation and the background radiation.

Study of optics of Mini-Z sulfur analyzer

"Mini-Z sulfur analyzer" from Rigaku is a benchtop WDXRF analyzer that is suitable for the analysis of ultra-low sulfur in fuel oil. This system is configured with an optic that is unique to Rigaku and which makes it possible to measure peak and background intensities, even though it has a fixed goniometer, to comply with ASTM, ISO and JIS regulations.

This system was designed to obtain as high intensities as possible and to provide the best repeatability at around 10 ppm sulfur concentration, which most of the regulations in the world are going to focus on.

However, it is anticipated that 5 ppm regulations will be put into practice in the near future as environmental concerns increase pressure on the automobile industry to lower the sulfur concentration in fuel oil.

Consequently, we have developed a new optic for the Mini-Z sulfur analyzer which obtains precision sufficient for the range of 1–5 ppm of sulfur. At ultra-low sulfur concentrations, it is important to lower the background and improve the signal-to-noise (S/N) ratio, where "signal" means net intensity of S- α .

Figure 1 shows the pulse height distribution curve of the original Mini-Z sulfur analyzer. A peak from the blank sample that is located at the same position as S- α can be observed. This peak is the signal of scattered X-rays generated when the *bremstrahlung* from the X-ray tube are irradiated onto the sample and is diffracted at the same angle as S- α in the goniometer. It is not S- α from sulfur contamination in the optics. Therefore, two measures were taken to improve the S/N of the Mini-Z sulfur analyzer, described below.

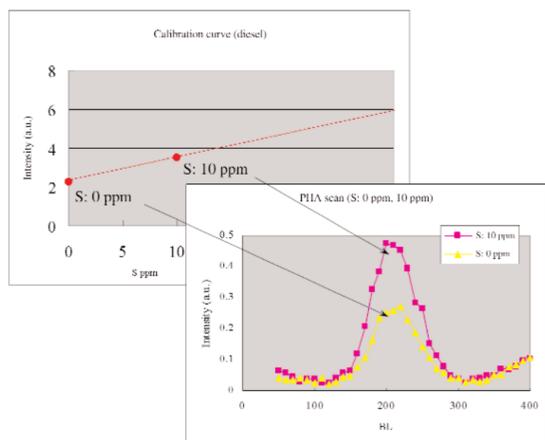


Figure 1. Calibration curve and pulse height distribution curve before adopting the measures in this study

The 10 ppm sample is diesel oil, and the blank sample is decalin. A pulse height distribution curve shows an energy spectrum of X-rays detected in the detector. 200 on the horizontal axis corresponds to the energy of S- α . A considerable amount of X-rays are detected at the same energy as S- α from the blank sample.

Specific measures to improve S/N

1. Cr target X-ray tube

Using the characteristic Cr- α line to excite the sulfur in place of Pd- α , we can avoid the significant loss of excitation efficiency even through the primary beam filter described in the next paragraph, because Cr- α has higher energy than Pd- α .

2. Primary beam filter

The filter was adopted to reduce the *bremstrahlung* from the X-ray tube that overlaps with S- α due to the energy correspondence. The thicker the filter adopted, the better the S/N that can be obtained, at the cost of overall X-ray intensity. We optimized the thickness of the filter to achieve the best LLD.

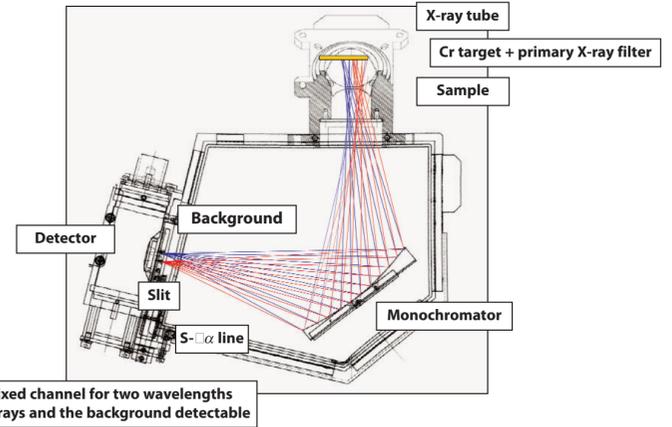


Figure 2. Optics of Mini-Z sulfur analyzer

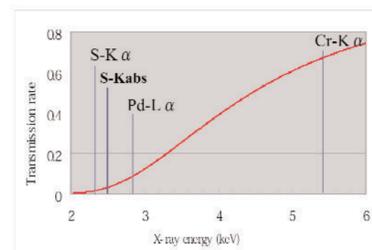


Figure 3. Transmission rate vs. X-ray energy

The relationship between the transmission rate of the filter adopted in this study and X-ray energy is shown. Almost all of the X-rays corresponding to S- α are absorbed by this filter. After replacing the Pd target with Cr, we optimized the thickness of filter so that the transmission rate of Cr- α is nearly 70%.

Results and conclusion

The following results were obtained by adopting two specific measures to improve the S/N ratio.

- The intensities from the blank sample that was observed as a peak in the pulse height distribution curve before adopting these two measures was significantly reduced (Figure 4).
- The S/N ratio at 10 ppm sample was significantly improved from 0.5 to 3.0.
- Lower limit of detection of 0.26 ppm at 300 second measurement time and 0.18 ppm at 600 second measurement time was achieved by improving the S/N ratio significantly.
- Due to the improvement of the S/N ratio, background fluctuation was reduced in oil sample measurements, and a good fit of the calibration curve was obtained in the 1–5 ppm range.
- A good fit was also obtained in the calibration curve with both diesel fuel and gasoline included (Figure 4).

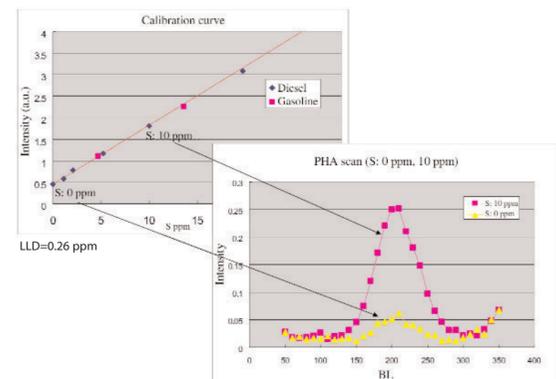


Figure 4. Calibration curve and pulse height distribution curve after adopting measures to improve the S/N ratio

These figures show the calibration curve and the pulse height distribution curve after adopting two measures described in this poster. The samples indicated as "Diesel" were prepared by diluting the standard sample from JPI (The Japan Petroleum Institute) with decalin. The samples indicated as "Gasoline" were SRM2298 and SRM2299, which are standard samples from NIST. By comparison with Figure 1, it is clear that the intensities of the blank sample were reduced significantly.

Table III. Repeatability test result (1 sampling, counting time: 300 seconds)

	1 ppm	2 ppm	5 ppm	10 ppm	50 ppm
σ' (ppm)	0.10	0.11	0.15	0.18	0.37
σ'' (ppm)	0.12	0.16	0.18	0.24	0.38

The standard deviations of ten consecutive measurements of diesel oils at several sulfur concentrations are listed. Counting time is 300 seconds. σ' shows the standard deviation obtained by measuring gross intensities. σ'' shows the standard deviation obtained by subtracting the background intensities from the peak intensities, in accordance with the ASTM-D2622. The repeatability obtained in this study is good enough even at concentrations lower than 10 ppm.

Summary

- Benchtop wavelength dispersive X-ray fluorescence spectrometer
- Both S- α peak and background measured
- S/N was improved to 3.0 at 10 ppm
- LLD: 0.26 ppm at 300 seconds
0.18 ppm at 600 seconds
- Repeatability: Std. Dev. = 0.12 ppm at 1 ppm
0.16 ppm at 2 ppm
0.18 ppm at 5 ppm