

## MEASUREMENT OF SULFUR CONTENT IN DIESEL and GASOLINE FUEL OIL USING Rigaku Mini-Z Sulfur Analyzer

### INTRODUCTION

Recently, transition to ultra low sulfur diesel fuel and ultra low sulfur gasoline fuel is accelerating for reducing air pollution and upgrading clean-up system of automobile exhaust gas.

The supply of sulfur free (maximum 10ppm) gasoline and diesel fuel oil began by the oil manufacturers since 2005 in Japan. The sulfur content of gasoline is restricted to maximum 30ppm from 2005 and the sulfur content of diesel fuel oil is restricted to maximum 15ppm from 2007 in USA. And the sulfur content of gasoline and diesel fuel oil is restricted to maximum 10ppm from 2009 in EU.

Rigaku's Mini-Z Sulfur Analyzer is a wavelength dispersive X-ray fluorescence spectrometer dedicated to sulfur content measurements in oil complying with ISO 20884, ASTM D2622 and JIS K2541-7. Since the background decreases substantially, the detection limit has been improved drastically and excellent long term stability can be achieved for low level sulfur. And this sulfur analyzer can cope with forecasted 5ppm regulation.

**Keywords:** wavelength dispersive, gasoline, diesel, sulfur free, sulfur content, benchtop type

### 1. APPARATUS

#### **Benchtop wavelength dispersive X-ray fluorescence spectrometer Mini-Z Sulfur Analyzer**

The sulfur content is obtained by measuring fluorescent x-ray of sulfur.

The sulfur analyzer adopted wavelength dispersive type X-ray fluorescent spectrometer using analyzing crystal and it gives very low background and trace amount of sulfur can be measured with good sensitivity. And the background subtraction which is specified in the standards such as ISO, ASTM and JIS can be utilized.

The operation is done through a touch panel and even beginner can analyze samples without training. The measurement operation is placing samples on the turret and simply press [Start] key.

## 2. APPLICATION DATA

### (1) Calibration Curve

Fig.1 shows the calibration curve for sulfur in diesel fuel oil and gasoline standard samples. Both peak and background were measured following the standards such as ISO, ASTM and JIS, and obtained net intensity subtracted peak intensity by background intensity to make the calibration.

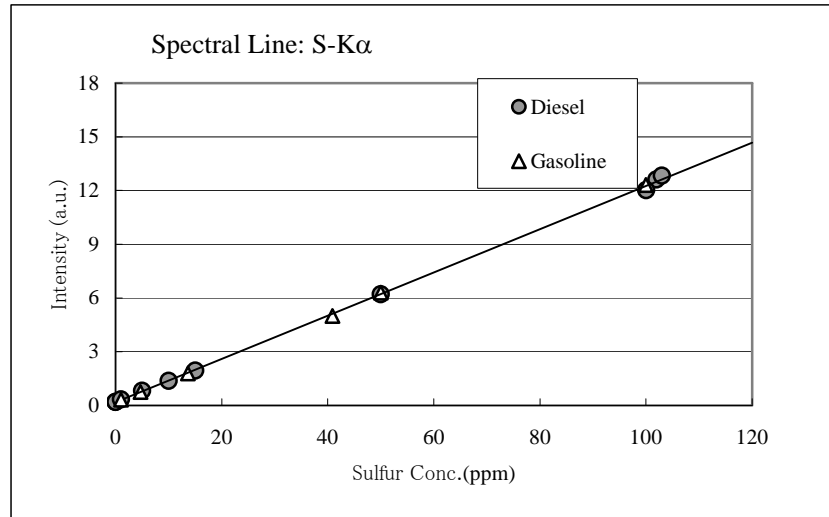


Fig.1 Calibration curve of sulfur for diesel fuel oil and gasoline

The plot data of both diesel and gasoline are lying on the same calibration curve and good linearity down to less than 10ppm was obtained.

### (2) Repeatability measurements

Table 1 shows the result of 10 times repeat measurements for three sulfur levels of diesel fuel oil.

Table 1 Result of repeatability measurements

Repeat	5ppm	10ppm	15ppm
1	4.35	9.99	15.03
2	4.41	10.02	15.62
3	4.55	9.94	15.71
4	4.53	10.34	15.54
5	4.47	10.42	15.81
6	4.65	10.09	15.57
7	4.98	10.09	15.87
8	4.82	10.33	15.46
9	4.78	10.43	15.34
10	4.70	10.38	15.82
Average (ppm)	4.62	10.20	15.58
Std .dev. (ppm)	0.20	0.19	0.26
RSD(%)	4.3	1.9	1.7

### (3) Sampling repeatability

Table 2 shows the result of sampling repeatability of 10 times by measuring diesel fuel oil samples. Oil samples were set to sample cells before every measurement.

Table 2 Result of 10 times sampling repeatability

Time	5ppm	10ppm	15ppm
1	4.90	10.03	14.91
2	4.91	9.75	15.47
3	4.58	9.65	15.04
4	4.76	9.60	14.68
5	4.62	9.38	15.53
6	4.80	9.36	15.76
7	4.81	10.02	15.13
8	4.47	9.58	14.84
9	4.55	10.00	15.48
10	5.09	9.80	14.89
Average (ppm)	4.75	9.72	15.17
Std .dev. (ppm)	0.19	0.25	0.36
RSD(%)	4.1	2.6	2.4

The result of sampling reproducibility is identical to the result of repeatability measurements so that the error cause by sampling can be ignored. And the standard deviations obtained are maximum 0.25ppm for the range 10ppm and less.

(4) Long term stability for 20 days

Table 3 shows the result of long term stability test for 20 days by measuring diesel fuel oil samples. The samples were measured once per day.

Table 3 Result of long term stability test

Day	5ppm	10ppm	15ppm
1	4.80	10.18	15.14
2	5.12	9.94	14.88
3	5.09	10.45	15.27
4	4.90	10.04	14.74
5	4.84	9.52	14.60
6	4.87	9.81	15.23
7	4.84	10.06	14.42
8	4.91	9.64	14.91
9	5.45	10.27	14.95
10	4.94	9.58	14.89
11	4.88	10.07	14.89
12	4.90	10.17	14.75
13	4.68	9.99	14.76
14	5.11	9.98	14.63
15	5.36	9.94	15.18
16	4.78	10.00	14.54
17	4.64	9.78	14.12
18	5.11	9.85	14.85
19	4.59	9.52	14.62
20	4.63	10.01	14.29
Average (ppm)	4.92	9.94	14.78
Std .dev. (ppm)	0.23	0.25	0.30
RSD(%)	4.7%	2.5%	2.1%
95% conf. interval(ppm) <sup>1)*</sup>	0.90	0.97	1.19

\*1) The definition of repeatability defined in the ISO, ASTM and JIS is “95% confidence interval” in statistics and the repeatability is expressed as follows.

$$95\% \text{ confidence interval} = 1.96 \times 2 \times \text{Standard deviation (ppm)}$$

Table 4 shows the allowable repeatability equation and the values of calculated repeatability for individual standards. The measured results above sufficiently satisfy the allowable repeatability. The 95% confidence interval for sulfur 5ppm obtained is less than 1ppm so that the sulfur analyzer can be used for the sulfur level of less than 5ppm.

Table 4 Repeatability of sulfur specified in individual standards

Standard	Allowable repeatability equation	5ppm	10ppm	15ppm
ISO 20884	$1.7 + 0.0248 X$ (5-60ppm)	1.82	1.95	2.07
ASTM D 2622	$0.00736(X\%+0.0002)^{0.4} \times 10000$ (3-930ppm)	4.03	5.00	5.74
JIS K2541-7	$1.9 + 0.0217 X$ (5-500ppm)	2.01	2.12	2.23

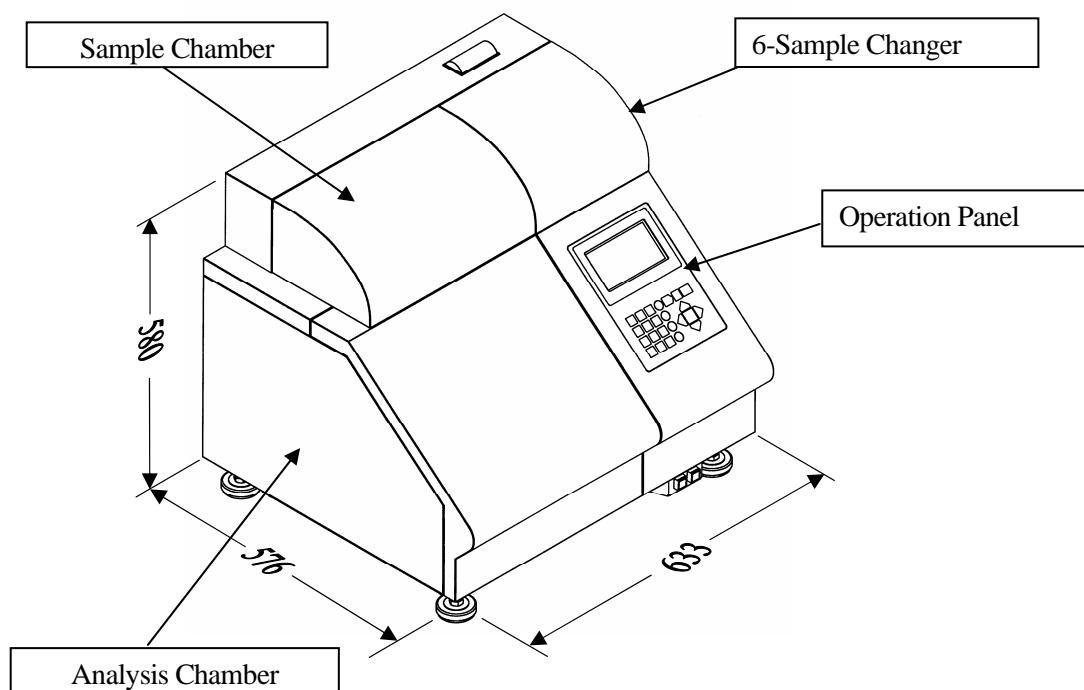
Note: X is average analyzed sulfur concentration in ppm.

### 3. MEASURING CONDITIONS

- (1) Measurement time : Peak 300 sec  
Background 300 sec
- (2) Sample amount : 4mL (measured in special liquid sample holder)
- (3) Analysis chamber : Helium path

#### 4. EXTERNAL APPEARANCE OF INSTRUMENT

(Unit: mm)



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