Application Note WDXRF1082

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XRF1082 - Sulfur analysis in crude oil and high-sulfur fuels by benchtop WDXRF according to ASTM D2622-16

Introduction

Crude oil is raw material for petroleum products and contains sulfur in concentration from 0.5 mass% to 5.0 mass% typically. Residual fuel oil and high-sulfur diesel fuel are mainly used for boilers and burners, agricultural machines, and long-distance mass transportation means, such as vessels and diesel locomotives of rail road, equipped with large engines. Sulfur compounds in petroleum cause various harmful influences such as air pollution, metal corrosion and catalyst degradation. Therefore, sulfur concentration of crude oil and high-sulfur fuels is monitored or controlled in refinery and production processes in the petroleum industry.

X-ray fluorescence (XRF) spectrometry has been used for quantitative analysis of sulfur in crude oil and high-sulfur fuels including bunker fuel, owing to simple sample preparation. In XRF analysis of oils, samples are simply poured into liquid cells and any complicated treatment such as chemical decomposition or dilution is not required. In addition, concentration of total sulfur is obtained in XRF analysis.

This application note demonstrates quantitative analysis of high-concentration sulfur in crude oil, high-sulfur diesel fuel and residual fuel oil according to ASTM D2622-16 on Rigaku Supermini200, a benchtop wavelength-dispersive X-ray fluorescence (WDXRF) spectrometer.

Instrument

The Supermini200 is a benchtop sequential WDXRF spectrometer designed specifically to deliver excellent performance while eliminating typical installation requirements, such as cooling water, special power supply, large floor space, etc.

Featuring a unique air-cooled 200 W X-ray tube, two detectors, programmable environment of vacuum or helium, and three analyzing crystals, the Supermini200 can analyze elements from fluorine to uranium.

The Windows-based software running the Supermini200 is shared with Rigaku's popular Primus family of higher-power WDXRF systems, which means that it has the same advanced algorithms, multiple language support and an intuitive user-friendly interface.

Measurements were performed on the Supermini200 using a PET analyzing crystal, included in the standard crystals, with the X-ray tube operating at 50 kV and 4.0 mA. The counting time was 50 seconds for peak and 25 seconds for background.

Sample preparation

Four milliliter of each sample was poured into a standard liquid cell (Chemplex® 1540) equipped with 3.6 µm Mylar® (Chemplex® 150).

Standard and sample preparation

Crude oil standards, “Number 2 diesel fuel” standards and residual oil standards provided by VHG Labs were used for calibration of crude oil, high-sulfur diesel fuel and residual fuel oil respectively. The calibration curves are shown in Figure 1 and the calibration results are tabulated in Table 1.

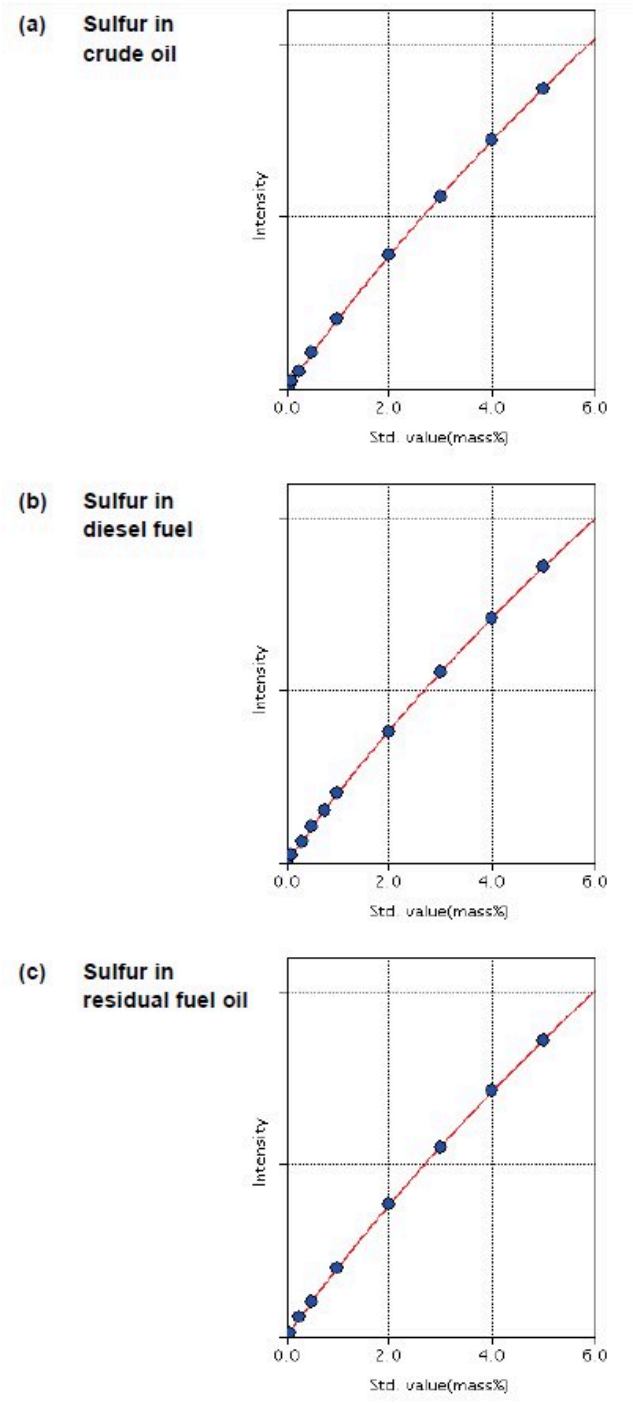

Figure 1: Calibration curve for each material (a) Crude oil; (b) Diesel fuel (high sulfur); (c) Residual fuel oil

Table 1: Calibration result for each material (in mass%)

Material	Calibration range	Accuracy
Crude oil	0 – 5.0	0.016

Diesel fuel	0 – 5.0	0.011
Residual fuel oil	0 – 5.0	0.022

The accuracy of calibration was calculated by the following formula:

$$Accuracy = \sqrt{\frac{\sum_i (C_i - \hat{C}_i)^2}{n-m}}$$

C_i: calculated value of standard sample
$\hat{C}_i$: reference value of standard sample
n : number of standard samples.
m: degree of freedom (linear 2, quad. 3)

Analysis results

In order to assess the repeatability of the method, two aliquots of a representative sample were prepared and quantified with the calibration; this process was repeated twenty times.

The test data are compiled in Table 2 (a) for crude oil, Table 2 (b) for high-sulfur diesel fuel and Table 2 (c) for residual fuel oil, which show the average and the difference of the results of each two-aliquot measurement. ASTM D2622-16 defines "repeatability (r)" by

Repeatability (r) = $0.1462 \cdot X^{0.8015}$ mg/kg (1)
X: total sulfur concentration (mg/kg) [1]

and states that the difference between successive test results obtained by the same operator with the same apparatus under constant operation conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values calculated by Equation (1) only in one case in twenty.
The test results shown in Table 2, where the difference of two aliquots does not exceed the repeatability (r) for each material, prove that the performance of the Supermini200 easily satisfies the requirement of ASTM D2622-16 for crude oil, high-sulfur diesel fuel and residual fuel oil.

Table 2: Repeatability test result (qualification test for ASTM D2622-16)

(a) Crude oil

Run #	Average (mass%)	Difference (mass%)
1	4.02	0.01
2	4.01	0.00
3	4.01	0.01
4	4.02	0.05
5	3.97	0.06
6	4.03	0.01
7	4.02	0.03
8	3.99	0.02

9	3.98	0.00
10	3.98	0.02
11	4.00	0.01
12	3.99	0.02
13	4.01	0.01
14	4.02	0.01
15	4.03	0.03
16	4.00	0.00
17	4.00	0.04
18	4.04	0.06
19	3.98	0.02
20	3.97	0.02
Avg. 4.00		
Maximum		0.06
r (repeatability)		0.07

(b) Diesel fuel

Run #	Average (mass%)	Difference (mass%)
1	3.99	0.03
2	3.97	0.02
3	3.95	0.03
4	3.97	0.02
5	3.95	0.03
6	3.98	0.03
7	4.01	0.06
8	3.95	0.01
9	3.96	0.02
10	3.94	0.05
11	3.99	0.05
12	3.94	0.01
13	3.93	0.01
14	3.94	0.02

15	3.93	0.02
16	3.95	0.01
17	3.95	0.01
18	3.94	0.04
19	3.98	0.03
20	4.01	0.04
Avg.	3.96	
Maximum		0.06
r (repeatability)		0.07

(c) Residual fuel oil

Run #	Average (mass%)	Difference (mass%)
1	4.02	0.05
2	3.97	0.01
3	3.99	0.05
4	4.04	0.01
5	4.05	0.01
6	4.06	0.06
7	4.00	0.02
8	3.98	0.01
9	3.99	0.03
10	4.02	0.01
11	4.01	0.04
12	3.97	0.01
13	3.98	0.04
14	4.02	0.00
15	4.02	0.03
16	4.04	0.03
17	4.01	0.01
18	4.02	0.03
19	3.99	0.06
20	4.05	0.04

Avg.	4.01	
Maximum		0.06
r (repeatability)		0.07

Conclusion

The application note demonstrates that high concentration sulfur in crude oil and petroleum-based fuels, including bunker fuel, can be routinely analyzed with excellent accuracy, sensitivity and repeatability using a benchtop WDXRF spectrometer with minimal site requirements.

In particular, the Rigaku Supermini200 benchtop WDXRF system, which does not require external water for cooling an X-ray tube or special power supply, meets the specification of ASTM D2622-16, which has become stricter in the recent versions of ASTM D2622.

Reference

ASTM D2622-16, Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry, ASTM International, (2016), 12pp.

Related products

Supermini200

Benchtop tube below sequential WDXRF spectrometer anal
yzes O through U in solids, liquids and powders