Application Note WDXRF1108

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XRF1108 - Sulfur analysis in crude oil and high-sulfur fuels by 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 ZSX Primus IVi, a wavelength dispersive X-ray fluorescence (WDXRF) spectrometer.

Instrument

The ZSX Primus IVi, a tube-below sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer, is optimized for routine analysis that today's petroleum laboratories need to perform. The programmable, switchable vacuum seal between the sample and optical chambers can keep the optical chamber under vacuum with the sample chamber under helium, and, therefore, minimizes helium gas consumption and time of atmosphere change in the sample chamber. The spectrometer is equipped with a 3 kW X-ray tube and the analyzing crystals covering O to Cm in the standard configuration. If higher sensitivity or precision is required, a 4 kW X-ray tube can be mounted.

The system software is designed for ease of use in routine analyses. The Flowbar in quantitative analysis guides users in establishing calibration. The Sample ID Table and the Program Operation help operators carry out daily analysis.

Measurements were performed on the ZSX Primus IVi with a 3 kW X-ray tube operating at 30 kV and 80 mA using a GeH analyzing crystal and the S4 slit, included in the standard configuration. The beryllium primary beam filter, inserted between the sample and the X-ray tube, protects the X-ray tube window against damage from sample falling during measurement. The counting time was 20 seconds for peak and 10 seconds for background.

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.

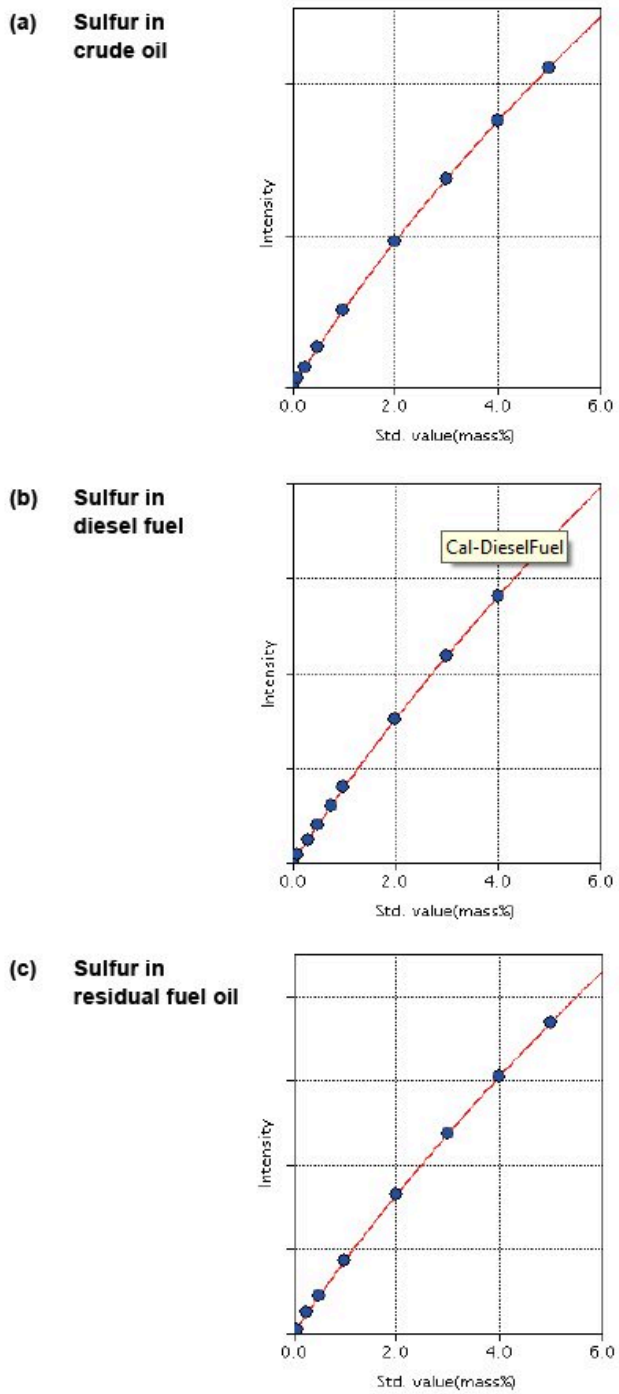

Figure 1: Calibration curve for each material (a) Crude oil; (b) Diesel fuel (high sulfur); (c) Residual fuel oil

Four milliliters of each sample was poured into a liquid cell (Chemplex® 1095) with analysis film of 3.6 µm Mylar® (Chemplex® 150).

Table 1: Calibration result for each type of petroleum products (in mass%)

Material	Calibration range	Accuracy
Crude oil	0 – 5.0	0.005
Diesel fuel	0 – 5.0	0.005
Residual fuel oil	0 – 5.0	0.012

The accuracy of calibration is 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

Repeatability tests were carried out using a representative sample for each material. For each sample, two aliquots were prepared and quantified with the calibration (Figure 1); this process was repeated twenty times. The test results are tabulated in Table 2 (a) for crude oil, Table 2 (b) for high-sulfur diesel fuel and Table 2 (c) for residual fuel oil, in which the average and the difference of two aliquots each are shown. "r" represents "repeatability" defined by

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

in ASTM D2622-16, which 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.

For high power instruments having >1000 watt X-ray sources, a non-mandatory repeatability for high power instrument is provided in Appendix of ASTM D2622-16.

Repeatability (r) = $0.08681 \cdot X^{0.8383}$ mg/kg

This value for each material is also shown in Table 2 for reference.

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

(a) Crude oil

Run #	Average (mass%)	Difference (mass%)
1	0.990	0.003
2	0.993	0.007

3	0.997	0.002
4	0.994	0.008
5	0.991	0.002
6	0.996	0.008
7	0.997	0.006
8	0.994	0.001
9	0.998	0.009
10	1.001	0.002
11	0.998	0.003
12	0.995	0.003
13	0.994	0.001
14	0.997	0.004
15	1.000	0.003
16	1.001	0.001
17	0.997	0.006
18	0.996	0.003
19	0.997	0.000
20	0.998	0.002
Avg.	0.996	
Maximum		0.009
r (repeatability)*		0.023
r (high power)**		0.020

(b) Diesel fuel

Run #	Average (mass%)	Difference (mass%)
1	3.98	0.02
2	3.98	0.02
3	3.98	0.01
4	3.99	0.01
5	3.99	0.01
6	3.97	0.03
7	3.97	0.01

8	3.98	0.01
9	3.98	0.01
10	3.97	0.01
11	3.96	0.01
12	3.96	0.02
13	3.96	0.02
14	3.95	0.00
15	3.98	0.04
16	3.97	0.06
17	3.93	0.02
18	3.94	0.03
19	3.95	0.02
20	3.95	0.01
Avg.	3.97	
Maximum		0.06
r (repeatability)*		0.07
r (high power)**		0.06

(c) Residual fuel oil

Run #	Average (mass%)	Difference (mass%)
1	3.93	0.01
2	3.94	0.01
3	3.95	0.01
4	3.96	0.02
5	3.96	0.02
6	3.95	0.01
7	3.95	0.01
8	3.93	0.04
9	3.92	0.01
10	3.92	0.00
11	3.94	0.03
12	3.92	0.00

13	3.89	0.00
14	3.89	0.03
15	3.90	0.01
16	3.91	0.00
17	3.91	0.03
18	3.93	0.02
19	3.93	0.03
20	3.91	0.04
Avg.	3.93	
Maximum		0.04
r (repeatability)*		0.07
r (high power)**		0.06

* This "***r***" is defined in the text of ASTM D2622-16 and mandatory for qualification.
** This "***r***" is defined in "High power Instrument Precision" Appendix of ASTM D2622-16 and is not mandatory for qualification .
The test results shown in Table 2, where the difference of duplicated aliquots does not exceed the repeatability (r), prove that the performance of the ZSX Primus IVi meets the requirement of ASTM D2622-16 for crude oil, high-sulfur diesel fuel and residual fuel oil.

Conclusion

High concentration sulfur in crude oil and petroleum- based fuels, including bunker fuel, can be routinely analyzed with high accuracy and precision on the ZSX Primus IVi, a sequential WDXRF spectrometer, with a 3 kW X-ray tube. This application note demonstrates that the performance of the ZSX Primus IVi meets the requirement 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

ZSX Primus IV*i*

High-power, tube-below, sequential WDXRF spectrometer wi
th new ZSX Guidance expert system software