Application Note WDXRF1080

View on rigaku.com

XRF1080 - Sulfur analysis in petroleum products by benchtop WDXRF according to ASTM D2622-16

Introduction

Crude oil contains sulfur in concentration from 0.5 mass% to 5.0 mass% typically, and control of the level of sulfur in refinery intermediates and final products is critical in a refinery.

Sulfur in petroleum-based fuels contributes to atmospheric pollution; therefore, sulfur content in fuels, especially in automobile fuels, is strictly controlled. Sulfur also causes damage to facilities such as catalysts in refinery processes. Therefore, control of sulfur content is very important in the petroleum industry from the standpoints of both environment and production cost.

X-ray fluorescence (XRF) spectrometry has been used for quantitative analysis of sulfur in petroleum products, owing to simple sample preparation. In XRF analysis of oil, 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 sulfur in petroleum products 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 200W 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 for low sulfur concentration was 300 seconds for peak and 150 seconds for background, for high sulfur concentration, 50 seconds and 25 seconds.

Standard and sample preparation

Calibration standards of polysulfides in mineral oil provided by VHG Labs were used for calibration for a low sulfur range from 0 mg/kg to 1000 mg/kg and a high sulfur range from 0 mass% to 5 mass% separately. The calibration curves are shown in Figure 1 and the calibration results are listed in Table 1.

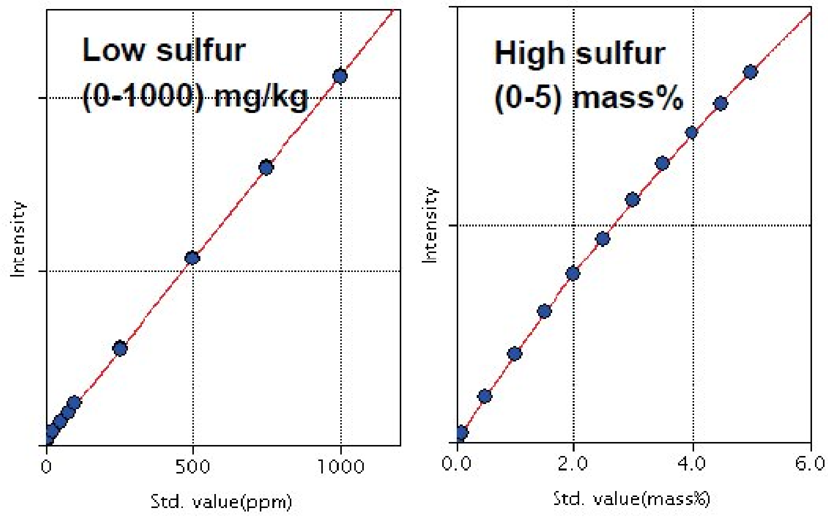

Figure 1: Calibration curve

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

Table 1: Calibration results

Element	Calibration range	Accuracy (LLD)
S (low conc.)	0 mg/kg – 1000 mg/kg	2.1 mg/kg (LLD 0.5 mg/kg)
S (high conc.)	0 mass% – 5 mass%	0.022 mass%

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)

The lower limit of detection (mg/kg) was calculated by the following formula:

$$LLD = 3 \cdot \frac{1}{m} \cdot \sigma_B = \frac{3}{m} \cdot \sqrt{\frac{I_B}{1000 \cdot t}}$$

$m{{ widgetHtmlContent }}nbsp; : sensitivity of calibration (kcps/[mg/kg])
$s_B{{ widgetHtmlContent }}nbsp; : standard deviation of blank intensity (kcps)
$I_B{{ widgetHtmlContent }}nbsp; : sensitivity of calibration (kcps/[mg/kg])
$t{{ widgetHtmlContent }}nbsp; : counting time (s)

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 for low sulfur concentration and high sulfur concentration were compiled in Table 2 and Table 3 respectively, which show the average and the difference of the results for each two-aliquot measurement. ASTM D2622-16 defines "repeatability (r)" by:

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

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 and Table 3, where the difference of two aliquots does not exceed the repeatability (r), prove that the Supermini200 easily satisfies the requirement of ASTM D2622-16.

Table 2: Repeatability test results for low sulfur concentration

Run No.	Average (mg/kg)	Difference (mg/kg)
1	9.8	0.3
2	9.9	0.0
3	10.0	0.0
4	10.0	0.1
5	9.7	0.4
6	9.8	0.6
7	9.9	0.5
8	9.7	0.1
9	9.7	0.1
10	9.8	0.2
11	9.5	0.4
12	9.7	0.1
13	9.7	0.0
14	9.7	0.1

15	9.7	0.1
16	9.7	0.0
17	9.8	0.1
18	9.8	0.0
19	9.8	0.1
20	9.8	0.1
Average	9.8	
Maximum		0.6
r (repeatability) defined by ASTM		0.9

Table 3: Repeatability test results for high sulfur concentration

Run No.	Average (mass%)	Difference (mass%)
1	4.50	0.05
2	4.55	0.02
3	4.52	0.07
4	4.45	0.05
5	4.41	0.06
6	4.46	0.02
7	4.49	0.02
8	4.46	0.03
9	4.50	0.00
10	4.49	0.01
11	4.49	0.01
12	4.47	0.00
13	4.47	0.04
14	4.51	0.03
15	4.48	0.03
16	4.52	0.02
17	4.50	0.01
18	4.49	0.01
19	4.50	0.00
20	4.50	0.01
Average	4.49	

Maximum	0.07
r (repeatability) defined by ASTM	0.08

Conclusion

This application note demonstrates that sulfur in petroleum products can be routinely analyzed in both low and high sulfur concentration ranges 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 specifications of ASTM D2622-16, which has become more stringent in the recent versions of ASTM D2622, which has become more stringent 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