Application Note WDXRF1106

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XRF1106 - Sulfur analysis in petroleum products by 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 causes 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 treatments such as chemical decomposition or dilution are 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 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 samples leaking during measurement. The counting time for low sulfur concentration was 200 seconds for peak and 100 seconds for background; for high sulfur concentration, 20 seconds and 10 seconds.

Standard and sample preparation

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

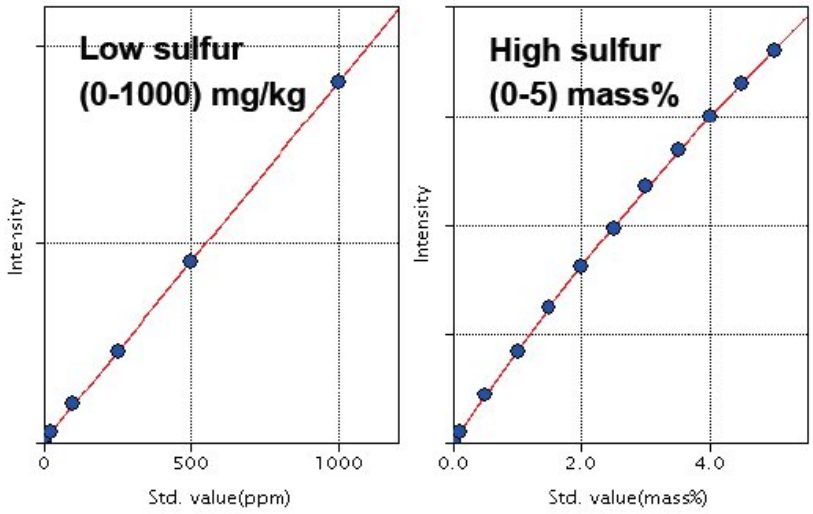

Figure 1: Calibration curve

Table 1: Calibration results

Element	Calibration range	Accuracy (LLD)
S (low conc.)	0 mg/kg – 1000 mg/kg	1.2 mg/kg (LLD 0.2 mg/kg)
S (high conc.)	0 mass% – 5 mass%	0.013 mass%

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)

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

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

$m{{ widgetHtmlContent }}nbsp; : sensitivity of calibration (kcps/[mg/kg])
$\sigma_B{{ widgetHtmlContent }}nbsp; : standard deviation of blank intensity (kcps)
$I_B{{ widgetHtmlContent }}nbsp; : blank intensity (kcps)

$t{{ widgetHtmlContent }}nbsp; : counting time (s); 100 s is used

Analysis results

Repeatability tests were carried out using representative samples with polysulfide in mineral oil.

Table 2: Repeatability test results for low sulfur concentration

Run No.	Average (mg/kg)	Difference (mg/kg)
1	9.9	0.0
2	9.9	0.1
3	10.0	0.3
4	10.2	0.1
5	10.2	0.2
6	10.1	0.1
7	10.2	0.1
8	10.2	0.1
9	10.0	0.3
10	10.1	0.4
11	10.1	0.4
12	9.9	0.0
13	10.0	0.1
14	10.2	0.3
15	10.2	0.4
16	10.0	0.2
17	10.1	0.1
18	10.1	0.1
19	10.0	0.3
20	9.9	0.0
Average	10.1	
Maximum		0.4
r (repeatability) defined by ASTM		0.9

Table 3: Repeatability test results for high sulfur concentration

Run No.	Average (mass%)	Difference (mass%)

1	4.42	0.00
2	4.43	0.02
3	4.44	0.00
4	4.43	0.02
5	4.43	0.00
6	4.43	0.00
7	4.45	0.04
8	4.44	0.05
9	4.42	0.01
10	4.44	0.03
11	4.43	0.05
12	4.42	0.02
13	4.44	0.04
14	4.47	0.02
15	4.46	0.04
16	4.42	0.03
17	4.41	0.00
18	4.43	0.03
19	4.43	0.03
20	4.42	0.01
Average	4.43	
Maximum		0.05
r (repeatability) defined by ASTM		0.08

For each sample, two aliquots were prepared and quantified with the calibration (Figure 1); this process was repeated twenty times. The test results for low sulfur concentration and high sulfur concentration are tabulated in Table 2 and Table 3 respectively. In the tables, the average and the difference of two aliquots each are shown and “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.

The test results shown in Table 2 and Table 3, where the difference of two aliquots does not exceed the repeatability (r) for each analyte, prove that the performance of the ZSX Primus IVi meets the requirement of ASTM D2622-16.

In Appendix of ASTM D2622-16, “r” for high power instruments, having 1000 watt sources or higher, is provided as nonmandatory information. For the samples used for the repeatability test, “r’s” calculated are 0.6 mg/kg for low sulfur concentration and 0.07 mass% for high sulfur concentration. Even if these values were used as the requirement, the analyses on the ZSX Primus IVi would be qualified.

Conclusion

Sulfur in petroleum products can be routinely analyzed in both low and high sulfur concentration ranges 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