Application Note WDXRF1107

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XRF1107 - Analysis of low-concentration sulfur in petroleum-based fuels by WDXRF according to ASTM D2622-16

Introduction

Sulfur in petroleum-based fuels contributes to atmospheric pollution. Sulfur content in fuels, especially in automobile fuels, is strictly controlled and regulations of sulfur content in fuel oil such as diesel fuel and gasoline have been tightened. Therefore, control of sulfur content is very important in refinery plants.

X-ray fluorescence (XRF) spectrometry has been used for quantitative analysis of sulfur in petroleum-based fuels, owing to simple sample preparation. In XRF analysis of fuel 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 low concentration sulfur in diesel fuel, gasoline and kerosene 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 200 seconds for peak and 100 seconds for background.

Standard and sample preparation

“Number 2 diesel fuel” standards, isooctane-based standards and kerosene-based standards provided by VHG Labs were used for calibration of diesel fuel, gasoline and kerosene respectively. The calibration curves are shown in Figure 1 and the calibration results are tabulated in Table 1.

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

Table 1: Calibration result for each type of petroleum products (in mg/kg)

Material	Diesel fuel	Gasoline	Kerosene
Calibration range	0 – 1000	0 – 1000	0 – 1000
Accuracy	0.8	1.3	4.8
LLD	0.2		

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 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.

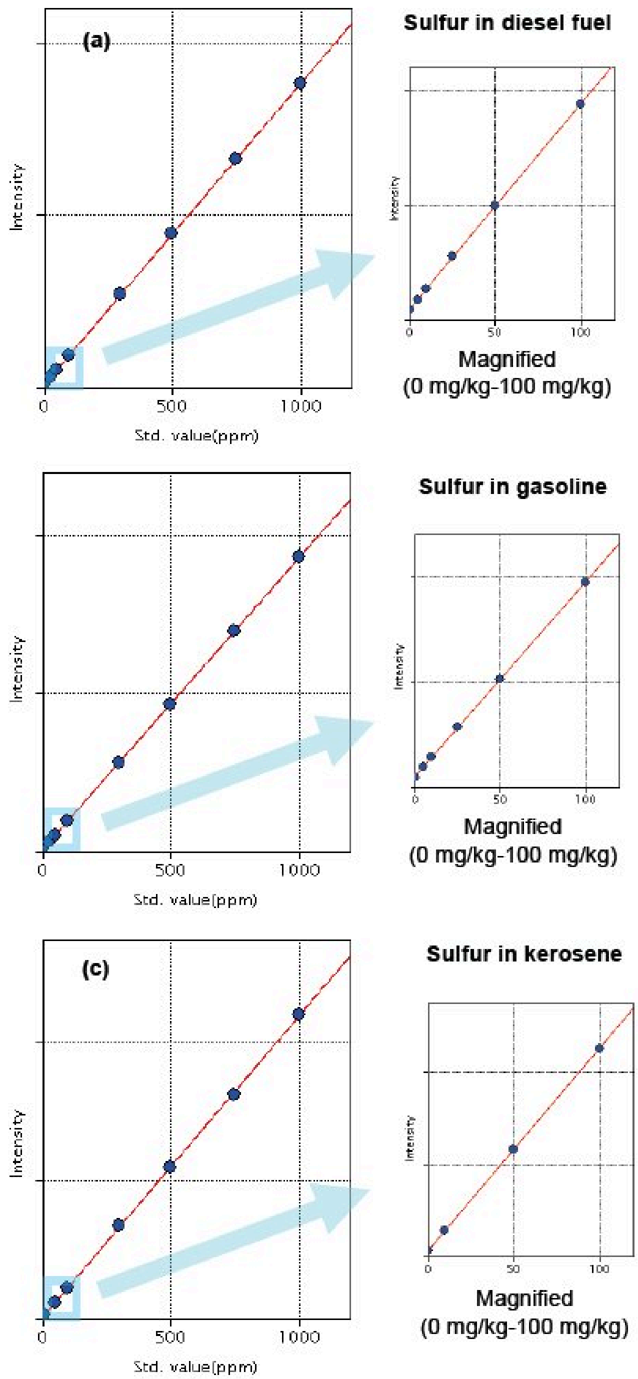

Figure 1: Calibration curve for each material (a) Diesel fuel; (b) Gasoline; (c) Kerosene

The test results are tabulated in Table 2 (a) for diesel fuel, Table 2 (b) for gasoline and Table 2 (c) for kerosene, 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.

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

(a) Diesel fuel

Run #	Average (mg/kg)	Difference (mg/kg)
1	9.7	0.4
2	9.6	0.1
3	9.4	0.4
4	9.4	0.4
5	9.7	0.2
6	9.6	0.4
7	9.6	0.4
8	9.6	0.4
9	9.5	0.2
10	9.6	0.0
11	9.7	0.2
12	9.8	0.1
13	9.7	0.1
14	9.6	0.1
15	9.7	0.4
16	9.7	0.4
17	9.7	0.4
18	9.6	0.6
19	9.6	0.5
20	9.7	0.2
Avg.	9.6	
Maximum		0.6
r (repeatability)*		0.9
r (high power)**		0.6
r (diesel)**		0.6

(b) Gasoline

Run #	Average (mg/kg)	Difference (mg/kg)
1	17.3	0.6
2	17.8	0.4
3	17.9	0.2
4	17.6	0.5
5	17.7	0.7
6	18.0	0.0
7	17.9	0.3
8	17.5	0.5
9	17.3	0.1
10	17.3	0.0
11	17.6	0.6
12	17.7	0.4
13	17.7	0.3
14	17.5	0.6
15	17.4	0.3
16	17.5	0.0
17	17.6	0.1
18	17.6	0.1
19	17.8	0.5
20	18.1	0.1
Avg.	17.6	
Maximum		0.7
r (repeatability)*		1.5
r (high power)**		1.0
r (gasoline)**		1.8

(c) Kerosene

Run #	Average (mg/kg)	Difference (mg/kg)
1	99.5	0.2
2	99.5	0.1
3	99.5	0.1

4	99.6	0.0
5	99.9	0.5
6	100.1	0.1
7	100.0	0.1
8	99.7	0.5
9	99.5	0.1
10	99.4	0.2
11	99.5	0.1
12	99.6	0.1
13	99.5	0.2
14	99.8	0.8
15	99.8	0.7
16	99.7	0.5
17	99.8	0.4
18	99.8	0.6
19	100.0	0.2
20	99.5	0.2
Avg.	99.7	
Maximum		0.8
r (repeatability)*		5.8
r (high power)**		4.1

* This “***r***” is defined in the text of ASTM D2622-16 and mandatory for qualification. ** This “***r***” is defined in Appendix of ASTM D2622-16 and is not mandatory for qualification.
There are three other (r) repeatability criteria. One is for high power instruments having >1000 watt X-ray sources for all types. The others are for diesel fuel and gasoline, which are not mandatory, are provided in Appendix of ASTM D2622-16.

High power: $r = 0.08681\ X^{0.8383}$ (mg/kg)

Diesel fuel: $r = 0.1037\ X^{0.8000}$ (mg/kg)

Gasoline: $r = 0.5006\ X^{0.4377}$ (mg/kg)

X: total sulfur concentration (mg/kg)

These values for the test are also shown in Table 2 (a) and Table 2 (b) for reference.
The test results shown in Table 2, where the difference of duplicated 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 for diesel fuel, gasoline and kerosene.

Conclusion

Low concentration sulfur in petroleum-based 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 strict 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