Rigaku

Application Note

XRF 5031

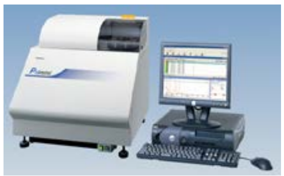
Determination of Sulfur in Bio-gasoline Using the Primini Biofuel

Application

bio-gasoline

Instrument

Benchtop wavelength dispersive X-ray fluorescence spectrometer
Primini Biofuel



Keywords

wavelength dispersive X-ray fluorescence (WDX)
bio-gasoline
biofuel
ETBE
oxygen content
sulfur

Introduction

The sulfur content in gasoline has been reduced from the view point of influence on environment and protection of automobile engines. The sulfur content in gasoline and diesel fuel is regulated below 10 ppm since 2009 in Europe.

On the other hand, utilization of non-fossil fuels such as bio-ethanol and bio-diesel has been increased in addition to effective use of conventional fossil fuels such as hydrocarbon fuels for countermeasures against global warming and creation of circulation-type society.

In production of bio-gasoline, there are two types of biofuels; one is to add ETBE (ethyl tert-butyl ether), synthesized from ethanol and isobutene, and the other is to directly add ethanol to gasoline. For example, ETBE is added to gasoline in Germany and France while ethanol is directly added to gasoline in the United States.

In X-ray fluorescence analysis, difference of additive ratio of ETBE or ethanol influences analysis results of sulfur owing to the variation of oxygen content in bio-gasoline. This note introduces a new method which has been developed to correct for the influence using scattering X-rays from samples.

Instrument

The Primini Biofuel is a benchtop wavelength dispersive X-ray fluorescence (WDX) spectrometer, which is dedicated for analysis of P, S and Cl.

The Primini Biofuel is equipped with a 50 W Pd target X-ray tube of air-cooling type, which does not require external cooling water. The tube voltage and current are 40 kV and 1.25 mA. An analyzing crystal of RX9, which gives high reflectivity of the elements of P, S and Cl, is employed. The detector used is a sealed proportional counter, which does not require the preparation of counter gas and drastically reduces background. The fluorescent X-rays from oil samples are measured under helium for the determination of the contents of the elements. The combination of features above enables extremely low detection limits for P, S and Cl to be achieved. The counting time for peak is 300 s and for background, 100 s for sulfur analysis.

For optional “Lite Matrix Correction”, additional analyzing crystal and detector are mounted on the spectrometer for the measurement of scattering X-rays from samples.

The software is developed with the ZSX software platform, featuring easy-to-use operation and modified to be dedicated for the analysis of P, S and Cl.

Sample preparation

The standard samples and unknown samples were prepared by blending di-n-butyl disulfide with paraffinic oil and alcohol. The blended oils were sufficiently mixed and 6 grams of the mixed oils were poured into plastic liquid cells for measurement. Polyester film with 2.5μm thickness (supplied from Chemplex®) was used for sample film.

Calibration and results

In making calibration for sulfur, a newly developed "Lite Matrix Correction" method was applied.
This method only requires standards for elements to be analyzed and does not require any special standards for correction. Figure 1 shows comparison of sulfur calibration curves for different base oils with and without the correction.

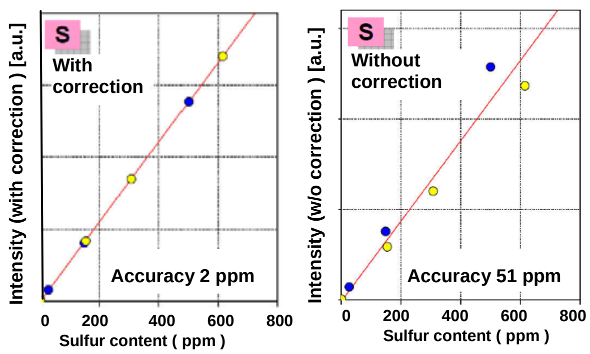


Figure 1 Calibration curves of sulfur with different base oils
- paraffinic oil base (blue)
- alcohol base (oxygen ~20%) (yellow)

The accuracy of calibration is calculated by the following formula.

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

C_i : calculated value of standard sample
$\hat{C}_i$: reference value of standard sample
n : number of standard samples

As shown in the Figure 1, the accuracy is greatly improved by applying the "Lite Matrix Correction" even for different oil matrices.

Sulfur content in oil samples containing about 5 ppm of sulfur with variety of ETBE and oxygen contents were analyzed using the calibration above as listed in Table 1. Five aliquots were prepared and analyzed for each sample for a repeatability test. As the results show, sulfur contents were accurately determined without regard to ETBE and oxygen contents.

Table 1 Analysis result of sulfur in variety of ETBE contents (repeatability test) (unit: ppm)

ETBE content	ETBE=0%	ETBE=7%	ETBE=100%
Target S content	5.25	5.18	5.24
Repeat n=1	5.31	5.25	5.39
2	5.40	5.17	5.41
3	5.53	5.34	5.19
4	5.53	5.45	5.21
5	5.55	5.13	5.58
Average	5.47	5.27	5.36
Std Dev.	0.11	0.13	0.16

Conclusions

The results above demonstrated that the benchtop wavelength dispersive X-ray spectrometer Primini Biofuel can give accurate determination of sulfur in bio-gasoline without regards to variation of oxygen content and ETBE.
The Primini Biofuel is a benchtop WDX spectrometer dedicated for trace analysis of P, S and Cl with software having simple operation user interface and the performance is comparable to large WDX spectrometer.
By adding optional "Lite Matrix Correction" function, accurate determination of sulfur can be performed for oils with variety of C/H and oxygen content.

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