Rigaku

Application Note XRF 5032

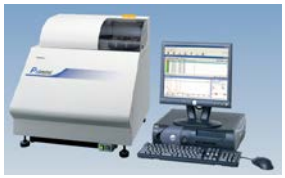
Analysis of P, S and Cl in Bio-diesel and Bio-ethanol Using the Primini Biofuel

Application

bio-diesel, bio-ethanol

Instrument

Benchtop wavelength dispersive X-ray fluorescence spectrometer
Primini Biofuel



Keywords

wavelength dispersive
X-ray fluorescence (WDX)
bio-diesel
bio-ethanol
bio-gasoline
biofuel
FAME
E100
oxygen content
phosphorus
sulfur
chlorine

Introduction

Utilization of non-fossil fuels such as bio-ethanol and bio-diesel has been increased, in addition to efficient use of conventional fossil fuels such as hydrocarbon fuels, for prevention of global warming and creation of circulation-type society.

The contents of phosphorus, sulfur and chlorine in conventional fuels have been reduced for protection of engines and catalysts in addition to the prevention of air pollution. Likewise, the contents of the elements for biofuels are regulated as shown in Table 1.

In the analysis of biofuels, content of oxygen and CH ratio influence the analysis results of these elements. We have developed a new method to correct for the influence using scattering X-rays from samples.

This note describes quantitative analysis of trace amount of P, S and Cl in biofuels using the Primini Biofuel, dedicated for P, S and Cl analysis.

Table 1 Regulated standards for biofuels (unit: ppm)

	Standard	P	S	Cl
Bio-diesel (B100*)	EN14214	<10	<10	-
	ASTMD6571-09	<10	<15	-
	JIS K 2390:08	<10	<10	^
Bio-ethanol (E100*)	EN15376	<0.5	<10	<20
	ASTMD4806-09	-	<30	<10
	JASIM361	-	<10	-

* 100% FAME is called B100 and 100% ethanol is called E100

Instrument

The Primini Biofuel is a benchtop wavelength dispersive X-ray fluorescence (WDX) spectrometer, which is dedicated for the analyses 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. The fluorescent X-rays from oil samples are measured under helium for the determination of the contents of the elements. The counting time for peak is 300 s and for background, 60 s for each element.

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

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 CRMs and reagents used for preparing standard samples and unknown samples are listed in Table 2. The blended oils for standards and samples were sufficiently mixed and then 6 grams of the mixed oils were poured into a plastic liquid cell for measurement. Polyester film with 2.5 µm thickness (supplied from Chemplex® Cat No.CH100) was used for sample film.

Table 2 Certified reference materials and reagents

CRM and reagent	Supplier
Oil analysis standard P 5000ppm	Chemplex
Di-n-butyl disulfide	Tokyo Chemical Industry
Oil analysis standard Cl 0.5wt%	CONOSTAN
Fatty acid methyl ester (FAME, B100)	VHG
Liquid paraffin	Nacalai Tesque
1-penthanol	Wako Pure Chemical Industries
1-butanol	Wako Pure Chemical Industries

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.

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 “Light Matrix Correction” even for different oil matrices. Accordingly, the same calibration can be used for both bio-diesel and bio-ethanol.

Figure 2 shows the calibration curves of phosphorus and chlorine also with the Lite Matrix Correction applied. Since a good single calibration curve can be obtained for each element without regard to CH ratio and oxygen content, the calibration can be created using standards with only white oil (liquid paraffin) as base oil for the analysis of bio-diesel and bio-ethanol.

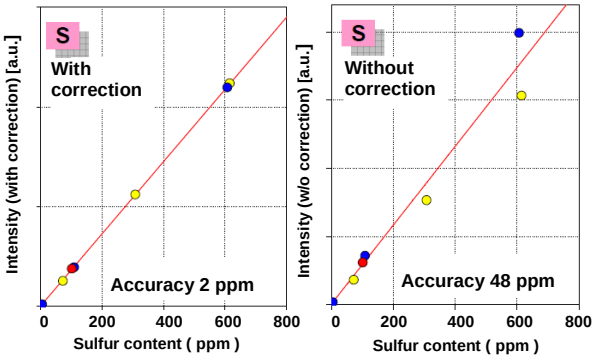


Figure 1 Calibration curves of sulfur with different base oils

- liquid paraffin
- 1-penthanol or 1-butanol
- FAME

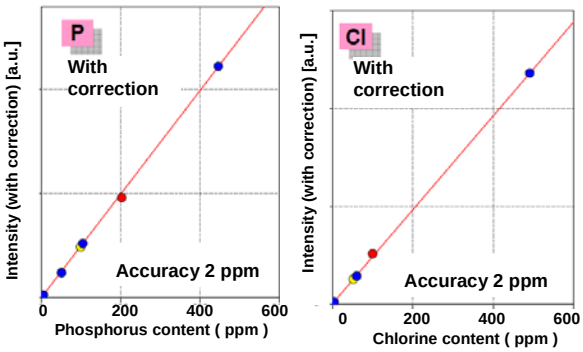


Figure 2 Calibration curves of phosphorus and chlorine with different base oils

- liquid paraffin
- 1-penthanol or 1-butanol
- FAME

Quantitative analysis results for each element in oil samples containing about 10 ppm using the calibration curves shown in Figure 1 and 2 are listed in Table 3. Five aliquots were prepared and analyzed for each sample for a repeatability test. As the results show, accurate results can be obtained for P, S and Cl in bio-diesel fuel (FAME, B100) even when the calibration created with liquid paraffin base standards are used.

Table 3 Analyzed result of P, S and Cl in FAME(B100) based oil (repeatability test) (unit: ppm)

Element	P	S	Cl
Target S content	10.4	10.4	10.1
Repeat n=1	10.50	10.40	10.23
2	10.47	11.02	10.52
3	10.72	10.59	10.34
4	10.75	11.26	10.23
5	10.09	11.19	10.88
Average	10.51	10.89	10.44
Std Dev.	0.26	0.38	0.27

Conclusions

The results above demonstrated that the benchtop wavelength dispersive X-ray spectrometer Primini Biofuel can give accurate determination for trace level of P, S and Cl for different base oils such as bio-diesel and bio-ethanol by using Lite Matrix Correction. Accordingly, blended bio-gasoline and bio-diesel can be analyzed using same calibration with the Lite Matrix Correction.

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 done for the oils with variety of C/H and oxygen content.

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