SHIMADZU
Excellence in Science

Application News

No. XRAY-002

X-Ray Analysis

Analysis of Sulfur in Petroleum Products According to ASTM D4294 & ISO 8754 using Shimadzu's EDX-7000

■ Introduction

The sulfur content of fuels is widely regulated to reduce atmospheric emissions of sulfur dioxide, or SO_2, and other sulfur oxides, or SO_x, during combustion of the fuel. Sulfur dioxide has wide-ranging negative health effects, particularly impacting the respiratory system as well as contributing to the formation of acid rain. The primary sources of SO_2 in the atmosphere are from sulfur contained in fossil fuels that are burned for power generation and transportation as well as naturally-occurring volcanic emissions. To limit SO_2 discharge into the atmosphere, various organizations and governments have imposed increasingly strict limits on the sulfur content of fuels. A recent example of this is the International Maritime Organization's (IMO) regulation set to take place in 2020 limiting the content of sulfur in marine fuel at 0.5%, reduced from the current 3.5% limit.

Because of its ease of use and minimal sample preparation, energy dispersive X-ray fluorescence, (EDXRF) spectrometry is a preferred method for the analysis of sulfur. This application note describes the use of Shimadzu's EDX-7000 for compliance with ASTM D4294 and ISO 8754.

■ Method

The method applied in this application note adheres to the methodology described in ASTM D4294, *Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-ray Fluorescence Spectrometry*, and ISO 5784, *Petroleum Products – Determination of Sulfur Content – Energy Dispersive X-ray Fluorescence*.

The measurement conditions for each standard method as well as the actual parameters used in this study are outlined in Table 1.

Several factors were assessed for method compliance, including repeatability (r), reproducibility (R), blank measurement, and a lower limit of detection (LLD).

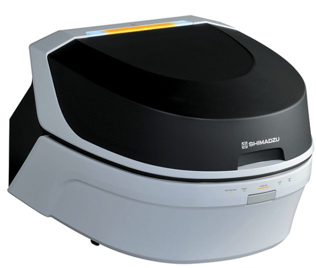

Table 1: Method specification and actual operating parameters.

Specification	ASTM D4294 Requirement	ISO 8754 Requirement	Actual Measurement Condition
Temperature	*Not Specified*	*Not Specified*	Room temperature (25° C)
Humidity	*Not Specified*	*Not Specified*	Normal Ambient Condition (~50 % RH)
Atmospheric Pressure	*Not Specified*	*Not Specified*	Normal Ambient Condition
Warm-up Time	"whenever possible the instrument is left on…"	"Continuously Switched On"	≥ 15 minutes
Sample Film	Polyester, Polypropylene, Polycarbonate, Polyimide films, "usually <10 µm"	"Normally 6 µm polyester, polypropylene, or polycarbonate"	5 µm Polypropylene
Atmosphere	*Air and Helium*	*Not Specified*	Ambient Air and Helium (99.999 % purity)
Analysis Time	100 to 300 seconds, concentration dependent	*Not Specified*	100 to 200 seconds, concentration dependent

For ASTM D4294, repeatability was assessed by analyzing one sample 20 times on the same instrument and performed by the same operator. Reproducibility was assessed by analyzing one sample 20 times on one instrument in one laboratory, and then the same sample was analyzed a further 20 times on a different instrument (of the same model) and in a different laboratory by a different operator. The result is the magnitude of the range of results for the 20 replicated about the true value, and the results were then compared to the calculated, statistical limit as per the method specifications, calculated based on equations 1 and 2. The blank was assessed by analyzing a blank sample 20 times. The blank measurement must be below 2 ppm. When analyte concentrations were ≥500 ppm, analysis was conducted with the analytical chamber purged with He and under standard atmospheric conditions. At concentrations <500 ppm, analysis was conducted only with the chamber purged with He.

$$r = 0.4347 \times S^{0.6446}$$

$$r = 1.6658 \times S^{0.3300}$$

Equation 1: Repeatability (r), in ppm, according to ASTM D4294 for base oil (a) and diesel fuel (b). The target concentration is represented as S.

$$R = 1.9182 \times S^{0.6446}$$

$$R = 1.6658 \times S^{0.3300}$$

Equation 2: Reproducibility (R), in ppm, according to ASTM D4294 for base oil (a) and diesel fuel (b). The target concentration is represented as S.

For ISO 8754, repeatability was assessed by performing two sets of 20 analyses (40 total analyses) of the same sample on the same instrument in the same laboratory by the same operator. Reproducibility was assessed in the same manner as that for ASTM D4294. The results were then compared to the calculated, statistical limit as per the method specifications, calculated based on equations 3 and 4. The analytical chamber was operated under ambient atmospheric conditions for all analyses.

$$r = 0.045 \times (S + 0.05)$$

$$r = 0.0215 \times (S + 0.15)$$

Equation 3: Repeatability (r) in weight percent (wt. %) according to ISO 8754 for sulfur in concentration range of 0.03 to 0.05 wt. % (a) and greater than 0.05 wt. % (b). The target concentration is represented as S.

$$R = 0.1781 \times (S + 0.05)$$

$$R = 0.0812 \times (S + 0.15)$$

Equation 4: Reproducibility (R) in weight percent (wt. %) according to ISO 8754 for sulfur in concentration range of 0.03 to 0.05 wt. % (a) and greater than 0.05 wt. % (b). The target concentration is represented as S.

The lower limit of detection (LLD) was calculated using equation 5.

$$LLD = 3 \times \frac{C}{NET}\sqrt{\frac{BG}{T \times A}}$$

Equation 5: Equation to calculate the Lower Limit of Detection (LLD). C is the concentration of S in ppm, NET is the fluorescent X-ray intensity of S (cps/µA), BG is the background intensity of S (cps/µA), T is the integration time (sec), and A is the current (µA).

■ Results

A summary of results of this study are presented in Tables 2 and 3 for ASTM D4294 and Tables 4 and 5 for ISO 8754.

Table 2: Results for repeatability (r) testing based on ASTM D4294 criteria.

Test	Sample	Conc.	Count Time (sec)	Method Criterion (ppm)	Result in Air (ppm)	% RSD	Result in He (ppm)	% RSD
Repeatability	Base Oil	50 ppm	300	5.4	-	-	5.0	2.89
Repeatability	Base Oil	100 ppm	200	8.5	-	-	7.1	2.08
Repeatability	Base Oil	500 ppm	200	24	16	0.89	12	0.71
Repeatability	Base Oil	0.5 wt. %	100	105	64	0.29	44	0.26
Repeatability	Base Oil	4.0 wt. %	100	405	257	0.17	159	0.12
Repeatability	Diesel	100 ppm	200	7.6	-	-	5.2	1.29
Repeatability	Base Oil	500 ppm	100*	24	23	1.26	13.5	0.72
Repeatability	Base Oil	0.5 wt. %	50*	105	80	0.35	41	0.22
Repeatability	Base Oil	4.0 wt. %	50*	402	220	0.19	91	0.12

*Analysis performed more rapidly than specified in method for given concentration.
Note: Samples represented by dashes (-) are more amenable to analysis with helium atmosphere.

Table 3: Results for reproducibility (R) testing based on ASTM D4294 criteria.

Test	Sample	Conc.	Count Time (sec)	Method Criterion (ppm)	Result (ppm) in Air	% RSD	Result (ppm) in He	% RSD
Reproducibility	Base Oil	50 ppm	300	24	-	-	5.4	2.44
Reproducibility	Base Oil	500 ppm	200	105	31	1.00	12	0.43
Reproducibility	Base Oil	4.0 wt. %	200	1776	388	0.25	667	0.09
Reproducibility	Diesel	100 ppm	200	41	-	-	17	1.85

Note: Samples represented by dashes (-) are more amenable to analysis with helium atmosphere.

Table 4: Results for repeatability (r) testing based on ISO 8754 criteria.

Test	Sample	Conc.	Count Time (sec)	Method Criterion (ppm)	Result in Air (ppm)	% RSD
Repeatability	Base Oil	0.03 wt. %	200	36	19	1.12
Repeatability	Base Oil	0.05 wt. %	200	45	23	1.23
Repeatability	Base Oil	0.2 wt. %	100	75	35	0.28
Repeatability	Base Oil	1.0 wt. %	100	247	100	0.15
Repeatability	Base Oil	4.0 wt. %	100	892	315	0.18

Table 5: Results for reproducibility (R) testing based on ISO 8754 criteria.

Test	Sample	Conc.	Count Time (sec)	Method Criterion (ppm)	Result (ppm) in Air	% RSD
Reproducibility	Base Oil	0.03 wt. %	200	143	38	0.99
Reproducibility	Base Oil	4.0 wt. %	100	3370	464	0.10

In addition to the above results, the results of measurement of 20 analyses of the blank sample yielded a maximum result of 1.9 ppm. Lower limits of detection (LLD) calculated using a 200 second integration time yield results of 5.61 ppm with a non-purged sample chamber, and 2.49 ppm with a helium-purged chamber.

■ Discussion

Calibration of the EDX-7000 with known standards yielded a linear and steep calibration curve, critical to effective quantitation (Fig. 1). Such a predictable and easily-modelled response on the instrument results in accurate and precise quantitation of unknown samples.

Repeatability results per ASTM D4294 for base oil show that the EDX-7000 can comply with the method at sulfur concentrations of ≥500 ppm using a non-purged analytical chamber and ≥50 ppm when purging the chamber with helium (e.g., Fig. 2). Furthermore, for sulfur concentrations of ≥500 ppm, the analytical time can be reduced by 50%, more stringent than the scope of the method, and still comply with repeatability requirements. For diesel fuel, repeatability complied with ASTM D4294 at sulfur concentrations of ≥100 ppm.

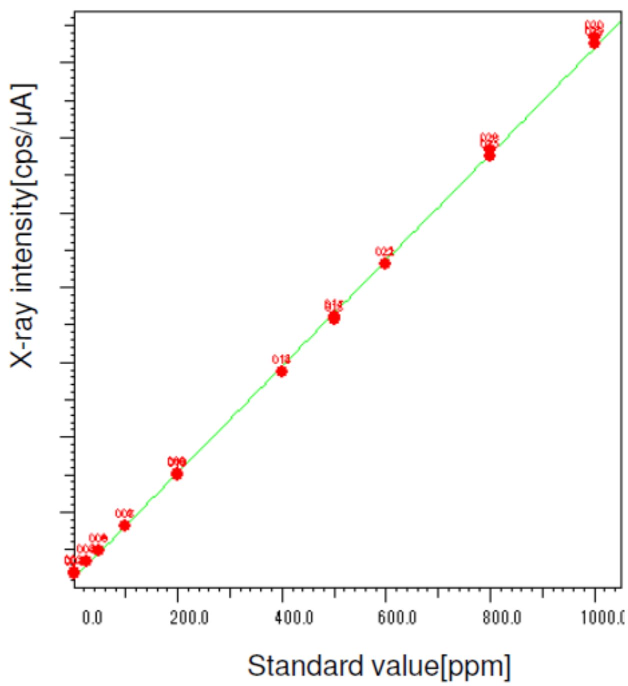

Figure 1: Example calibration curve of known samples using a helium-purged sample chamber.

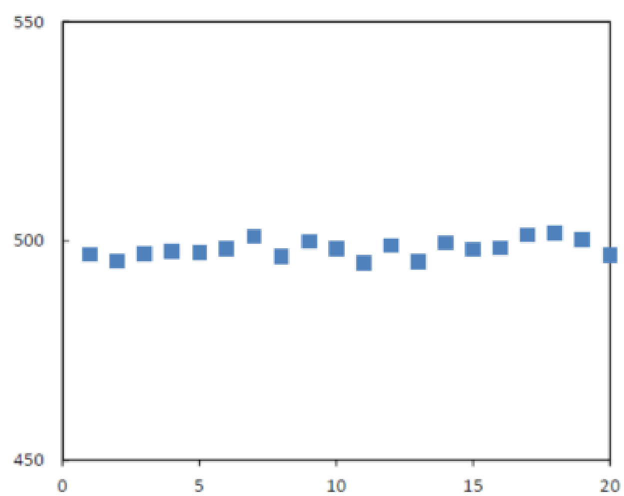

Figure 2: Repeatability of 500 ppm sulfur sample using helium-purged sample chamber.

Reproducibility results per ASTM D4294 for base oil show that the EDX-7000 can comply with the method at sulfur concentrations of ≥500 ppm using both a non-purged and a helium purged chamber. For diesel fuel, the concentration range is lower at ≥100 ppm sulfur using a helium purge.

For both repeatability and reproducibility as per ISO 8754, the EDX-7000 complied across the entire concentration range of 0.03 to 4 weight percent sulfur using ambient (non-purged) conditions.

Calculations of the LLD demonstrate sensitivity of the EDX-7000 for sulfur as low as 2.49 ppm. This concentration is far lower than the upcoming requirements of > 0.5 wt. percent (5000 ppm). Even when operating the instrument without the use of the helium-purged chamber, sensitivity was only diminished slightly, to 5.61 ppm. Again, this value is well within the scope of upcoming IMO regulations.

■ Conclusion

The method and data outlined above demonstrate the applicability of Shimadzu's EDX-7000 towards ASTM D4294 and ISO 8754 for measuring total sulfur in petroleum products. As regulations on sulfur in fuels and petroleum products become stricter, fast and easy methods for testing become increasingly important. Shimadzu's EDX-7000 provides a simple way for analysis of sulfur, and other elements, in petroleum products.

First Edition: January 2019

SHIMADZU

SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com