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Application News

Energy Dispersive X-Ray Fluorescence Spectroscopy

Controlling the Sulfur Content in Ultra Low Sulfur Diesel (ULSD) Fuels

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Introduction

Sulfur enters our atmosphere as gaseous sulfur dioxide through the burning of fossil fuels such as diesel (1)[a]. This sulfur dioxide or SO_2 affects the environment, man-made structures, our health, and even the industries that generate the toxic gas (1). Sulfur dioxide combines with water vapor in the air to form sulfurous and sulfuric acid. These acids fall back to earth in water vapor and slowly devour away stone and cement edifices, statues, and ancient ruins around the world (2). The gas easily corrodes steel and iron structures as well (3). More importantly, sulfur emissions affect our health and environment. Sulfur-laden emissions have been correlated with higher incidences of asthma, lung disease, heart disease, and bronchitis (4), (5). It is directly responsible for the particulate smog in large metropolitan cities such as Beijing and Los Angeles (6). Finally, sulfur poisons the catalysts used in oil and gas refineries and in the catalytic diesel particulate filters of vehicles that are designed to eliminate the very problem of pollution (7).

The United States (US), the European Union (EU), and Asia are slowly implementing regulations to restrict the amount of sulfur content in diesel fuels for both vehicular and, eventually, non-vehicular use. For example, the US Environmental Protection Agency (US-EPA) implemented a 15 µg/mg (or ppm) limit to be phased in beginning June 1, 2006 (8). Moreover, the EU implemented a 10 ppm limit on diesel for vehicular use in 2005 (8). The EU is expected to ratify this most stringent of sulfur regulations for all uses in 2009.

Hence, analytical testing laboratories at fast-paced production facilities and refineries are facing new challenges. In order to adhere to these new restrictions, fuel-related industries must test their oils and fuels with reliable and fast instrumentation. Moreover, the instruments must maintain high accuracy and precision at low detection levels. Unfortunately, many highly accurate tools have pronounced disadvantages. For instance, inductively coupled plasma (ICP) is one of the most accurate analytical tools for detecting elemental concentrations in the parts per billion (ppb) range. However, samples must be digested or dissolved before analysis. This process often includes high temperature ashing and hazardous, corrosive acids or bases (9). Sample preparation can also take several hours and may unknowingly introduce contamination. Today, many analytical laboratories have initiated screening

[a] Sulfur is also converted to sulfur trioxide (SO_3) and hydrogen sulfide (H_2S).

methods on less expensive instruments to expedite sampling and testing in their fast-paced environments.

Energy Dispersive X-ray Fluorescence spectroscopy (ED-XRF or EDX) is one of the best, cost-effective screening tools today. EDX has three distinct advantages as a screening tool: (1) little sample preparation, (2) short analysis time, and (3) reproducibility. For example, a typical diesel sample can be placed into the sample chamber without preparation (other than pouring the fuel into a 10 mL sample cup) and measured with printed results within 5-7 minutes. Moreover, in simple studies, a fuel with particular sulfur content can be measured repeatedly with high precision.

Objective

Reproducibly measure the concentration of sulfur in diesel fuel blend and create a typical process control routine that is easily implemented in the analytical laboratory of a plant refinery.

Materials

NIST SRM 2724b[b]	Ten sealed glass ampoules – 10 mL diesel fuel with 426.5 ppm
Analytical Services[c]	a. SDFM – 25 ppb sulfur in diesel (3L bottle) b. SEPA-P(L) – 7 ppm sulfur in diesel (1L bottle) c. SEPA-P(H) – 296 ppm sulfur in diesel (1L bottle)
Consumables	a. SPEX[d] 3529 31 mm X-Cell 22x32.0 mm overall dimension with 24.5 mm window and 8 mL maximum volume. Holders include a snap top ring to hold window film. b. SPEX 3526 Ultralene window film with 4 micrometer thickness.

Table 1: Materials

The NIST standards were used to develop the 5-point calibration curve. The Analytical Services bulk fuels (SEPA) were used to test against the standard curve. The Analytical Services SDFM bulk was used as the blank for the standard curve.[e]

Experimental

The Shimadzu EDX-720 x-ray fluorescence spectrometer was used for testing. The instrument included 1, 3, 5, and 10 mm collimators. Other options included a He kit, vacuum kit, auto-sampler, and a CCD camera for sample positioning.

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[b]National Institute of Standards and Technology, 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300; Email: srminfo@nist.gov; Phone: (301) 975-2200. http://ts.nist.gov/measurementservices/referencematerials/index.cfm

[c] Analytical Services, Inc., P.O. Box 7895, The Woodlands, TX 77387; Telephone/Fax: (281)419-9229, Toll Free: 866-419-9229. http://www.analyticalservicesinc.com/index.cfm?fuseaction=home.main

[d] SPEX CertiPrep, 203 Norcross Avenue Metuchen, NJ 08840; Phone: 1-800-LAB-SPEX extension 465 (Sample Prep). http://www.spexcsp.com/sampleprep/

[e] The SDFM sample contains 25 ppb of sulfur. This concentration is below the limit of detection for x-ray fluorescence.

Parameter	Setting	Comments
Instrument	Shimadzu EDX-720	
Power	15 kV/1000 mA, 10 mm collimation	Higher current for better light element excitation
Primary filter	Aluminum	Removal of RhLα and RhLβ_1. See figure 1.
Detector	Si(Li)	Be window
Environment	Helium	Constant purge during measurement
Calibration Curve	Five-point calibration curve 28, 14, 7, 3.5, 0 ppm	
Standards	NIST 2724b (Points 1-4) Analytical Services SDFM, <25 ppb (blank, point 5)	SRM 2724b – 10 mL sealed ampoule at 426.5 ppm
Samples	d. SEPA-P(L) – 7 ppm sulfur in diesel (1L bottle) e. SEPA-P(H) – 296 ppm sulfur in diesel (1L bottle)	
Measurement	300 seconds live counting time, 120 seconds pre-measurement He purge	

Table 2: Experimental parameters

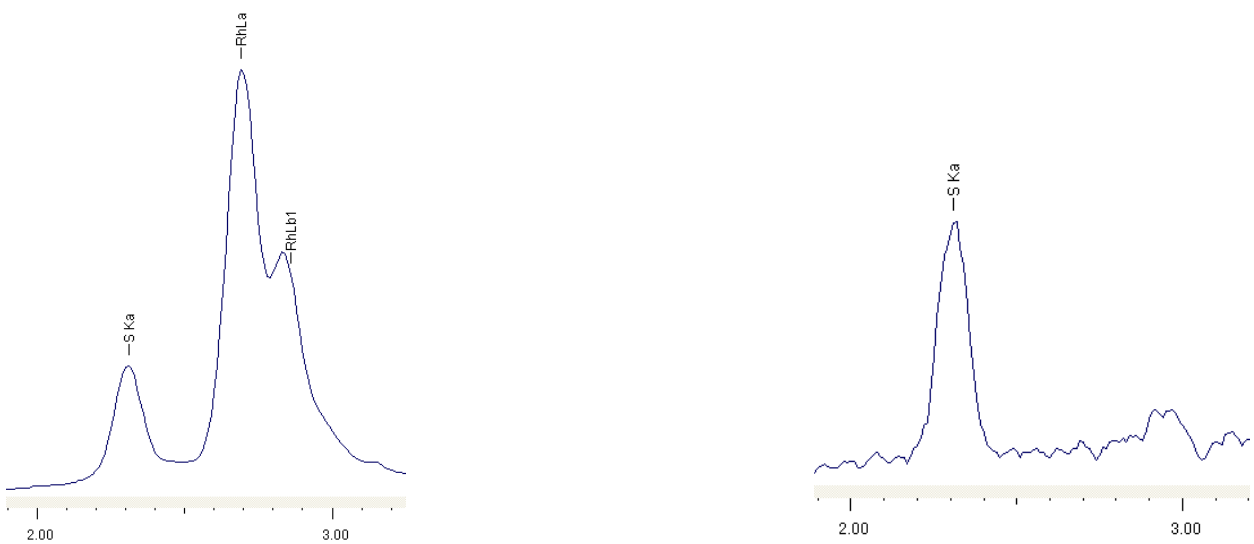

Figure 1: Sulfur peak without primary Al filter (left) and with primary Al filter (right).

Results & Discussion

Calibration Curve

Samples for the calibration curve were measured for 300 seconds under a helium-purged atmosphere. The sample chamber was initially purged for 120 seconds before measurement. Total analysis time was 420 seconds, or about 7 minutes. Two curves are shown below. The first curve used in the analysis of the unknown samples shows good linearity (figure 2). However, the second curve (figure 3) shows the nonlinearity over a wider range. The nonlinear response is due to matrix effects of the fuel. Coexistent multiple curves can be utilized at high and low ranges (figure 4) to measure samples with high variability of sulfur concentrations in order to avoid these effects. The software is easily setup to choose the appropriate calibration curve depending on sample concentration. The Critical Accuracy must be at or below 1.0000 for a reliable curve. The accuracy of the curve is better as this number approaches zero.

Figure 2 shows the accuracy as 0.2311. The results are reported and evaluated in terms of the statistics, the reproducibility, and use in a process control situation.

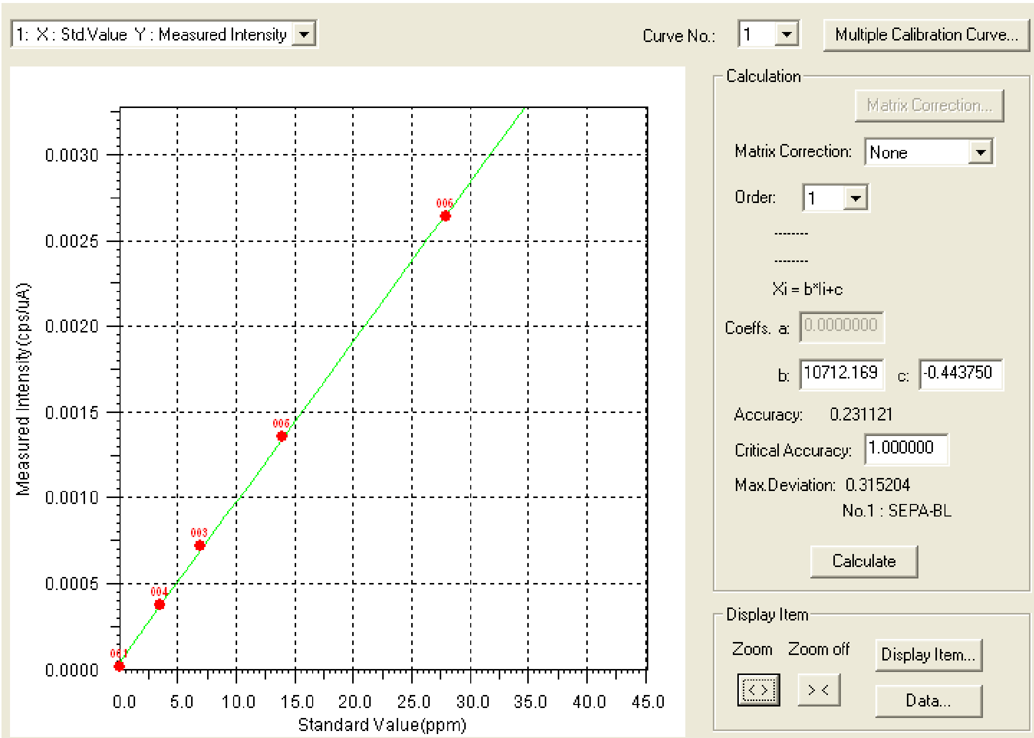

Figure 2: Calibration curve – sulfur content in diesel fuel (parts per million, ppm).

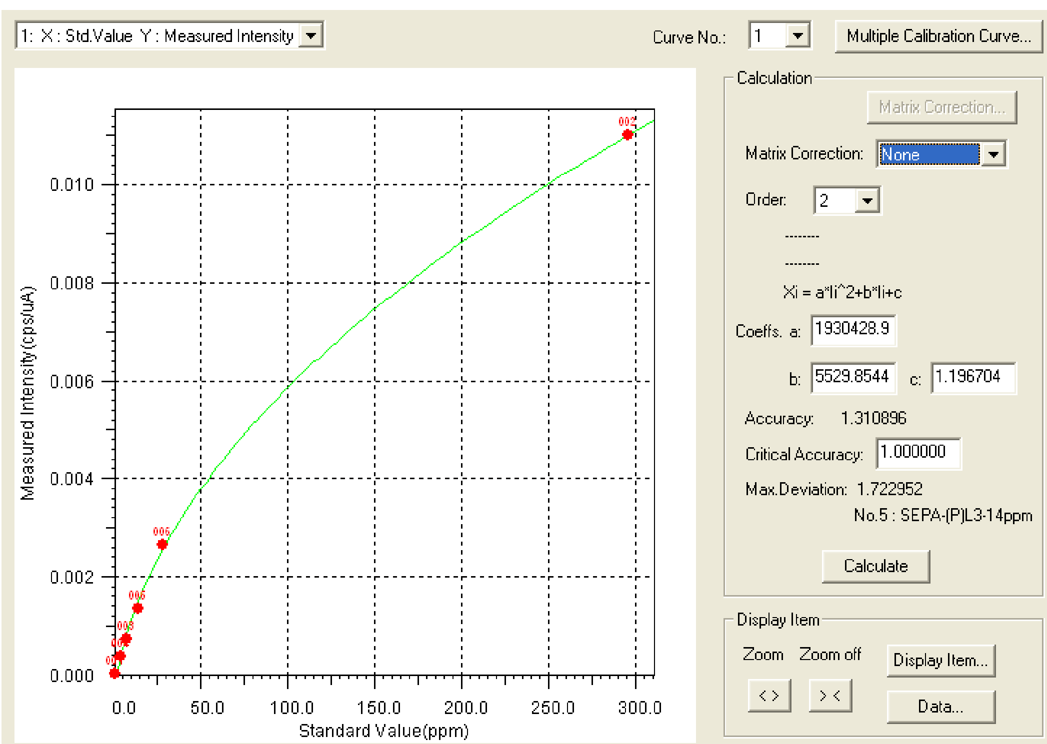

Figure 3: Extended calibration curve exhibiting the non-linearity and the requirement of two separate curves needed to examine fuels with highly variable concentrations of sulfur.

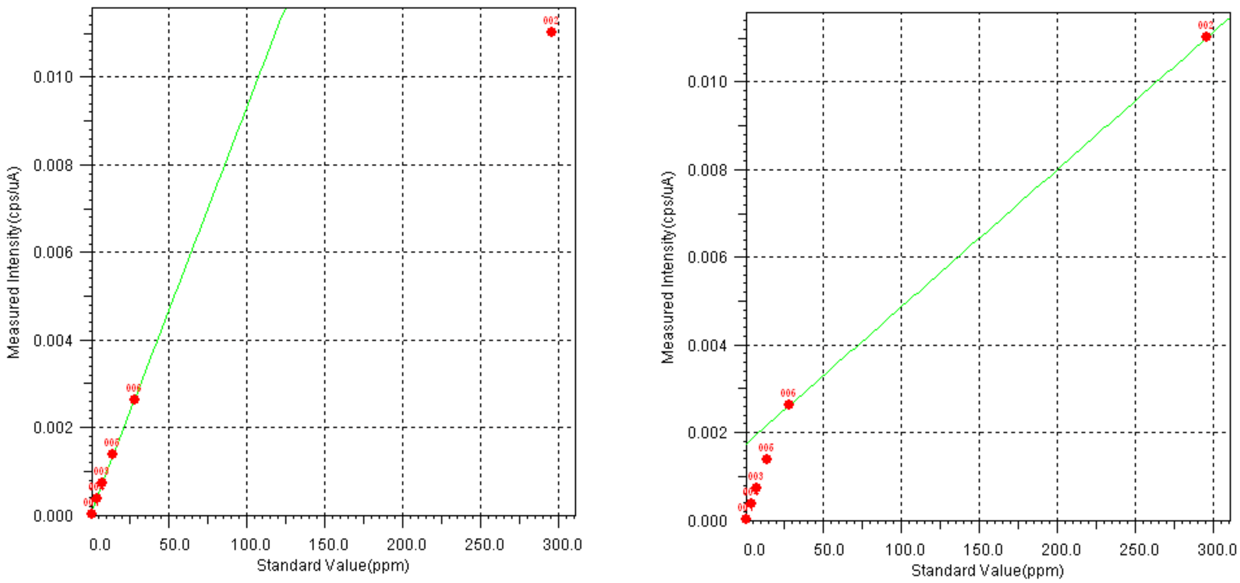

Figure 4: Example of the use of multiple curves for one element – Skα. This is a divided curve with an intensity threshold of 0.0026 cps/µA. The trend lines (green) were extended for clarity.

Statistics & Reproducibility

The sample was measured in two ways to yield the raw data listed below. First, the sample was measured "dynamically". That is, the sample was manually positioned before each measurement. Next, the measurements were performed statically. The sample was left in place and measured 10 times. All samples were measured under a constant helium purge of approximately 2 mL/min. The initial wait time after a sample was placed into the analysis chamber and the lid closed was 120 seconds.

Sample	Date	Sulfur, ppm
7ppm	8/6/2008	6.75
7ppm	8/6/2008	6.71
7ppm(01)	8/6/2008	4.59
7ppm(02)	8/6/2008	5.59
7ppm(03)	8/6/2008	9.87
7ppm(04)	8/6/2008	7.23
7ppm(05)	8/6/2008	5.84
7ppm(06)	8/6/2008	5.46
7ppm(07)	8/6/2008	7.77
7ppm(08)	8/6/2008	7.68
7ppm(09)	8/6/2008	5.97
7ppm(10)	8/6/2008	7.11
Average		*6.71*
Std. Dev.		*1.39*

Table 3: Summary of all data

Sample	Date	Sulfur, ppm
7ppm	8/6/2008	6.75
7ppm	8/6/2008	6.71
7ppm(04)	8/6/2008	7.23
7ppm(05)	8/6/2008	5.84
7ppm(07)	8/6/2008	7.77
7ppm(08)	8/6/2008	7.68
7ppm(09)	8/6/2008	5.97
7ppm(10)	8/6/2008	7.11
Average		*6.88*
Std. Dev.		*0.72*

Table 4: Summary of data excluding outliers

The average of all samples was 6.71 ppm. When the outliers were excluded the average was 6.88 ppm. There was a 4.1% error using the average (all samples) against the nominal value of 7 ppm. This shows good accuracy of the method. Moreover, the samples compared to the average show good reproducibility.

Process Control

The chart below shows the results as plotted as a "process control" chart. Engineers often place controls on the output in a typical process environment. In this case, the output is sulfur content. The hypothetical specification is 7 ppm, or about one-half the US EPA restriction of 15 ppm[f] (8). The process is within specification if the content is no higher than 9.1 ppm (+1.5σ higher than specification) or 4.9 ppm (-1.5σ lower than specification). The process may be deemed "out of control" if it surpasses a certain limit defined in the process laboratory. For example, this process is out of control if the sulfur content is above 11.2 ppm (+3σ of the specification) or below 2.8 ppm (-3σ of specification). Data points #2 and #4 (red, darker points) were out of specification but not out of control. The software is easily modified to flag the technician or manager to re-analyze the sample. Hence, the EDX-720 as a screening tool may be easily implemented in a process control environment where the specification is well below the US EPA restriction of 15 ppm.

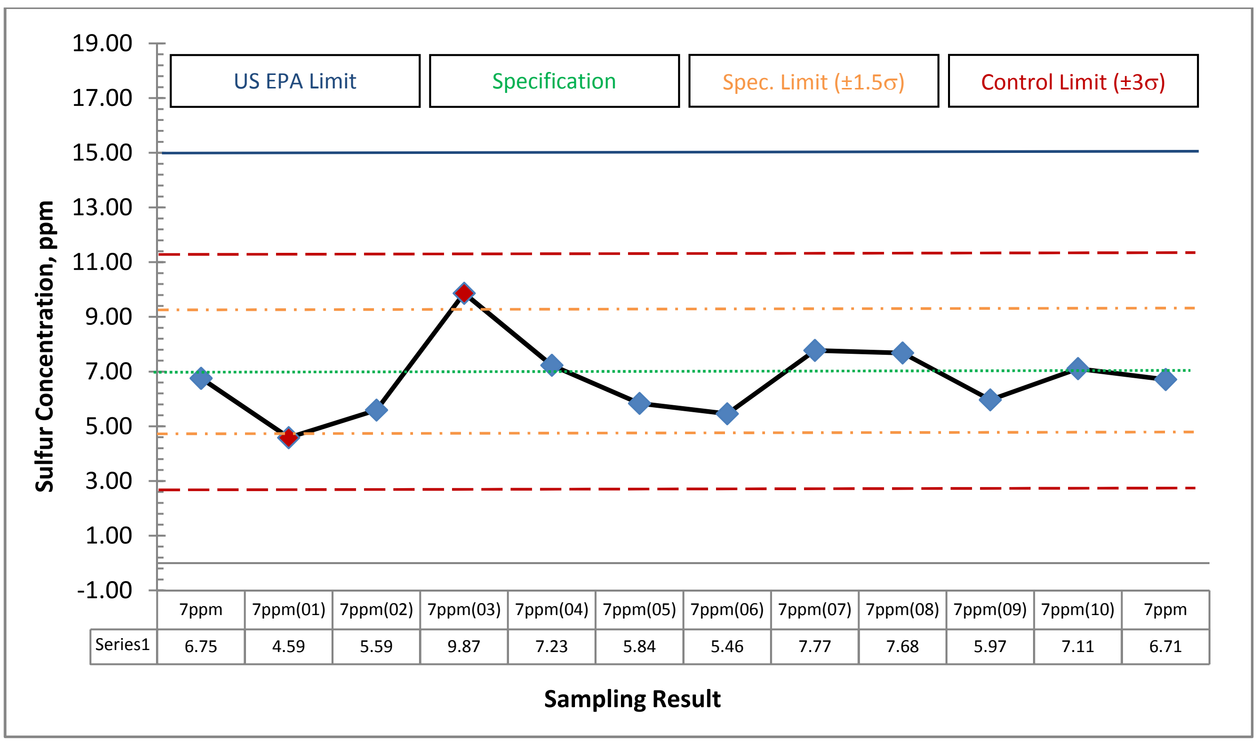

Figure 5: Example of a typical process control diagram.

[f] Facilities often employ restrictions below the actual restriction to ensure that proper levels are met. See the NIST article, reference 3 for more information.

Conclusion

The Shimadzu EDX series of energy dispersive x-ray fluorescence spectrometers are effective tools in the analysis of low ppm levels of sulfur in diesel fuel and similar matrices. This study shows that the EDX can accurately measure fuel blends with 7 ppm sulfur, approximately 50% below the US EPA restriction and 30% below the 2009 proposed EU directive. Moreover, the measurements were reproducible, both dynamically and statically. Hence, EDX can be readily utilized as a dependable, low-cost screening tool.

Some positive attributes of the EDX include a low maintenance schedule and rapid analysis time per sample (3-7 minutes). Finally, with a “footprint” of 750 (D) x 580 (W) mm the bench top EDX-720 uses very little laboratory space.

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