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## Low-Level Sulfur in Fuel Determination Using Monochromatic WD XRF—ASTM D 7039-04

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**ABSTRACT:** A monochromatic wavelength dispersive X-ray fluorescence (MWDXRF) technique has been successfully developed for measuring low-level sulfur in fuel. In this technique, two doubly curved crystal (DCC) optics were used to provide monochromatic excitation and fixed channel wavelength dispersive analysis. Using highly efficient DCC optics, compact bench top MWDXRF analyzers for sulfur analysis have been successfully produced. A new ASTM standard test method for low-level sulfur determination in diesel and gasoline, D7039-04, has been developed based on this technique. Data for ultra-low-sulfur fuel were collected and analyzed using this new method. In this paper, the results of repeatability, reproducibility, and bias are presented and discussed. The repeatability for 10-ppm sulfur fuel was shown to be around 1 ppm. The pooled limit of quantification (PLOQ) for ultra-low-sulfur diesel was found to be less than 1.5 ppm in this study. The reproducibility of 15-ppm sulfur diesel fuel was determined to be better than 3 ppm (95 % confident level). The limit of detection for a single analyzer was found to be 0.36 ppm. The effect of matrix composition was investigated. The correction due to matrix for low-level sulfur diesel and gasoline is generally not significant.

**KEYWORDS:** sulfur, diesel, X-rays, D7039, fluorescence, optics

### Introduction

To deliver low-sulfur fuel to meet the new EPA regulation, it is important to monitor the sulfur level during the fuel-refining process and transport in a pipeline terminal. X-ray fluorescence (XRF) analysis has been demonstrated to be a reliable and accurate method for on-line measurement of sulfur in petroleum processes. However, conventional XRF using energy dispersive spectrometry (EDS), without the use of X-ray optics, is limited in detection of low-level sulfur in oil due to a relatively poor signal-to-background ratio (S/B). Another serious issue for any XRF/EDS system is that the strong scattering of the primary beam from the sample can adversely inundate the energy dispersive detector resulting in large detector dead times during measurement. This limits the intensity of the primary beam due to the counting limitations of the energy detector. Alternatively, XRF with a wavelength dispersive spectrometer (WDS) gives improved sensitivity and precision over EDS systems. However, high performance WDS systems require high power X-ray tubes with water-cooling and extensive maintenances. These systems are not suitable for distribution terminal quality control and on-line applications.

XRF analysis using monochromatic excitation can provide a much better S/B than the polychromatic excitation for EDS and WDS XRF techniques described above by eliminating the scattering of bremsstrahlung (continuum X-rays) from the X-ray tube. Laboratory monochromatic XRF methods have been hindered by the lack of efficient X-ray focusing

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monochromators until recently. With innovative point-to-point focusing doubly curved crystal (DCC) optic devices [1,2], intense monochromatic focused beams can be achieved using low power compact X-ray sources. The basic configuration of a compact monochromatic WDS XRF sulfur analyzer with single channel analysis based on DCCs is shown in Fig 1. It consists of an X-ray tube, a point-focusing DCC for X-ray excitation, a sample mount, a focusing DCC for collection of characteristic X-rays from the sample, and an X-ray counter. The X-ray tube has power of 30–75 W and its spot size is in the range of several hundreds of microns. In this system, the first-point focusing DCC captures a narrow bandwidth of X-rays from the source, typically a characteristic line of the X-ray tube, and focuses an intense monochromatic beam to a small spot onto a sample. The target material of the X-ray tube is chosen to have proper characteristic line for the excitation of sulfur atoms. During sample excitation, sulfur  $K\alpha$  secondary characteristic fluorescence X-rays are emitted from the excitation volume of the sample. The second DCC, the collection crystal, collects the sulfur  $K\alpha$  X-rays and focuses them at the detector. The X-ray detector can be a proportional counter or a solid-state detector. The intensity of the detected X-rays has linear relationship with the sulfur elemental concentration in the specimen. With proper calibration, the sulfur concentration in a sample can be directly determined.

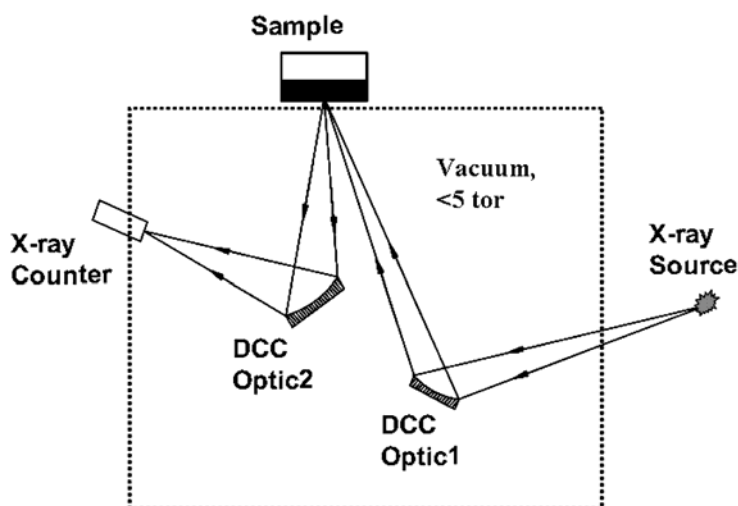


FIG. 1—*Principle of Monochromatic Wavelength Dispersive XRF for sulfur analysis.*

The most important advantage of the monochromatic wavelength dispersive X-ray fluorescence (MWDXRF) approach is that the S/B is improved by using the monochromatic excitation of the X-ray source characteristic line. The primary beam is highly monochromatic, and the bremsstrahlung photons from the X-ray tube with energies corresponding to the sulfur fluorescence peak can only reach the detector by an unlikely two-step successive scattering process. Therefore the S/B ratio is drastically improved compared to polychromatic excitation. The other advantages of this unique MWDXRF sulfur analysis system are that it has no moving parts, is very compact, and requires very little maintenance.

An ASTM standard, D 7039-04, has been recently designated for this MWDXRF technique. In this paper, data for sulfur analysis in diesel and gasoline using D7039-04 are presented and discussed.

## Materials and Methods

Samples used in this study included commercially available sulfur in diesel standards, gravimetric samples prepared in-house, NIST SRMs, and refinery diesel and gasoline products. The commercial sulfur diesel standards were gravimetrically based and were obtained from AccuStandard in New Haven, CT, and Analytical Service Inc. in Woodlands, TX. The in-house samples were made by mixing n-butyl sulfide ( $C_8H_{18}S$ ) with decalin ( $C_{10}H_{18}$ ), tetralin ( $C_{10}H_{12}$ ), or decane ( $C_{10}H_{22}$ ). The NIST SRMs included 1616a, 2723a and 2299.

Bench top MWDXRF analyzers were used in this study. Measurements were performed in two different laboratories. Five different bench top instruments were used in the XOS R&D laboratory and one instrument was used for measurements acquired in a refinery lab.

For laboratory measurements, samples were measured directly with minimal sample preparation. Prior to analysis, the samples were prepared by placing ~4 mL of liquid sample into a Chemplex XRF disposable plastic liquid sample cell fitted with a Chemplex cardboard-mounted mylar window (3.6- $\mu$ m thickness). The analytical volume of the MWDXRF method is small due to the focusing nature of the incoming X-ray beam. The full size of the excitation beam is about 1 mm x 1 mm on the Mylar window and the sulfur X-rays 1/e escape depth for fuel is ~0.1 mm. Therefore, only a small amount of the specimen near the center of the film is analyzed during measurement. The sample cell was vented immediately after sample preparation if gasoline or another volatile sample was used. The Mylar film surface was kept dust free, flat, and wrinkle free near the center area of the sample cell to avoid errors during measurement.

## Results and Discussion

### *Calibration and Linearity*

The bench top analyzer was first calibrated using commercial gravimetrically based diesel standards. Two sets of commercial diesel standards and a set of in-house prepared standards were used to generate three different calibration curves for comparison. The first set of standards, made from No. 2 diesel (Vendor A), included sulfur concentration levels of 0 ppm (blank), 5 ppm, 10 ppm, 100 ppm, 500 ppm, 1000 ppm, and 3000 ppm. The second set, made from a synthetic diesel fuel matrix (Vendor B), included sulfur levels of close to 0 ppm (blank), 20 ppm, 50 ppm, 100 ppm, 200 ppm and 500 ppm. The in-house standards were made by mixing different ratios of decalin and n-butyl disulfide ( $C_8H_{18}S$ ) gravimetrically with resulting sulfur concentration levels of close to 0 ppm (blank), 10 ppm, 48.6 ppm, 87.6 ppm, 320 ppm, and 946 ppm. The measured sulfur fluorescent X-ray intensity, in counts, for each standard is listed in Table 1.

Based on the repeatability statement in the ASTM D 7039-04 method, the precision of the MWDXRF method is a function of the concentration and it can be best fit by a square root function. Therefore, a weighted linear least square fit is needed to obtain a proper calibration curve over a wide range of concentration levels. Since X-ray counting is governed by Poisson statistics, and the uncertainty due to Poisson statistics is comparable to the precision statement of the ASTM D 7039-04 method, a satisfactory fitting result can be achieved by using the Poisson fluctuation as a weighted error bar. The linear regression function can be written as:  $Y = A + B \cdot X$ , where Y is the X-ray counts obtained in 300 s, X is the concentration, A is the calibration intercept, and B is the slope of the calibration curve. Weighted linear regression

results are compared with non-weighted fitting results (Table 2). The regression output includes the intercept, the slope, and the linear correlation probability R.

TABLE 1—*Sulfur X-ray intensity with corresponding concentration for three sets of calibration standards.*

No. 2 Diesel Set (Vendor A)		Synthetic Diesel Set (Vendor B)		In-house Set, Decalin-based	
Concentration, ppm	Measured Counts	Concentration, ppm	Measured Counts	Concentration, ppm	Measured Counts
0.2	301	0.5	291	0	244
5	943	20	3 042	10.0	1 582
10	1 611	50	7 186	48.6	6 905
100	13 965	100	14 020	87.6	1 2334
500	68 507	200	27 772	320	4 4114
1000	136 784	500	68 464	946	1 29686
3 000	407 712	...	...	...	...

TABLE 2—*Comparison of linear regression using non-weighted and weighted data.*

Calibration Set	Intercept, A, Counts		Slope, B, Counts/ppm		Linear Correlation Probability, R	
	Weighted	Non-weighted	Weighted	Non-weighted	Weighted	Non-weighted
No. 2 Diesel Standard	287 ± 13	418 ± 132	136.2 ± 0.2	135.8 ± 0.1	1.000	1.000
Synthetic Diesel Standard	234 ± 19	342 ± 57	137.1 ± 0.5	136.4 ± 0.3	1.000	1.000
Decalin-based Standard	242 ± 8	273 ± 29	136.9 ± 0.2	136.8 ± 0.1	1.000	1.000

It is clearly shown that non-weighted linear fit gives high uncertainty of the intercept. This can adversely affect the accuracy of the low ppm measurement. Particularly for the two commercial calibration standard sets, the biases for the low ppm measurements can be as much as 1 ppm if non-weighted fitting is used. The linearity of the calibration curve is exceptional for all three sets of standard. There is no significant difference among the three calibration curves. The in-house standard has the smallest fitting error. The final calibration for this study was set at  $A = 242$  and  $B = 136.9$ . The calibration line with the data points is shown in Fig. 2. The relationship between the X-ray counts and the sulfur concentration is given:  $W$  (in ppm) =  $((\text{counts}/T) - B/300)/(A/300)$ , where  $T$  is the measurement time in seconds.

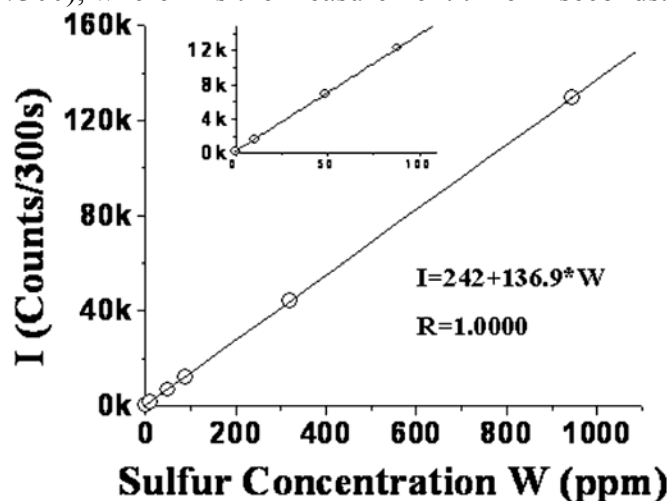


FIG. 2—*The calibration curve for a bench top sulfur analyzer: the open circles are the calibration data points and the solid line is the linear fit with weighted error bars.*

### *Repeatability and Precision*

Repeatability measurements were performed at two sites: the XOS R&D laboratory and a refinery laboratory.

### *XOS Results*

All the measurements were done with the bench top analyzer with the calibration curve shown in Fig. 2. Three bottles of diesel samples with sulfur levels of 5 ppm, 10 ppm, and 300 ppm were measured periodically over 20 days. For each measurement, a specimen was taken from a sample and placed into the bench top analyzer and a reading was obtained. Two successive measurements were performed on each day for each sample. The two successive measurements were done within 15 min. of each other. Forty measurements were obtained in total for each concentration level and the results are shown in Fig. 3. The difference between each pair of measurements, total 60 pairs, is shown in Fig. 4.

Single site repeatability can be determined from the data shown in Figs. 3 and 4. The results are listed in (Table 3). The definition of repeat measurement standard deviation is based on ASTM D 6300. There is no significant difference between the paired repeat standard deviation and the standard deviation of the 40 total measurements. This indicates that there is no observable measurement drift over 20 days. The standard deviation of the 40 measurements for the 5-ppm and 10-ppm samples are very close to the Poisson standard deviation based on the X-ray photons\counts. Conversely, at high concentrations, the Poisson fluctuation is small, and other instrumental factors become important. Table 3 shows that at 300 ppm the difference between the measured standard deviation and the Poisson standard deviation is significant. EPA recently issues the precision criteria for selecting an ASTM testing method for measuring sulfur in diesel fuel. With at least 20 tests over 20 days, the maximum standard deviations for the selected method are 0.7 ppm and 7 ppm for a 5–15-ppm sulfur diesel fuel and 200–500-ppm sulfur diesel fuel, respectively. The precision obtained above for both low-level and high-level sulfur is well within the EPA precision criteria.

### *Refinery Site Results*

Data were also collected from a different bench top sulfur analyzer at a refinery laboratory over a period of one month. Again, all the measurements were carried out with one calibration curve. For the repeatability evaluation, two diesel products and a gasoline product were used. The gasoline and one of the diesel samples contain ~ 50 ppm sulfur. The other diesel sample has ~ 10 ppm sulfur. For each sample, two successive readings were obtained within 10 min. from two different specimens by the sample operator. A total of 26, 36, and 32 pairs of results were obtained over a month for the 50-ppm diesel, 10-ppm diesel and the gasoline samples respectively. The difference between each pair was calculated and the results are shown as histograms for the three samples (see Fig. 5). The repeat measurement standard deviation and the site repeatability were found and the results are listed in Table 4.

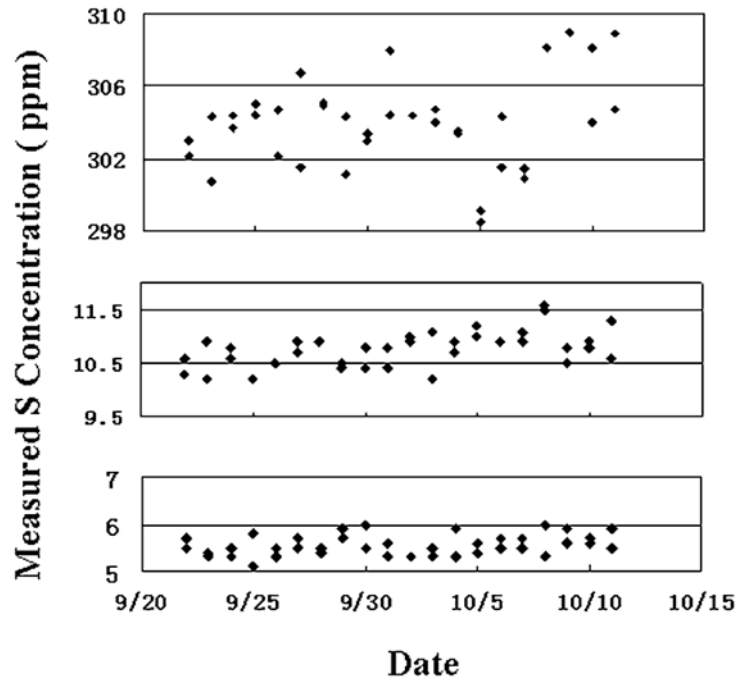


FIG. 3—Twenty pairs of repeats over 20 days for diesel samples with sulfur level at 5 ppm, 10 ppm, and 300 ppm.

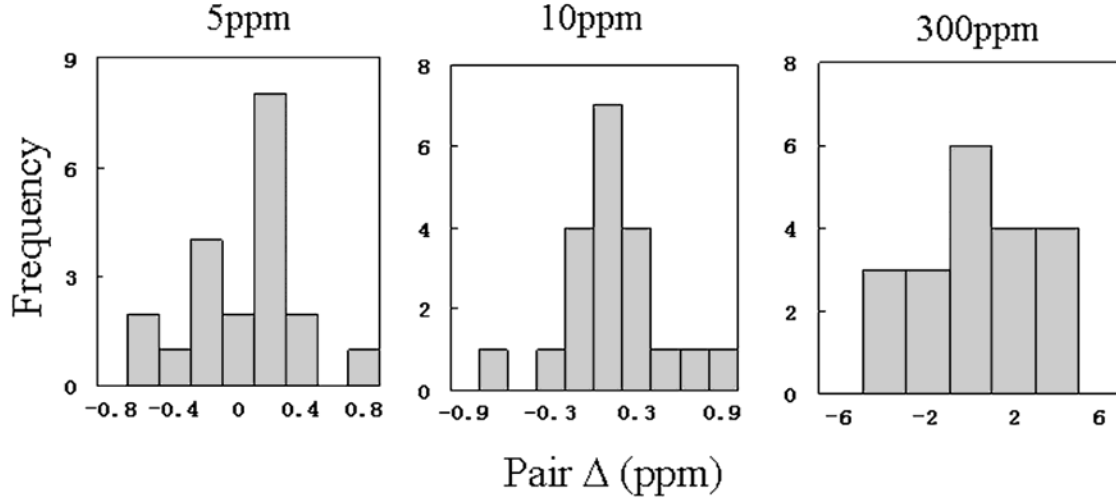


FIG. 4—The Histograms for the difference ( $\Delta$ ) between each pair at 5 ppm, 10 ppm, and 300 ppm sulfur level.

TABLE 3—Repeatability of a MWDXRF bench top analyzer for single site.

Diesel C, ppm	$\sigma$ of repeats, ppm	Repeatability, ppm	$\sigma$ of whole set, ppm	Poisson $\sigma$ , ppm
5	0.24	0.71	0.22	0.23
10	0.25	0.74	0.34	0.30
300	1.5	5.3	2.9	1.5

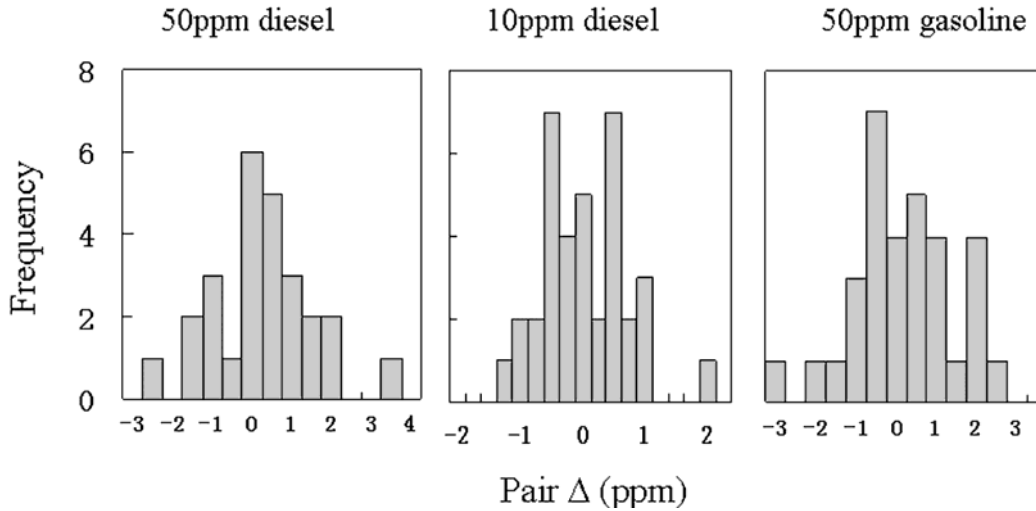


FIG. 5—Histograms for the difference between the two values of each pair.

TABLE 4—The repeat measurement standard deviation and the repeatability at a refinery lab.

Sulfur level, ppm	Repeat $\sigma$ , ppm	Repeatability, r, ppm
50, diesel	0.88	2.7
50, gasoline	0.87	2.6
10, diesel	0.46	1.3

The precision of the analyzer was also evaluated. Two gasoline samples with ~50 ppm and ~10 ppm sulfur and one diesel sample with ~10 ppm sulfur were used for the study. For each measurement, a specimen was obtained from the sample and placed into the analyzer. Each measurement was taken at least 7-h apart. A total of 26–28 measurements were carried out for each sample over the period of one month. The results for the three samples are shown as histogram plots in Fig. 6. The site precision was determined and the results are listed in Table 5. Again there is no significant difference between the repeatability and the site precision, indicating no observable drift for the instrument. The measurement results were also in good agreement with the XOS data.

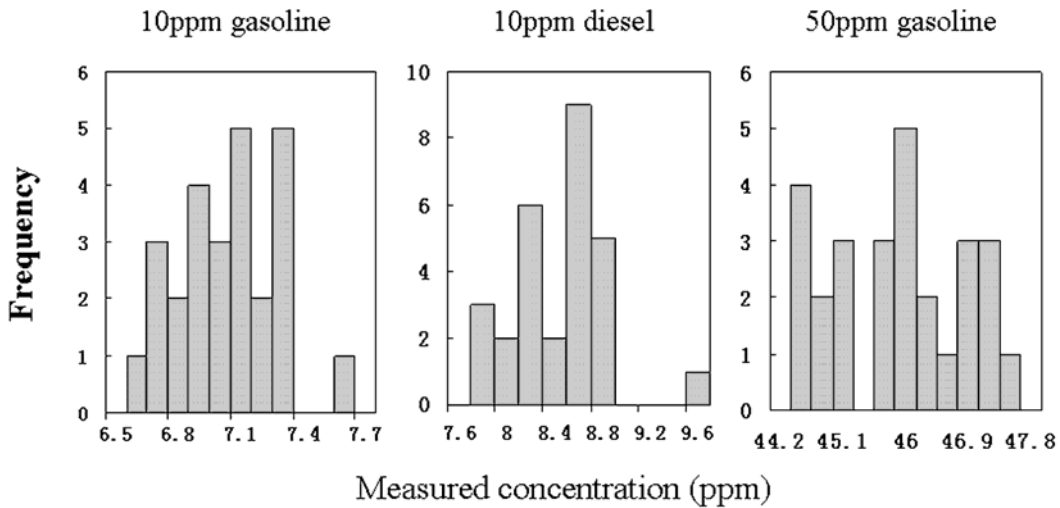


FIG. 6—Histogram plot for extensive repeat measurements on 10- and 50-ppm sulfur gasoline, and 10-ppm sulfur diesel.

TABLE 5—*Site precision for low-sulfur gasoline and diesel.*

Sulfur level, ppm	Mean, ppm	$\sigma$ , ppm	Precision, ppm
50, gasoline	45.8	0.96	2.5
10, gasoline	7.0	0.24	0.6
10, diesel	8.4	0.40	1.0

*Repeatability and Reproducibility for Ultra-low-sulfur Diesel Cross Check Samples*

An in-house round robin study was conducted using the ultra-low-sulfur diesel crosscheck samples from the ASTM D2 study group. Five bench top instruments were used with a different operator for each instrument. Calibration standards from different commercial sources were used for the calibration of these instruments. There were a total of 8 diesel samples from the crosscheck program. NIST SRM2723a was added to the 8-sample group so a total of 9 samples were used in the study. Two successive repeat measurements were made for each sample on each analyzer. The measurement results are listed in Table 6.

TABLE 6—*Measured sulfur concentrations (ppm) of the ultra-low-sulfur diesel cross check samples and SRM 2723a with five analyzers.*

Analyzer	Sample								
	ULSD04 03	ULSD04 04	ULSD04 05	ULSD04 06	ULSD04 07	ULSD04 08	ULSD04 09	ULSD04 010	SRM 2723a
A	1.26	14.50	9.94	0.39	3.26	14.30	0.31	15.51	10.00
	1.33	13.92	9.74	0.47	4.11	14.42	0.17	15.77	9.80
B	1.70	14.33	10.94	0.63	4.11	15.16	0.69	15.42	10.50
	1.55	13.66	11.13	0.68	4.14	15.54	0.48	15.32	10.40
C	1.24	13.77	10.07	0.11	4.09	16.30	0.43	15.28	10.70
	1.40	13.33	10.55	0.23	4.55	16.18	0.23	15.52	10.40
D	2.00	13.85	10.80	0.80	3.38	16.03	0.65	15.25	10.80
	1.95	14.58	10.85	0.63	3.68	16.88	0.65	13.93	9.80
E	1.40	14.60	9.60	1.00	3.90	14.00	0.60	15.80	10.10
	1.70	15.50	10.30	1.10	4.10	13.40	0.60	16.30	10.90

Following the guidelines of ASTM D 6300, repeatability ( $r$ ) and reproducibility ( $R$ ) were determined from the data shown in Table 6. The results are given in Table 7 along with the mean of each sample and the standard deviations of  $r$  and  $R$ . The repeatability results show significant improvement over that of the ASTM D 7039-04. The reproducibility results are similar to that of inter-laboratory study (ILS) in 2002 [3]. Further interlaboratory round robin studies will be needed to confirm the reproducibility.

TABLE 7—*Standard deviations, repeatability, and reproducibility for ultra-low-sulfur diesel fuel, in ppm.*

Sample ID	ULSD0 403	ULSD0 404	ULSD0 405	ULSD0 406	ULSD0 407	ULSD0 408	ULSD0 409	ULSD0 4010	SRM 2723a
Mean	1.55	14.20	10.39	0.60	3.93	15.22	0.48	15.41	10.34
$\sigma_r$	0.12	0.48	0.28	0.08	0.33	0.35	0.10	0.46	0.42
$\sigma_R$	0.29	0.64	0.56	0.33	0.40	1.21	0.20	0.63	0.40
$r$	0.44	1.75	1.03	0.29	1.19	1.29	0.38	1.68	1.53
$R$	1.05	2.33	2.05	1.21	1.45	4.40	0.72	2.28	1.45

### Accuracy and Bias

The accuracy and bias of the analyzer was evaluated using three NIST SRMs and a commercial gravimetric standard. One specimen was taken from each sample and 10 readings were recorded. The mean of the 10 data points was obtained and was compared with the reference value. The comparison is shown in Table 8. Biases for these reference samples were found to be non-significant except for the gasoline sample.

TABLE 8— *Accuracy and bias: comparison of the measured concentrations and the referenced values.*

Sample	Reference Value, ppm	Measured Value, ppm	Bias, ppm	Bias significance
SRM 1616a, kerosene	146.2 ± 1.8	149 ± 2.50	2.8	n
SRM 2723a, diesel	11.0 ± 1.1	10.8 ± 0.6	-0.1	n
SRM 2299, gasoline	13.6 ± 1.5	11.6 ± 0.6	-2.0	y
Commercial standard, diesel	300 ± 3.0	303.2 ± 3.0	3.2	n

### Matrix Effects

The absorption of both the excitation beam and the characteristic sulfur X-rays of the sample is matrix dependent. In general, the matrix effect is minor and there is no need for correction. However, if the sample measured has a high oxygen content or very different hydrogen-to-carbon H/C ratio compared to the calibrant, a correction will be necessary. Due to the monochromatic excitation, the matrix correction is simple if the major composition of the matrix is known. The primary fluorescence intensity for an element in the matrix can be simply found from the first principle for monochromatic excitation [4]:

$$I_i(E_i) = \frac{\eta(E_i)}{G_0} \frac{Q_i(E_i)I(E_o)}{(\mu(E_o) + G\mu(E_i))} W_i \quad (1)$$

where  $\eta(E)$  is detector efficiency,  $Q(E_i)$  is the fundamental parameter for element I and  $I(E)$  is the excitation beam intensity,  $W_i$  is the concentration of the element by weight,  $\mu(E)$  is the average mass absorption coefficient at energy E for the matrix, and  $G_0$  and  $G$  are geometrical factors related to the beam and sample configuration. The term  $\mu_M = (\mu(E_o) + G\mu(E_i))$  is the only parameter related to the matrix.

The current sulfur analyzer has a Cr  $K\alpha$  excitation beam and the fluorescence element is sulfur. The G factor for the beam configuration in the analyzer design is  $\sim 0.87$ . For diesel and gasoline, the matrix consists of C, H and O. Assuming their weight percentage as  $W_C$ ,  $W_H$ , and  $W_O$  respectively, the matrix effect term can be written based on the mass absorption coefficients for C, H, and O at  $E_o = 5.4\text{keV}$  and  $E_i = 2.3\text{ keV}$  [5] and is the following:

$$\begin{aligned} \mu_M &= 198W_C + 0.35W_H + 440W_O \\ &= \frac{182R_{C,H}(1 - W_O)}{(R_{C,H} + 1)} + \frac{0.35(1 - W_O)}{(R_{C,H} + 1)} + 440W_O \end{aligned} \quad (2)$$

where  $R_{C,H}$  is the C/H mass ratio in the matrix. The matrix correction factor,  $C_M$ , then can be defined as  $C_M = \mu_M(\text{specimen})/\mu_M(\text{calibrant})$ , and the correct sulfur X-ray counts of the specimen is  $I_c = C_M * I_r$ , where  $I_r$  is the recorded counts from the analyzer.

To validate Eq 2, measurements were carried out for eight gravimetric diesel standards with known C/H ratios to determine the C factor experimentally. The experimental C factor can then be compared with the C factor calculated from Eq 2. Relatively high sulfur concentration samples were used since the relative precision of the method is better for high concentration. The study results are listed in (Table 9). Measurements on gasoline samples with added ethanol were also performed to validate the effect of oxygen. The results are also given in Table 9. Please keep in mind, decalin is the matrix for the calibration material and the correction factor for decalin samples is 1.

TABLE 9—*Effects of C, H, and O composition.*

Sample	C/H ratio, $R_{C,H}$	$W_O$	Sulfur Concentration $W$ , ppm	Expected Counts, $I_a$	Recorded Counts, $I_r$	$C_M = I_a/I_r$
Diesel, Kerosene, SRM1616a	6.18	0	300	41312	41720	0.991
Decane	5.51	0	146	20229	20708	0.977
Mixture of Decane and Decalin	5.42	0	951.5	130502	135731	0.961
Decalin	6.03	0	950.55	130372	133464	0.977
Mixture of Decalin and Tetralin	6.67	0	946.1	129763	129694	1.000
Tetralin	8.09	0	948.5	130091	128036	1.016
Gasoline	9.93	0	951.5	130502	125231	1.042
Gasoline + 3.31% ethanol	6.56	0	205	28312	28032	1.005
Gasoline + 6.71% ethanol	6.68	0.0115	195.4	27384	26768	1.018
Gasoline + 8.30 % ethanol	6.81	0.0233	188.4	26294	25331	1.033
	6.85	0.0288	185.2	25966	24706	1.046

The experimental values of  $C_M$  are plot vs.  $R_{C,H}$  at different oxygen levels and compared with the theoretical value from Eq 2 (See Fig. 7). The experimental results follow the theoretical curves quite well. Therefore the theoretical curve can be used as a general guideline for practical use. The C/H mass ratio is in the range of 5.3–6.7 for diesel products and 5.7–7.3 for gasoline. If the synthetic diesel calibration set (commercial standards with C/H mass ratio of 6.18) is used, the biases due to the matrix effect will be no more than 2 % in the extreme case. The biases will be insignificant for low-sulfur diesel and gasoline, and there is no need for matrix correction. For gasoline with oxygenates, the matrix correction will also be insignificant, provided the oxygen content is less than 2 %, which corresponds to no more than ~11 % of MTBE or ~6 % of ethanol.

#### *Limits of Detection*

The minimum limits of detection of an analyzer can be determined by measuring the standard deviation of the background. Decalin was used for background measurement. Twenty repeat measurements were carried out on this sample and the measured X-ray intensities are given in

Fig. 8. Each measurement was done with a 300s counting time. The average X-ray counts in 300s for the background is  $B = 241$  counts with standard deviation of  $\sigma_B = 16.9$  counts. From the calibration curve in Fig. 2, the background can be written in term of ppm:  $\sigma_B = 16.9 / A = 0.12$  ppm. Therefore the minimum detection limit is given as:

$$LOD = 3\sigma_B = 0.36 \text{ ppm}$$

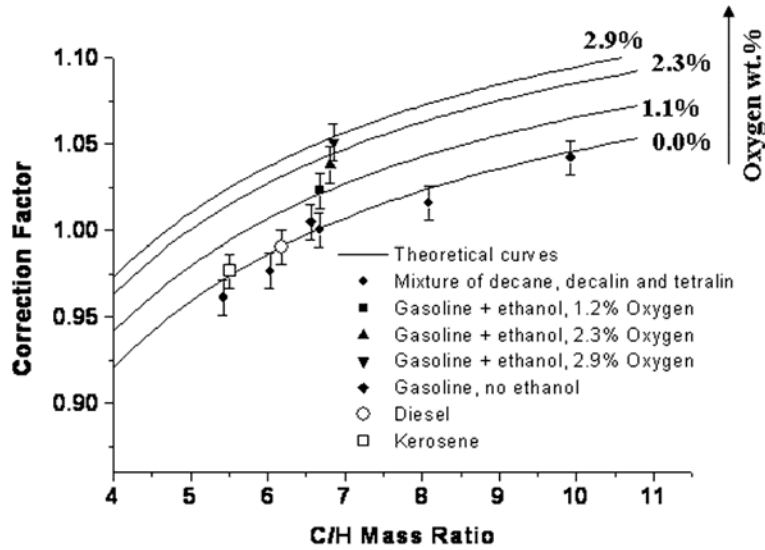


FIG. 7—Matrix effects: measured correction factor and the theoretical correction curves for C/H mass ratio and total oxygen wt. %

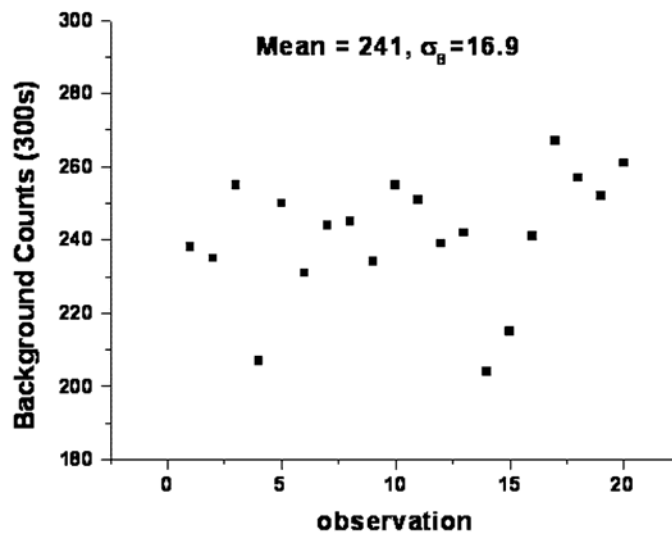


FIG. 8—Measured background X-ray counts.

## Conclusion

Compact bench top analyzers have been successfully produced for low-sulfur determination in fuel. A new ASTM method, D 7039-04, was the basis for the study in this paper. The bench top analyzer provides a wide dynamic range for sulfur measurements. The linearity of the technique is excellent and it holds from 0–3000 ppm. During the calibration, linear regression with a weighted error bar is necessary for obtaining good accuracy for low ppm sulfur measurements. The repeatability for 10-ppm sulfur in fuel was shown to be around 1 ppm. The PLOQ for ultra-low-sulfur diesel was found to be less than 1.5 ppm in this study. The precision of an analyzer over one month without further calibration remains the same as that of repeat measurements taken over very short intervals, such as minutes. The reproducibility of 15-ppm sulfur diesel fuel was determined to be better than 3 ppm (95 % confident level). The limit of detection for a single analyzer was found to be 0.36 ppm. The correction factor due to matrix composition was measured and compared to the theoretical curve. The correction factor predicted by the theoretical curved is accurate within the measurement error. The correction due to the matrix for low-sulfur diesel and gasoline is generally not significant.

## Acknowledgments

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