Determination of Sulfur in Biodiesel and Petroleum Diesel by X-ray Fluorescence (XRF) Using the Gravimetric Standard Addition Method−II[†]

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Sulfur in petroleum diesel is typically detected by wavelength dispersive X-ray fluorescence (XRF) spectrometry by comparing the response of the unknown to a linear calibration curve composed of a series of matrix-identical standards. Because biodiesel contains about 11% oxygen by mass and diesel is oxygen-free, the determination of sulfur in biodiesel using petroleum diesel calibrants is predicted to be biased $\sim -16\%$ due to oxygen absorptive attenuation of the X-ray signal. A gravimetric standard addition method (SAM) was hypothesized to overcome this bias because it should be matrix-independent. Samples of both petroleum diesel (SRM 2723a and European Reference Material EF674a) and biodiesel (candidate SRM 2773, NREL 52537, and NREL 52533) were analyzed, comparing the traditional calibration curve method to the gravimetric SAM approach. As expected, no significant difference was found between the two methods when measuring sulfur in petroleum diesel. Sulfur determinations in biodiesel with petroleum diesel calibrants were lower by $\sim 19\%$ relative to the gravimetric SAM at the 3, 7, and 12 μg/g levels. It is concluded that XRF using gravimetric SAM yields accurate sulfur measurements in biodiesel samples. In addition, the gravimetric SAM approach is insensitive to differences in the C/H ratio.

Introduction

The maximum allowable sulfur content in U.S. on-highway diesel fuel was lowered to 15 μg/g in June 2006.[1] The sulfur content of biodiesel is typically lower than 15 μg/g but ranges from $\sim$0.2 to $\sim$25 μg/g depending upon the feedstock and the supplier.[2] Accurate and precise sulfur determinations at these levels present a challenge to the petroleum industry. Wavelength dispersive X-ray fluorescence (XRF) spectrometry has been the method of choice because it is rapid, precise, inexpensive, and accurate if properly calibrated. Calibration consists of a response curve based on a series of standards or certified reference materials (CRMs) of different concentrations. For a straight-line calibration curve, the response of the unknown is then compared to the calibration curve and the concentration calculated from the relation

$$[S] = \frac{\bar{y}_{sample} - \beta_0}{\beta_1} \qquad (1)$$

where β_0 and β_1 are the intercept and slope calculated by weighted least-squares regression and $\bar{y}_{sample}$ is the mean sample response. Sulfur determinations in biodiesel present additional problems because there are currently no biodiesel CRMs. Also, biodiesel contains $\sim$11% (mass fraction) oxygen that causes absorptive attenuation of the sulfur signal relative to petroleum-based diesel, which is essentially oxygen-free. Theoretically, sulfur determinations in biodiesel using petroleum diesel for calibration are predicted to be biased low by $\sim$16% relative.[3] Consequently, the American Society for Testing and Materials (ASTM) specification for biodiesel (D6751-06a) cautions against using XRF for sulfur determinations.[4]

The purpose of this study was to assess experimentally the predicted bias and investigate the performance of the gravimetric standard addition method (SAM) described in paper I,[5] which in theory is matrix-independent.

Experimental Section

All determinations were performed on an X-ray Optical Systems SINDIE 4000 monochromatic wavelength dispersive XRF instrument specifically designed for the measurement of sulfur in liquid fuels. This instrument is very similar to the newer SINDIE 7039 described in detail by Chen.[3] The spectrometer design incorporates crystal monochromators for both the primary and secondary X-ray beam to improve selectivity and decrease the background. A standard three-place top-loader balance was used for gravimetric mass determinations above 1 g. A five-place balance was used below 1 g.

All samples were measured for 300 s using 37 mm polyethylene cells with 3.6 μm polyester film as specified by the manufacturer.

(1) Federal Register. Rules and Regulations, Part III Environmental Protection Agency 40 CFR Part 80. May 1, 2006; Vol. 71, number 83.

(2) American Petroleum Institute. Backgrounder on renewable fuels for diesel engines. June 29, 2006 (http://www.api.org/aboutoilgas/otherfuels/upload/renewablefuelsdiesel.pdf).

(3) Chen, Z. *J. ASTM Int.* **2005**, *2*, 8.

(4) American Society for Testing and Materials (ASTM). ASTM D6751-06a; p 4.

(5) Kelly, W. R.; MacDonald, B. S.; Guthrie, W. F. *Anal. Chem.*, in press.
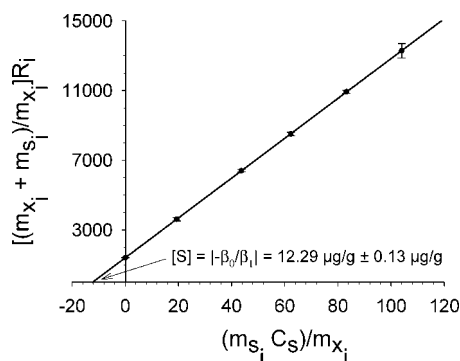
Figure 1. Gravimetric standard addition determination of sulfur in NREL biodiesel sample 52533. Error bars on points are one standard deviation ($n = 6$). C_s is the sulfur concentration in the "spike"; m_{si} and m_{xi} are the masses of the "spike" and unknown sample; and R_i is the instrument response of the ith sample. The uncertainty given with the sulfur concentration is an expanded uncertainty with an approximate confidence level of 95%.

All mixing and additions were made directly in these cells. The raw response counts were recorded and regressed by weighted linear least-squares using an Excel Least-Squares Add-In.[6] From this calibration line, the sulfur content of each unknown was calculated. Biodiesel unknowns included NIST candidate SRM 2773 and two biodiesel samples from the National Renewable Energy Laboratory (NREL).

Calibration samples were prepared from gravimetric mixtures of the following NIST diesel SRMs as well as their neat counterparts as described recently[7] (NIST CRMs [certified values $\mu g/g \pm U$; U is the expanded uncertainty], RM 8771 [0.071 ± 0.014], SRMs 2723a [11.0 ± 1.1], 2770 [41.57 ± 0.39], 2724b [426.5 ± 5.7], and 1624d [3882 ± 20]). The choice of standards used in each case was based on estimates of the unknown sulfur concentration; calibration samples were gravimetrically prepared to bracket the unknown using binary mixtures of SRMs that yielded the lowest uncertainties.[7,8]

All gravimetric standard addition samples were prepared by spiking $n - 1$ ($n = 5$ or 6) samples of the unknown with SRM 1624d, a high-sulfur diesel fuel, which introduced negligible changes to the matrix. It was gravimetrically added to ~4 g of biodiesel using a plastic syringe to deliver 1–5 drops (~0.032 g/drop). The sulfur content of the unknown was calculated from the slope and intercept of the weighted regression from the relation

$$[S] = \left| \frac{-\beta_0}{\beta_1} \right| \tag{2}$$

Figure 1 illustrates the geometric interpretation using actual data from a biodiesel determination.

The performance of the XRF and the gravimetric procedures used for both the calibration samples and gravimetric standard addition samples were assessed using SRM 2723a, European Reference Materials ERM-EF673a and ERM-EF674a, and uncertified LGC 3022.[9] The sulfur contents of SRM 2723a and EF674a were also determined by gravimetric standard additions using SRM 2770 as a spike to verify the accuracy of the SAM design.

Results and Discussion

Replicate sulfur determinations in three biodiesels and two petroleum diesel CRMs using the traditional calibration curve

Table 1. Sulfur Determination in Biodiesel and Diesel Samples Based on Calibration Curves

sample	[S] ($\mu g/g$)	U^a	k^a	v_{eff}	$u_c{}^a$	m^b	n^b
Biodiesel Samples							
SRM 2773 (Candidate)							
SRM 2773−1	6.04	0.19	2.44	6.05	0.079	6	4
SRM 2773−2	6.17	0.26	2.46	5.85	0.11	6	4
SRM 2773−3	6.18	0.15	2.37	6.95	0.064	6	4
SRM 2773−4	6.42	0.36	2.47	5.77	0.15	6	4
Unknown Biodiesels from NREL							
NREL 52537	2.86	0.22	2.50	5.52	0.086	6	6
NREL 52533	9.78	0.29	2.38	6.84	0.12	6	6
Petroleum Diesel Samples							
SRM 2723a (Certified Value 11.0 ± 1.1)							
SRM 2723a	10.68	0.48	2.53	5.27	0.19	6	5
European Reference Material EF 674a (Certified Value 11.0 ± 0.9)							
EF674a−1	11.44	0.18	2.45	5.95	0.075	5	4
EF674a−2	11.48	0.36	2.42	6.29	0.15	6	4

^{a} U is the expanded uncertainty expressed as an approximate 95% confidence interval; $U = ku_c$, where u_c is the standard uncertainty and k is the coverage factor obtained from Student's t distribution with v_{eff} effective degrees of freedom.[8] ^{b} m is the number of replicates on each of n calibration samples.

Table 2. Sulfur Determinations in Biodiesel and Petroleum Diesel Samples Based on the SAM^a

sample	[S] ($\mu g/g$)	U	k	v_{eff}	u_c	m	n
SRM 2773−4	7.49	0.39	2.78	4	0.14	6	6
SRM 2773−5	7.75	0.52	3.18	3	0.16	6	5
NREL 52537	3.59	0.26	2.78	4	0.093	6	6
NREL 52533	12.29	0.13	2.78	4	0.046	6	6
SRM 2723a	10.94	0.34	3.18	3	0.11	6	5
EF674a−3	11.69	0.92	3.18	3	0.29	6	5

^{a} See the footnotes in Table 1 for an explanation of the column headings.

approach are given in Table 1. The number of calibrants, n, is given in the last column, and the number of replicate determinations, m, is given in the penultimate column. All data were subjected to the Grubbs outlier test using a significance level of 0.05; one measurement of ERM-674a failed (see Table 1). It was assumed that the data conformed to Poisson counting statistics, and the weights used in all cases were proportional to $1/C_i$, where C_i is the sample concentration. For the SAM approach, C_i was determined iteratively. The effective degrees of freedom (v_{eff}) were calculated from the Welch−Satterthwaite formula, taking into account the variances of the unknown, the slope, the intercept, and the covariance of the last two quantities. All determinations have expanded uncertainties, expressed as approximate 95% confidence intervals, well below 1 $\mu g/g$, which are comparable to or better than those obtained by isotope dilution mass spectrometry at similar concentration levels.[9–11] There was excellent agreement among replicates.

To address the oxygen-induced bias issue, the sulfur contents of the three biodiesels were determined by SAM. This method has been used very successfully and almost exclusively with aqueous solutions to overcome matrix interferences. A graphical representation of this procedure is shown in Figure 1 for NREL sample 52533. The results of these experiments are tabulated in Table 2. The expanded uncertainties are well below 1 $\mu g/g$. A comparison of the two approaches is summarized in Table 3 which juxtaposes the results obtained from a traditional calibra-

(6) Kromer, P. LeastSquaresAddIn, Microsoft Excel, 1999 (http://mrflip.com/resources/ExcelFunctions/).

(7) Kelly, W. R.; MacDonald, B. S.; Leigh, S. D. *J. ASTM Int.* **2007**, *4*, 2.

(8) Taylor, B. N.; Kuyatt, C. E. Guidelines for evaluating and expressing the uncertainty of NIST measurement results. National Institute of Standards and Technology (NIST) Technical Note 1297, 1994 (http://physics.nist.gov/Pubs/guidelines/TN1297/tn1297s.pdf).

(9) Hearn, R.; Berglund, M.; Ostermann, M.; Pusticek, N.; Taylor, P. *Anal. Chim. Acta* **2005**, *532*, 55–60.

(10) Kelly, W. R.; Vocke, R. D.; Mann, J. L.; Turk, G. C. *Metrologia* **2007**, *44*, 08008.

(11) Certificate of Analysis for NIST SRM 2723a (https://srmors.nist.gov/view_cert.cfm?srm=2723A).

Table 3. Bias between Calibration Curve and SAM Determinations

	calibration curve method			gravimetric SAM method			
sample	[S] (μg/g)	u_c	v_{eff}	sample	[S] (μg/g)	u_c	v_{eff}	bias %[a]

sample	[S] (μg/g)	u_c	v_{eff}	sample	[S] (μg/g)	u_c	v_{eff}	bias %[a]
				Biodiesel Samples				
				SRM 2773				
mean[b]	6.20	0.053	16.60	1	7.49	0.14	0	−17.2 ± 4.2
				2	7.75	0.16	3	−19.9 ± 5.1
				NREL 52537				
1	2.86	0.086	5.52	1	3.59	0.093	4	−20.3 ± 7.1
				NREL 52533				
1	9.78	0.12	6.84	1	12.29	0.046	4	−20.4 ± 2.4
				Petroleum Diesel Samples				
				SRM 2723a				
1	10.68	0.11	5.27	1	10.94	0.11	3	−2.4 ± 3.3
				EF674a				
1	11.44	0.075	5.95	1	11.69	0.29	3	−2.1 ± 7.5
2	11.48	0.15	6.25					−1.8 ± 7.2

[a] Bias values were estimated by dividing the calibration curved derived result by that from the SAM minus 1 multiplied by 100. Expanded uncertainties at the 95% confidence level for the bias were calculated from the respective u_c values using effective degrees of freedom computed via the Welch−Satterthwaite formula.[12] The theoretically predicted bias for SRM 2773 is −16%. [b] The mean value was computed as a mean of means from the four data in Table 1.

tion curve with those obtained by SAM. For the biodiesel samples, there is an apparent −18 to −20% bias in the sulfur concentration relative to the commonly used calibration curve method.

The sulfur contents of petroleum diesel CRMs, SRM 2723a and EF674a, were also measured by the calibration curve method and SAM as a check on the validity of this approach and are consistent with the certified values as shown in Table 4. For these petroleum diesel samples, there are no resolvable differences between the two approaches.

Conclusions

The bias in sulfur measurements of biodiesel by XRF using calibration curves with petroleum diesel calibrants is experimentally demonstrated to be ∼ −19% at the 3, 7, and 12 μg/g levels (Table 3), in close agreement with the theoretical prediction.[3] It is demonstrated that the oxygen matrix effects can be overcome with SAM as shown in Table 3 and Figure 1.

(12) Guthrie, W. F. Proceedings of the 8th International Conference on Temperature: Its Measurements and Control, 2:887892, 2002 (http://www.itl.nist.gov/div898/pubs/author/guthrie/guthrie-2002-01.pdf).

Table 4. Summary of Sulfur Determinations in Control Samples

	this study		certified values		
sample	[S] (μg/g)	U	[S] (μg/g)	U	bias %[a]
Calibration Curve Determinations					
SRM 2723a	10.68	0.48	11.0	1.1	−2.9 ± 7.6
EF674a−1	11.44	0.18	11.0	0.9	4.0 ± 8.6
EF674a−2	11.48	0.36			4.4 ± 8.9
LGC 3022−1	32.82	0.57	33.53[b]	0.84[b]	−2.1 ± 2.8
LGC 3022−2	32.53	0.81			−3.0 ± 3.2
			33.72[c]	0.63[c]	−2.7 ± 2.3
					−3.5 ± 2.8
			31.0[d]	1.5[d]	5.9 ± 5.3
					4.9 ± 5.5
			33.17[e]	0.48[e]	−1.1 ± 1.8
					−1.9 ± 2.4
EF673a−1	52.95	0.99	52.4	1.3	1.0 ± 3.0
EF673a−2	51.96	0.95			−0.8 ± 2.9
Gravimetric Standard Additions Determinations					
SRM 2723a	10.94	0.34	11.0	1.1	−0.5 ± 8.5
EF674a−3	11.69	0.92	11.0	0.9	6.3 ± 10.4

[a] Bias is expressed in percent relative computed by comparing the XRF measurements to the certified value or, in the case of LGC 3022, which is not certified, to the National Metrology Institute values. Expanded uncertainties at the 95% confidence level for the bias were calculated from the respective u_c values using effective degrees of freedom computed via the Welch−Satterthwaite formula.[12] For certified values without explicitly cited effective degrees of freedom, coverage factors of $k = 2$ and effective degrees of freedom of $v_{eff} = 60$ were assumed. [b] LGC determination by ID−ICP−MS.[9] [c] BAM determination by ID−TIMS.[9] [d] IRMM determination by ID−TIMS.[9] [e] NIST determination by ID−TIMS (unpublished).

Thus, while theoretical correction factors may *reduce* bias, they may not eliminate it completely. Two distinct advantages of the gravimetric SAM approach are that it neither requires the analyst to know the C/H ratio nor the oxygen content in the sample. It appears SAM is a better approach to minimize bias.

The XRF results in Table 4 show excellent agreement with values determined by isotope dilution for the four reference materials.[9,11] Of particular note is the observation that the uncertainties from XRF measurements are comparable to the certified expanded uncertainties. This suggests that the benefits of high-accuracy standards produced by the National Metrology Institutes can now be realized in the data produced in industrial laboratories using a relatively simple and inexpensive XRF instrument.