

A Method for the Preparation of NIST Traceable Fossil Fuel Standards with Concentrations Intermediate to SRM Values

¹ W. Robert Kelly, ² Bruce S. MacDonald, and ³ Stefan D. Leigh

¹ Analytical Chemistry Division
Chemical Science and Technology Laboratory

² Measurement Services Division
Technology Services

³ Statistical Engineering Division
Information Technology Laboratory

National Institute of Standards and Technology
Gaithersburg, Maryland 20899

A Method for the Preparation of NIST Traceable Fossil Fuel Standards with Concentrations Intermediate to SRM Values

W. Robert Kelly, Bruce S. MacDonald, and Stefan D. Leigh

Abstract: A procedure is presented whereby the fossil fuel community may design and mix SRMs in different proportions and thereby produce in their laboratory standards for sulfur in distillate fuel oil, residual fuel oil, and coal of almost any desired concentration with uncertainties that are calculable and traceable to NIST SRM certified values. The expanded uncertainty, U , of a binary blend is always less than the U of the component with the largest U , and in some cases it is less than either of the SRM components. Because the sulfur content of all fossil fuel SRMs was certified at NIST with high accuracy and precision by isotope dilution thermal ionization mass spectrometry, in almost all cases the total expanded uncertainties of the standards produced from binary mixtures are an order of magnitude smaller than the reproducibility of current methods used in commercial laboratories. The use of this method gives the SRM user a continuum of concentrations available for calibrants and quality control test samples. Unlike calibrants prepared from high purity components, this method enables the SRM user to create a customized series of calibrants in the fossil fuel matrix of interest. This should reduce or eliminate biases that result from differences in matrix composition among standards and unknowns.

List of Notations

Latin Symbols		Greek Symbols	
f_i	mass fraction of component i	μg	microgram or 10^{-6} grams
k	coverage factor	∂	partial derivative
M	Analyte concentration in a binary mixture	Abbreviations	
M bar	Calculated concentration of mixture	EDXRF	Energy Dispersive X-Ray Fluorescence
n	number of determinaitons	EPA	Environmental Protection Agency
s	standard deviation	CI	Confidence Interval
t	student's t	NIST	National Institute of Standards and Technology
U	Expanded uncertainty	RM	Reference Material
u_c	standard uncertainty	SRM	Standard Reference Material [®] a NIST certified reference material
U_{mix}	Expanded uncertainty calculated for a binary mixture	WDXRF	Wavelength Dispersive X-Ray Fluorescence
Var(M)	Variance in M		
v_{eff}	effective degrees of freedom calculated from the Welch-Satterthwaite equation		
X	Concentration in component x		
Y	Concentration in component y		
X bar	Mean concentration of X		
Y bar	Mean concentration of Y		

Introduction

Instrumental chemical determinations are commonly performed by measuring the response of an unknown and comparing it to the response produced by a standard of known concentration or to a response calibration curve constructed using several standards that cover the concentration range of the unknowns. A polynomial function is frequently used to interpolate between the predetermined calibration points. The accuracy and precision of the results depend on the accuracy of the standards, the precision of the method, and quantified systematic (Type B) uncertainties. One source of systematic error results from difference in response of the analyte in the sample from that in the standard. This can result from attenuation of the signal emitted or in the case where there is a sample preparation step, the yields being different for sample and standard. For example, in the determination of sulfur in liquid fossil fuels by x-ray fluorescence (XRF) it is well established that the emission of $K\alpha$ line is dependent on the C/H ratio in the sample. In the case of combustion techniques the analyte yields may not be identical for different matrices because the conversion efficiency of various forms of sulfur to SO_2 may be different. Both of these systematic uncertainties, which are difficult to quantify, can be greatly reduced or eliminated as the difference between the matrix of the standard and sample approaches zero.

Like other national metrology laboratories, NIST frequently receives requests for additional standards at concentrations specific to the needs of the user. To augment the existing suite of Standard Reference Materials (SRMs) for fossil fuels which currently include coals, cokes, crude oils, residual fuel oils, middle distillates, and gasolines, with additional standards at sulfur concentrations that might be needed by the user community would require a major effort. The approach (nicknamed the *Designer Method*) presented in this paper is intended to solve this problem. It will permit the user to design and prepare standards at any concentration desired and with uncertainties that can be calculated and traced to NIST SRM certified values. This is an excellent example of transfer of the high accuracy capability of isotope dilution thermal ionization mass spectrometry (IDTIMS), a method which requires expensive instrumentation and is labor intensive, to the user community via SRMs which permits finite resources to be leveraged to meet a broad continuum of need. This approach could be implemented immediately with existing SRM stocks, and be maintained in the future with fewer SRMs and a much smaller expenditure of resources. Standards at the level of accuracy obtained by IDTIMS are necessary for this method to be useful. The well established technique of IDTIMS determination of sulfur will be able to meet the accuracy requirements both now and into the foreseeable future.¹⁻³ The method proposed here will permit exact matrix matching of sample and standard at almost any concentration desired. This capability will permit the analyst to reduce the numeric interpolation to zero with a concomitant reduction in uncertainty. Although we focus exclusively on sulfur in fossil fuels, the method is also being developed for other analytes in fossil fuels such as mercury.

Reduction of the sulfur content in diesel and gasoline motor fuels is the single most important factor in efforts to reduce primary and secondary air pollution from existing and future diesel and gasoline engines. The International Council on Clean Transportation (ICCT)⁴ states the following:

Worldwide, many jurisdictions have recognized the public health and environmental costs of allowing motor vehicle fuels to contain high levels of sulfur. The European Union, United States, and Japan have led the way in sulfur reduction, and will reach near-zero sulfur levels later in this decade.

In addition to the ICCT, statements similar to the above have been made by the EPA and the World Wide Fuel Charter⁵ and numerous trade organizations including the Alliance of Automobile Manufacturers and the Engine Manufacturing Association. The regulated upper sulfur limit in US on-road diesel fuel was dropped to 500 µg/g in 1993, and in June 2006 it was reduced to 15 µg/g. A further reduction to near-zero (< 5 µg/g) could be proposed before the end of this decade. Japan and Europe adopted a 50 µg/g limit in 2004 and 2005. Europe will phase in a 10 µg/g limit between 2005 and 2009 and Japan will adopt the same limit in year 2007. The incremental measurement challenges increase non-linearly as sulfur concentrations decrease from 500 to near zero levels. As the sulfur levels drop the demand for calibration standards will increase both in number and absolute accuracy. Petroleum refineries will need to ensure they are in compliance with regulations, but at the same time they will want to avoid reducing the sulfur content more than required because of the high costs of desulfurization by hydrogenation. The preparation of only three or four diesel fuel standards by NIST will permit the user community to prepare gravimetrically for themselves a continuum of concentrations between the end members which will meet all requirements that might arise both now and in the future. In principle, the minimum number to cover an entire range of need would be two SRMs for a given matrix - one on the low side and one on the high side of the range needed.

Almost all the methods used for sulfur in fossil fuel must be externally calibrated, and in many cases it is necessary to matrix match standards and unknowns to obtain bias-free results. The EPA is moving towards a Performance Based Quality System approach for the determination of sulfur in diesel fuel. This means that an analytical laboratory need not use only an EPA method for compliance, but may employ other methods demonstrated to yield accurate results. If these methods are sufficiently well calibrated, then they are considered to demonstrate the requisite accuracy. Likewise the sulfur content of coal and residual fuel oil must be determined accurately by both buyer and seller to ensure compliance with EPA regulations for sulfur emissions and contract specifications.

The “Designer” Method

This *Designer* method for making standards at user defined concentration levels is a simple, but effective, method of meeting calibration and quality control sample needs. Take two miscible diesel or kerosine SRMs and mix them gravimetrically to yield any target sulfur concentration between the two end member concentrations. This permits essentially a continuum of concentrations to be prepared between the two end member concentrations, and solves the long-standing problem of meeting and satisfying the demand for diesel fuel standards of many different sulfur concentrations. The actual preparation of the gravimetric mixes should be straightforward and their accuracy can be checked. It requires only a four-place balance with an uncertainty of less than 0.5 mg (see Appendix A). Ampoules could be poured directly into wide-mouth bottles on a balance because it is not necessary to mix to a specified value, but rather only necessary to be near a specified value and to know the mass of the mixing proportions accurately. After additions to the bottle it should be closed and mixed completely.

In this proposed method the two SRMs are of a same matrix; therefore, there is no change in the resulting matrix of the mixture, no matter the relative proportions. This is extremely important in matrix dependent methods, like XRF, a common and widely used technique. For example, XRF is subject to bias if there are differences in the C/H ratio between standards and unknowns.⁶ This method of making calibrants avoids this problem. The accuracy of the blends would need to be checked by measuring the blends and comparing the interval between the measured values of the successive blends to the interval between their corresponding gravimetric value (NIST traceable). If the difference between intervals is less than the repeatability of the method, then the blends are considered successful.

In this paper examples of mixing ratios have been limited to 4 to 1, although more extreme mixing ratios are possible. For example, if only three SRMs were certified with sulfur concentrations of 10, 100, and 1000 $\mu\text{g/g}$, then this would permit the preparation of samples with sulfur concentrations of 10, 28 - 82, 100, 280 - 820, and 1000 $\mu\text{g/g}$ sulfur. The high accuracy of the IDTIMS technique permits the certification of the end members to accuracies of approximately ± 1 to ± 5 $\mu\text{g/g}$ or better over the concentration range of 10 to 1000 $\mu\text{g/g}$. This translates to expanded uncertainties of the mixtures that would be very small relative to the requirements of the petroleum community. In some cases, over a limited concentration range the absolute uncertainty of the blends can actually be smaller than that of either end member SRM as discussed in the next section.

The approach presented in this paper will permit users to design and mix standards at desired concentrations from binary mixtures of NIST SRMs, and to calculate the concentration and uncertainty in the resulting mixture which are then directly traceable to NIST values.

Mixing and Statistical Considerations

There are several conditions that must be met: 1) the blends must be homogeneous, 2) there can be no sample loss during blending, 3) the resulting mixture must be of sufficient volume for the instrument being used, and 4) the mass of the two end members should be of sufficient size to make the weighing uncertainty negligible. In the case of XRF, a commonly used technique, the sample size needed is commonly about 5 mL, or about 4 grams. Condition #4 will be met if the sample mass of each end member is $> 0.2500 \pm 0.0005$ gram (see Appendix A).

For the technique to be useful, in addition to the obvious need to know the concentration of the mixture, one must also be able to characterize credibly the uncertainty of the mixture. The concentration of a mixture, M , composed of two SRM end members, X and Y , is given by the following mass balance relation:

$$M = f_1 X + f_2 Y = f_1 F_1(x_1, x_2 \dots x_j) + f_2 F_2(y_1, y_2 \dots y_k) \quad (1)$$

where f_1 and f_2 are the mass fractions of the respective end members subject to the condition that their sum equals unity. The concentrations, X and Y , are themselves determined from experimentally measured quantities ($x_1 \dots x_j$ and $y_1 \dots y_k$), calculated using functions F_1 and F_2 for NIST SRMs. The functions are essentially identical because the experimental technique is the same for all determinations, but there are differences in the way the input data are used in some cases. For example, regression by least squares is used for low level determinations such as SRM 2723a.⁷ In general, deviations in M resulting from deviations in the input variables of X and Y can be approximated by the Taylor series expansion in the vicinity of the means^{8,9}:

$$M - \bar{M} = f_1 (X - \bar{X}) \frac{\partial M}{\partial X} + f_2 (Y - \bar{Y}) \frac{\partial M}{\partial Y} + \text{higher order terms} \quad (2)$$

where the overstrike designates means of the represented random variables. Equation (2) involves only two variables, but it should be noted that it may be necessary to consider all the variables in equation (1). For the sake of brevity the treatment is presented for two variables only. Squaring, denominating by n (sample size), and taking the Expectation yields the relationship:

$$\text{Var}(\mathbf{M}) = \frac{1}{n} \left[f_1^2 \sigma_X^2 \left(\frac{\partial \mathbf{M}}{\partial \mathbf{X}} \right)^2 + f_2^2 \sigma_Y^2 \left(\frac{\partial \mathbf{M}}{\partial \mathbf{Y}} \right)^2 + \dots \right. \\ \left. + 2 f_1 f_2 \sigma_{XY} \left(\frac{\partial \mathbf{M}}{\partial \mathbf{X}} \right) \left(\frac{\partial \mathbf{M}}{\partial \mathbf{Y}} \right) + \dots \right] \quad (3)$$

The third term is a covariance term which is negligible if X and Y are independent or uncorrelated. If they are not independent, then it may be necessary to try to approximate it. In equation (3) both Type A and Type B uncertainties will appear and some cross products will be non-zero such as some uncertainties which correlate like those of the IDTIMS spike calibration. This has been evaluated by Monte Carlo simulation and found to be negligible.

Neglecting the covariance and higher order terms, a total expanded uncertainty¹⁰, U, can be expressed as the following:

$$U = t(v_{\text{eff}}) \left[f_1^2 \frac{s_X^2}{n_X} \left(\frac{\partial \mathbf{M}}{\partial \mathbf{X}} \right)^2 + f_2^2 \frac{s_Y^2}{n_Y} \left(\frac{\partial \mathbf{M}}{\partial \mathbf{Y}} \right)^2 \right]^{1/2} \quad (4)$$

The first term is the appropriate Student's *t* factor for the *effective degrees of freedom*, $t(v_{\text{eff}})$, which can be calculated from the Welch-Satterthwaite relationship, equation (5) below.

$$v_{\text{eff}} = \frac{\left(f_1^2 \sum_{i=1}^j \left(\frac{\partial \mathbf{M}}{\partial x_i} \right)^2 s_{x_i}^2 + f_2^2 \sum_{q=1}^r \left(\frac{\partial \mathbf{M}}{\partial y_q} \right)^2 s_{y_q}^2 \right)^2}{f_1^4 \sum_{i=1}^j \left(\frac{\partial \mathbf{M}}{\partial x_i} \right)^4 \frac{s_{x_i}^4}{n_{x_i} - 1} + f_2^4 \sum_{q=1}^r \left(\frac{\partial \mathbf{M}}{\partial y_q} \right)^4 \frac{s_{y_q}^4}{n_{y_q} - 1}} \quad (5)$$

The Welch-Satterthwaite relation reduces the uncertainty propagation by a small

amount in most cases; it is reduced near the middle of the range where v_{eff} approaches $(df_x + df_y - 2)$ if the degrees of freedom and the variances are approximately equal. The minimum in v_{eff} becomes more asymmetric as the variances become unequal.

Figure 1a shows the difference between using the Welch-Satterthwaite relation versus using the simpler multiplier of 2 which is favored by some laboratories. The drop lines in the figure illustrate the difference in magnitude of the two approaches. The Welch-Satterthwaite is a more conservative approach typically yielding a bigger coverage factor leading to a larger expanded uncertainty. The figure illustrates that the difference between the two approaches differs little for 50-50 mixtures and that the curves approach each other as n increases.

However, as will be seen in subsequent examples, from a practical point of view either approach is acceptable relative to the magnitude of the reproducibility of ASTM methods at this time. Figure 1b is a hypothetical example of the uncertainty propagation derived using the Welch-Satterthwaite relation to calculate a 95 % confidence interval for a mixture composed of 10 and 100 $\mu\text{g/g}$ end members both having the same absolute uncertainty of 1 $\mu\text{g/g}$ (lines a, b, and c). Note that the minimum in the absolute uncertainty occurs at the equal mass mixture which occurs at 55 $\mu\text{g/g}$. If the uncertainties in the end members are equal, then the minimum in the absolute uncertainty always occurs at the 50-50 mixture (see Appendix B) and is equal to the common end member uncertainty divided by the square root of 2 times the student's t factor for the effective degrees of freedom which approaches the sum of the end member degrees of freedom. Line c shows the effect of two different degrees of freedom of the end members. Line d shows the effect of a difference in the uncertainties of the end members on the uncertainty curve for $n=12$. This large value for n was used only to achieve visual separation of the curve from the other curves. As the difference between the uncertainties of the end members becomes larger the resulting propagated uncertainty becomes linear with concentration because the standard deviation approaches either f_1s_1 or f_2s_2 depending on which dominates.

In this paper a third approach will be used which is simple, easy, conservative, and closely approximates the output from the more complicated Welch-Satterthwaite approach discussed above. This approach uses data directly from the SRM certificates. The SRM certificates report the total expanded uncertainty, U , where u_c is the combined standard uncertainty and k is the coverage factor as shown in equation (6).⁹

$$U_i = k_i u_{c_i} \tag{6}$$

The first quantity is rigorously defined, but there is some latitude in choosing the value for k . On all sulfur in fossil fuel certificates published since 1994 at NIST the value for k was determined using Welch-Satterthwaite and is typically about 2.3 although it may

approach 4.3 for very low (< 10 µg/g) concentrations. In this paper the total expanded uncertainties for the mixes are calculated as:

$$U_{\text{mix}} = \left[(f_1 k_1 u_{c_1})^2 + (f_2 k_2 u_{c_2})^2 \right]^{1/2} \quad (7)$$

Therefore, if one uses the uncertainty directly from the SRM certificates, then equation (7) can be recast into equation (8) below in which one takes the expanded uncertainty (U_i) directly from the appropriate certificates.

$$U_{\text{mix}} = \left[(f_1 U_1)^2 + (f_2 U_2)^2 \right]^{1/2} \quad (8)$$

Figure 2 shows the difference among the different approaches for the case of mixing two NIST crude oil SRMs that were recently certified. The dark red line is a plot of equation (8) for the mixing of the two crude oil SRMs. It is clear that in this case equation (8) is an excellent approximation to the more complicated calculation involving equation (5). In this paper, equation (8) will be used to determine the total expanded uncertainty for sulfur in the fossil fuel mixtures.

Sulfur in Diesel and Kerosine

NIST currently has six different diesel fuel SRMs and one kerosine SRM certified for sulfur concentration. The certified values and uncertainties are listed in Table 1. There are 21 possible binary end member combinations and these are listed in Table 2. The uncertainties are small enough to permit mixes below 50 µg/g with expanded uncertainties below 1 µg/g. Varying the mixing fractions f_1 and f_2 of the two components chosen for each combination yields of course an infinite number of mixtures intermediate between each choice of end points. Figure 3a is a log-log plot of the uncertainty versus the mixture concentration for ten mixes. It demonstrates that there is essentially complete and continuous coverage between 2 µg/g and 3900 µg/g with the existing SRMs in Table 1 using limiting mixing ratios of 4 to 1 and 1 to 4. With the existing SRMs there is considerable overlap; for example, compare mixes 3 and 13, 1 and 18, 2 and 10, and 4 and 8.

The interest at the low sulfur end has increased greatly with the implementation of the ultra low sulfur diesel regulations in June 2006. Figure 3b is an expanded scale version of Figure 3a that shows the possible coverage below 50 µg/g sulfur. At the present time complete coverage is possible between 2 and 40 µg/g sulfur with uncertainties of less than 1 µg/g using mixtures of just three standards - RM 8771, SRM 1616b and SRM 2770.

Table 1. Diesel and Kerosine SRMs

SRM	Mean Sulfur Concentration in $\mu\text{g/g}$	Absolute Uncertainty 95 % CI (U)	% Relative Uncertainty 95 % CI (U)
RM 8771	0.071	0.014	20
2723a	11.0	1.1	10
1616b	8.41	0.12	1.4
2770	41.57	0.39	0.94
2724b	426.5	5.7	1.3
1617a	1730.7	3.4	0.20
1624d	3882	20	0.52

Figure 3a and 3b serve to indicate that it may be possible in the future to meet the entire ensemble of needs of the industry with only three or four SRMs of judiciously chosen sulfur concentration. The total expanded uncertainty in all the distillate fuel oil mixes is an order of magnitude smaller than the reproducibility of the current ASTM methods. The U_{mix} is always lower than the U of either end member and in some cases lower than the U of both end members. Mixes 12 and 19 in Table 2 are unique because the uncertainty of these mixes decreases with increasing sulfur content.

As will be seen in Figure 3a, the current relatively large uncertainty of 5.7 $\mu\text{g/g}$ for SRM 2724b dominates the uncertainty budget of any mixture in which it is included, but mixtures using the 8771-1671a pair give the same coverage. The same also applies to SRM 2723a (see FIG. 3b). But with even the relatively large uncertainty for SRM 2723a note from Table 2 that mixture #4 gives coverage between 2 to 9 $\mu\text{g/g}$ with an expanded uncertainty of less than 1 $\mu\text{g/g}$. Both of these SRMs may be re-certified in the near future using our improved analytical capabilities which may reduce the uncertainty by a factor of two or more.

Sulfur in Residual Fuel Oil

Residual fuel oil is a heavy oil of relatively high caloric content left over from the refining of crude oil. It is used to fire boilers in electric generating plants, particularly in the northeastern US. The sulfur emissions from these plants are regulated by the EPA

Table 2. Possible Ranges in Mixtures and Uncertainties with Existing Diesel Fuel and Kerosine SRMs

Mixture #	SRM End Members	S Concentration of End Members $\mu\text{g/g}$	Range in Mixture $\mu\text{g/g}$	^a Range in Uncertainty $\mu\text{g/g}$
1	8771/1624d	0.071 - 3882	776 - 3106	4 - 16
2	8771/1617a	0.071 - 1730.7	346 - 1385	0.7 - 3
3	8771/2724b	0.071 - 426.5	85 - 341	1 - 5
4	8771/2770	0.071 - 41.57	8.4 - 33	0.08 - 0.3
5	8771/2723a	0.071 - 11	2.3 - 8.8	0.2 - 0.9
6	8771/1616b	0.071 - 8.41	1.7 - 6.7	0.03 - 0.1
7	1616b/2723a	8.41 - 11	8.9 - 10.5	0.2 - 0.9
8	1616b/2770	8.41 - 41.57	15 - 35	0.1 - 0.3
9	1616b/2724b	8.41 - 426.5	92 - 343	1 - 5
10	1616b/1617a	8.41 - 1730.7	353 - 1386	0.7 - 3
11	1616b/1624d	8.41 - 3882	783 - 3107	4 - 16
12	2723a/2770	11 - 41.57	17 - 35	0.9 - 0.4
13	2723a/2724b	11 - 426.5	94 - 343	1 - 5
14	2723a/1617a	11 - 1730.7	355 - 1387	1 - 3
15	2723a/1624d	11 - 3882	785 - 3108	4 - 16
16	2770/2724b	41.57 - 426.5	119 - 350	1 - 5
17	2770/1617a	41.57 - 1730.7	379 - 1393	0.8 - 3
18	2770/1624d	41.57 - 3882	810 - 3114	4 - 16
19	2724b/1617a	426.5 - 1730.7	687 - 1470	5 - 3
20	2724b/1624d	426.5 - 3882	810 - 3114	6 - 16
21	1617a/1624d	1730.7 - 3882	2161 - 3452	5 - 16

^a Uncertainties apply to values in previous column and are total expanded uncertainties derived by application of equation (8) to end member certified uncertainties.

and a typical compliance fuel has a sulfur content of approximately 1%. It is quite common for a seller to blend two or more different fuel oils to a target sulfur value specified by the buyer. Therefore, it is absolutely essential to determine accurately the sulfur content of the resulting mixture to ensure that the target value for the consignment blend will be met. Since the first residual fuel oil standards were certified

Table 3. Residual Fuel Oil and Crude Oil SRMs

SRM	Mean Sulfur %	Absolute Uncertainty 95 % CI (U)	% Relative Uncertainty 95 % CI (U)
Residual Fuel Oil			
1623c	0.3806	± 0.0024	0.63
1619b	0.6960	± 0.0077	1.1
1621e	0.9480	± 0.0057	0.60
1622e	2.1468	± 0.0041	0.19
2717a	2.9957	± 0.0032	0.11
1620c	4.561	± 0.0015	0.33
Crude Oil			
2722	0.21037	± 0.0084	0.40
2721	1.5832	± 0.0044	0.28

for sulfur by NIST in the early 1960s, their number has increased to six which now covers the entire sulfur range of interest from 0.4 to 4.5 % sulfur. The complete list of currently available standards is given in Table 3. At the bottom of Table 3 are the first crude oil samples to be certified by NIST for sulfur. There are 15 possible binary combinations using the six residual fuel oil SRMs. This large number makes the optimal choice of end members somewhat difficult, but the graphical display of the solution presented in Figure 4 is straightforward. The solution requires three criteria to be met simultaneously: 1) complete coverage over the entire concentration range represented by the standards, 2) the uncertainties of the mixes must be as small as possible, and 3) the composite range be determined with the fewest number of SRMs.

Table 4. Recommended Binary Blends and Uncertainties from Residual Fuel Oil SRMs

Mixture #	SRM End Members	End Members %	Range % S	Absolute Uncertainty 95 % CI (U) $\mu\text{g/g}$
Residual Fuel Oil				
2	1623c/1621e	0.3806/0.9480	0.49 - 0.84	23 - 43
3	1623c/1622e	0.3806/2.1468	0.73 - 1.79	22 - 32
4	1623c/2717a	0.3806/2.9957	0.90 - 2.47	21 - 26
13	1622e/2717a	2.1468/2.9957	2.32 - 2.83	33 - 28
14	1622e/1620c	2.1468/4.5610	2.63 - 4.08	46 - 109
15	2717a/1620c	2.9957/4.5610	3.31 - 4.25	41 - 110
Crude Oil				
	2722/2721	0.21037/1.5832	0.48 - 1.31	12 - 32

The red lines in Figure 4 show the 5 end member mixes that cover the entire range. The solid circles are the end members. Note that the distances between the end of the red lines and the SRM compositions (red circles) increase as the values of the end members increase. This figure also makes it easy to see which three end members could be used to make identical concentration mixes with identical uncertainties. This condition occurs at the intersection of lines. For example, line 4 intersects both lines 3 and 13. There is much redundancy for mixes in the 1.3 to 2 % concentration range. Table 4 lists the 6 best binary end member choices based on the graphical solution presented in Figure 4. Table 4 lists the ranges in both the concentrations and the computed uncertainties of the resulting mixes. The last entry in Table 4 gives results for the mixing of the two crude oil SRMs, originally presented earlier in Figure 2. Table 5 gives the ranges and uncertainties for remainder of the mixes.

Table 5. Remainder of Residual Fuel Oil Mixtures
(Use Precluded by Graphical Analysis in Figure 3)

Mixture #	SRM End Members	End Members % S	Range % S	Absolute Uncertainty 95 % CI (U) $\mu\text{g/g}$
Residual Fuel Oil				
1	1623c/1619b	0.3806/0.6960	0.44 - 0.63	26 - 57
5	1623c/1620c	0.3806/4.561	1.22 - 3.73	37 - 112
6	1619b/1621e	0.6960/0.9480	0.75 - 0.90	63 - 50
7	1619b/1622e	0.6960/2.1468	0.99 - 1.86	60 - 38
8	1619b/2717a	0.6960/2.9957	1.16 - 2.54	58 - 31
9	1619b/1620c	0.6960/4.561	1.47 - 3.79	71 - 117
10	1621e/1622e	0.9480/2.1468	1.19 - 1.91	46 - 36
11	1621e/2717a	0.9480/2.9957	1.36 - 2.59	45 - 29
12	1621e/1620c	0.9480/4.561	1.67 - 3.84	57 - 112

Sulfur in Coal

The determination of sulfur in coal is another case where the methods used in industry require external calibration. Commonly, the coal mining industry is interested in sulfur determinations in coal within a very narrow range of sulfur content which frequently falls between two standards requiring interpolation of varying degrees. An actual recent example of this is shown in the upper right corner of FIG. 5. A coal company produces coal of 4.2 % sulfur (unwashed) and after washing has a sulfur content of 3.5 %. Both of these values are between SRMs 2684b (3.076 % S) and 2685b (4.73 % S). The method described here may allow calibration mixes at or very near the concentrations of interest.

Table 6 lists the 8 coal SRMs that are currently available. The coal SRMs have larger uncertainties than do residual fuel oils of comparable sulfur content because of their intrinsic heterogeneity resulting from variable mineral and moisture content. Because of this intrinsic heterogeneity, the best way to use this technique for coal standards would be to add the two components directly to the combustion crucible and combust the total sample. The moisture content would be determined on separate

samples. The effect of moisture content on the sample mass determination has been studied in detail, and it was demonstrated that coals may exhibit “anomalous” drying profiles.¹¹ Only coals of the similar rank should be blended to make calibration standards. The mixing of SRMs of different matrices can not be assumed to yield blends that will yield the expected derived value when analyzed by a given method and, although sometimes possible, it is not recommended. This is clearly a problem when the instrument-response characteristics of the selected SRM end members are different. For example, coal and coke SRMs are not recommended for blending for subsequent analysis by methods that use high temperature combustion techniques because of their different burn profiles. But if the unknown sample were a mixture of coal and coke, then a calibration curve should be constructed from similar blends.

Table 6. Coal SRMs

SRM	Sulfur Mean %	Absolute Uncertainty 95 % CI (U)	% Relative Uncertainty 95 % CI (U)
Sub-Bituminous Coal			
1635	0.3616	± 0.0017	0.47
2682b	0.4917	± 0.0079	1.6
Bituminous Coal			
^a 2693	0.4571	0.0067	1.5
^a 2692b	1.170	± 0.020	1.7
^a 1632c	1.462	± 0.051	3.5
^a 2683b	1.955	± 0.041	2.1
2684b	3.076	± 0.031	1.0
2685b	4.73	± 0.068	1.4

^a The uncertainties for these three SRMs were calculated as 95 % prediction intervals.

Figure 5 shows the coverage that is possible with the existing standards. The mean concentrations of the existing seven SRMs have been projected onto the abscissa to show the gaps in concentration that exist. The solid green circles on the mixing lines denote 50-50, 60-40, and 40-60 mixtures. Drop lines and the connecting

horizontal lines indicate the coverage that is possible. One might wish to restrict mixing of coals to much smaller ranges because of weighing considerations. Nevertheless, it should be both possible and practicable to cover almost the entire range of sulfur concentrations with the SRMs now available.

Conclusions

The *Designer* method makes possible the construction of multipoint calibration curves at or near the concentration of interest. This method should be ideal for analytical techniques that require multi-point calibration curves such as XRF and combustion techniques or where the analyst wishes to bracket an unknown concentration with several calibrants. This last feature means that non-linear response of instruments can be easily overcome. The ability to design and prepare in one's own laboratory diesel fuel calibrants with a specific sulfur concentration and uncertainties that are calculable and traceable to NIST values gives the analyst the ability to bracket very closely any unknown diesel fuel which should translate to an unprecedented flexibility and accuracy capability in the petroleum sector laboratories.

In addition, just as NIST certified values are currently used to verify analytical methods,¹² the *designer* blends can be used to create NIST traceable test samples and Quality Control (QC) Test-Standards. These mixtures can be used to verify calibrations and the accuracy of subsequent results of unknowns derived from the calibration. Quality Control (QC) Test-Standards must be different from the blends used for the calibration curve, though they may be composed of the same parent SRMs.

Although the method described here is ideally suited for miscible liquids, it can be used for complete combustion methods for sulfur in coals and other solids. In the case of coal, one would weigh the two different coals directly into the combustion crucible. This technique is being investigated for use with other analytes such as mercury in coal and trace elements in fuels.

The method described here should significantly improve calibration while reducing the number of certified standards that must be maintained by national metrology laboratories.

References:

1. Paulsen, P. J. and Kelly, W. R., Anal. Chem. 1984, **56**, 708-713.
2. Kelly, W. R., Vocke, Jr., R. D., Sieber, J. R., and Gills, T. E. 1993, FUEL, **72**, 1567-1569.
3. Kelly, W. R., Paulsen, P. J., Murphy, K. E., Vocke, Jr., R. D., and Chen, L.-T. Anal. Chem. 1994, **66**, 2505-2513.
4. International Council on Clean Transportation, see documents on low sulfur gasoline and diesel fuel (www.cleantransportcouncil.org)
5. World Fuel Charter, December 2002, 51 pp. 1 - 51 (www.autoalliance.org or www.enginemanufacturers.org)
6. ASTM D 2622-03 Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry, 2003, 1-6, American Society of Testing and Materials, West Conshohocken, PA
7. Kelly, W. R., Vocke, R. D., Mann, J. L., and Guthrie, W. F., in preparation
8. Bevington, P. R. and Robinson, D. K. Data Reduction and Error Analysis for the Physical Sciences, 2nd Edition, McGraw-Hill, Boston, 1992.
9. Ku, H. H. J. Res. NBS, 1966, **70C**, 263-273.
10. Taylor, B. N. and Kuyatt, C. E. NIST Technical Note 1297, 1994.
11. Mann, J. L., Kelly, W. R., and MacDonald, B. S. Anal. Chem. 2002, **74**, 3585-3591.
12. Taylor, J. K. Standard Reference Materials: Handbook for SRM Users. National Bureau of Standards Special Publication No. 260-100, U.S. Department of Commerce, Washington, DC, 1985.

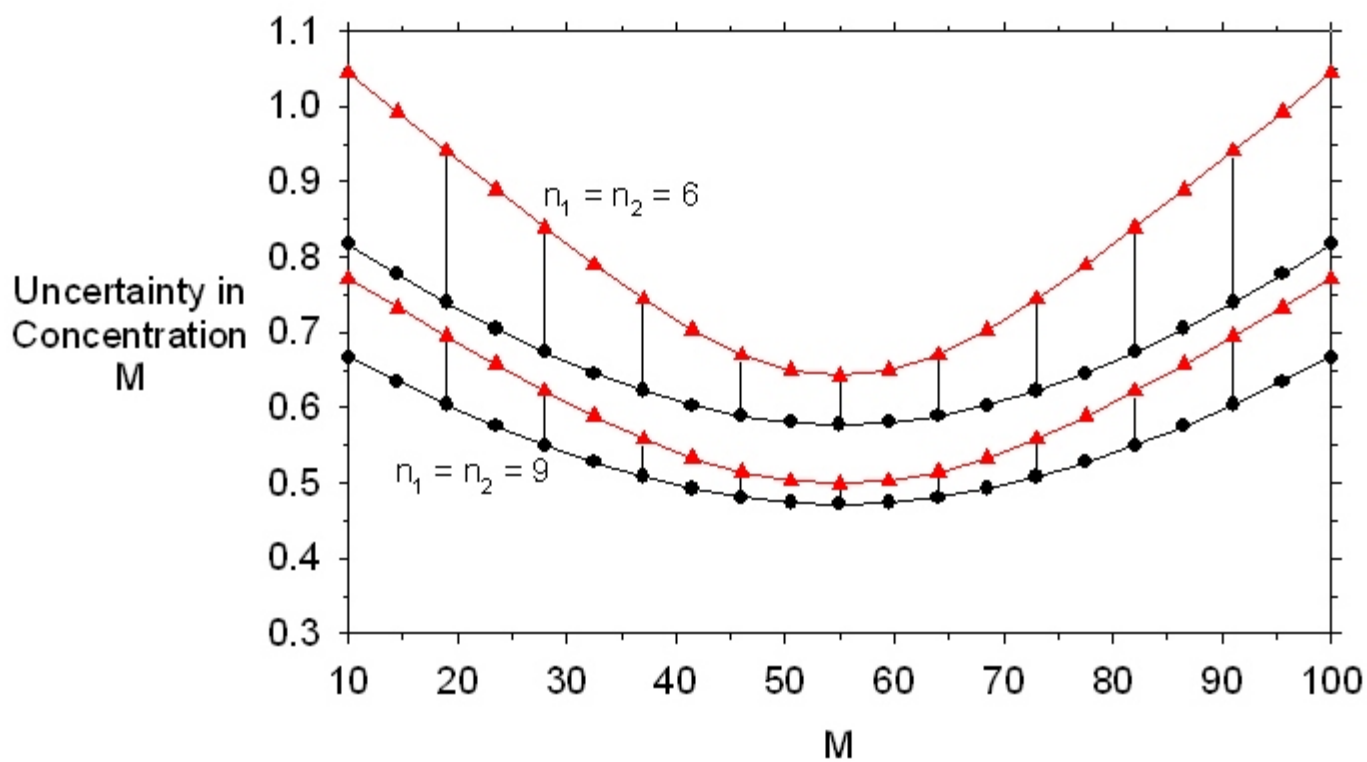


FIG 1a. Comparison of coverage factors. Filled circles are 95 % confidence intervals calculated using a coverage factor equal to 2 ($k = 2$). Filled triangles are 95 % C.I. calculated using a coverage factor calculated using the Welch - Satterthwaite equation. Vertical tie lines illustrate the difference between the two approaches.

Hypothetical Example of Mixing End Members of
10 $\mu\text{g/g}$ and 100 $\mu\text{g/g}$

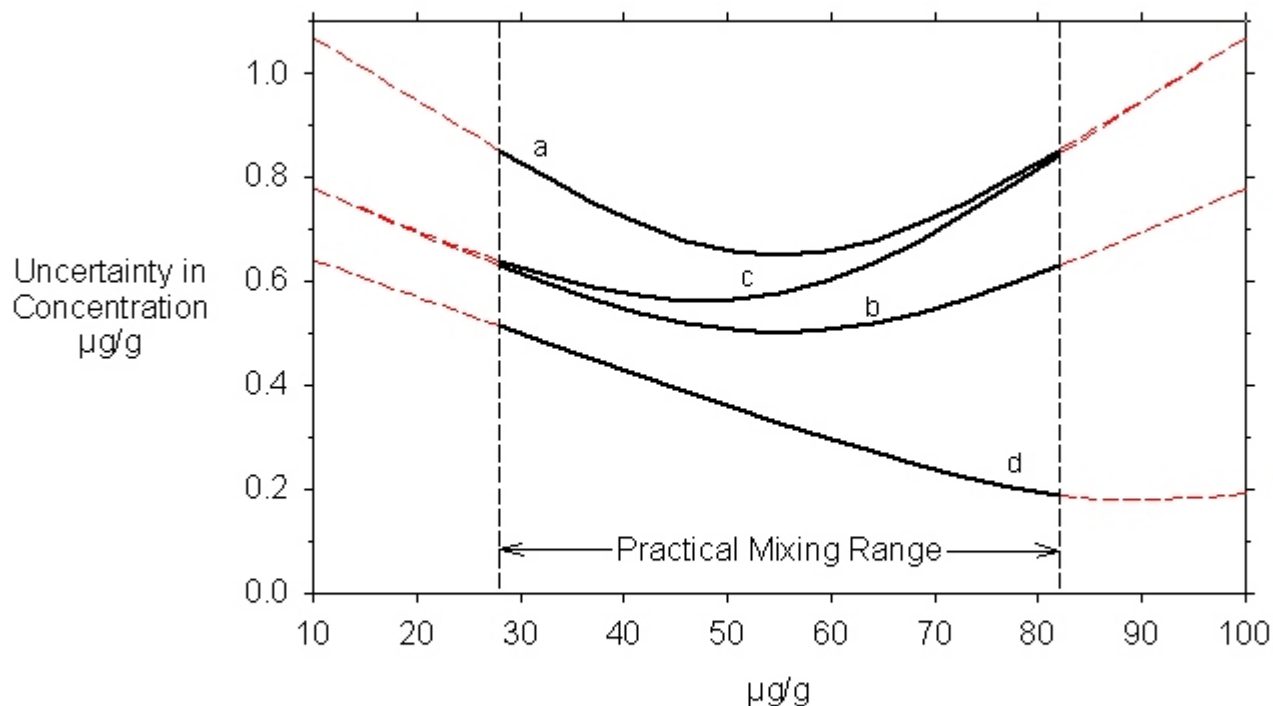


FIG 1b. Example of uncertainty propagation of mixing two different end members. The uncertainties of the end members for lines a, b, and c were taken equal to unity. The value of n was 6 and 9 for lines a and b; for line c the values of n for the left and right end members were 9 and 6. Line d shows the effect of differences in end member uncertainty which were taken to be 1 and 0.3 with $n = 12$.

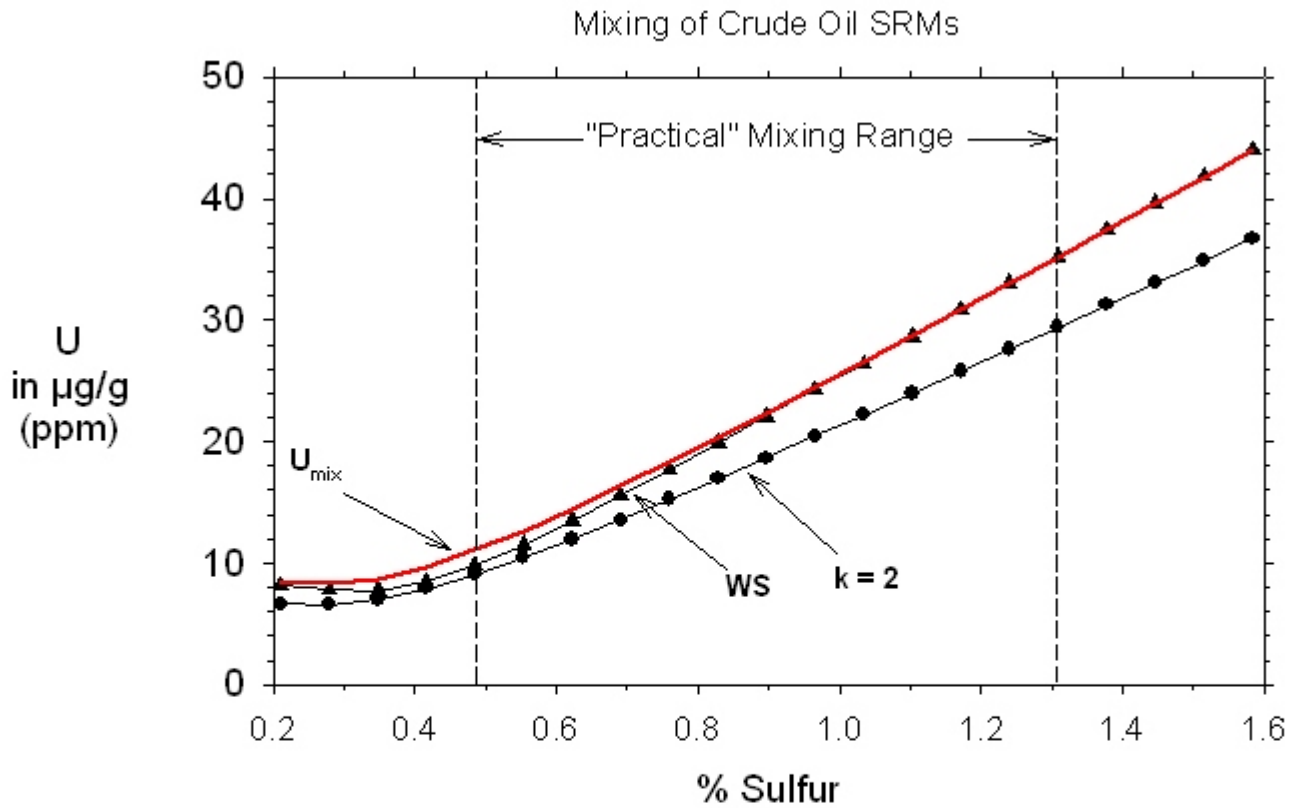


FIG. 2. Example of Mixing SRMs 2722 and 2721 of 0.21037 ± 0.00084 and 1.5832 ± 0.0044 % Sulfur. The line labelled WS is the total uncertainty using the Welch-Satterthwaite equation. The red line U_{mix} uses the total expanded uncertainty (U) from the SRM certificate. The relative uncertainty ranges from 0.2 to 0.4 %. A coverage factor of $k = 2$ results in the lower curve. A coverage factor of 2.4 is a good approximation to the line U_{mix} .

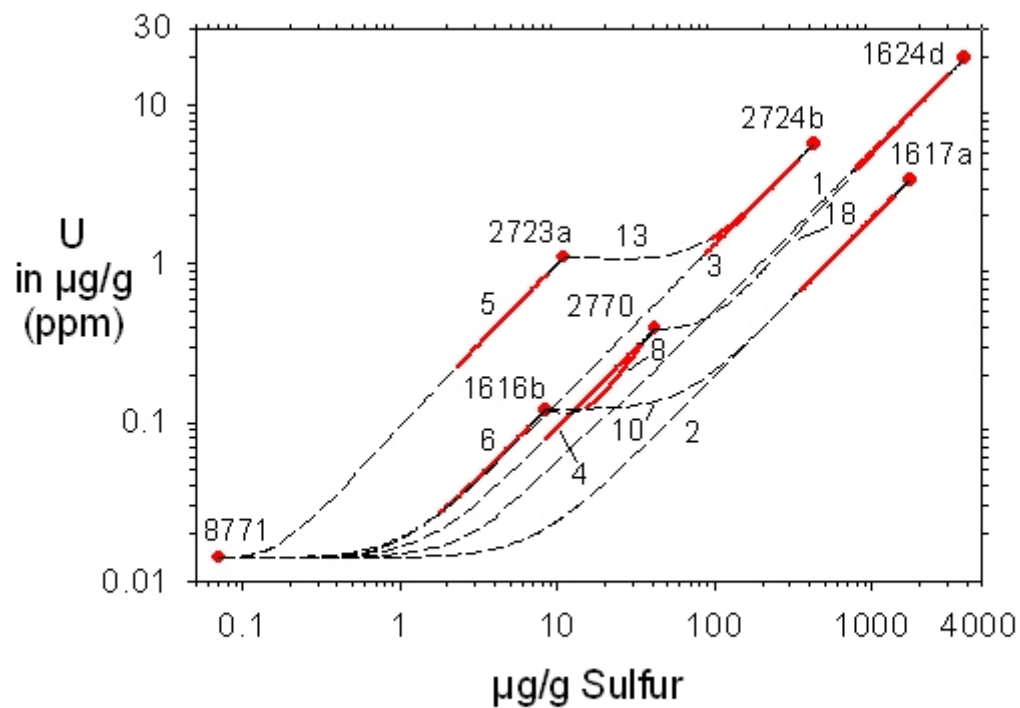


FIG. 3a. Log-Log plot of 10 of the possible 21 mixtures for distillate fuel oils. SRMs are denoted by red circles and four or five character alphanumeric. Numbers near the tie lines indicate the mixes for Table 2.

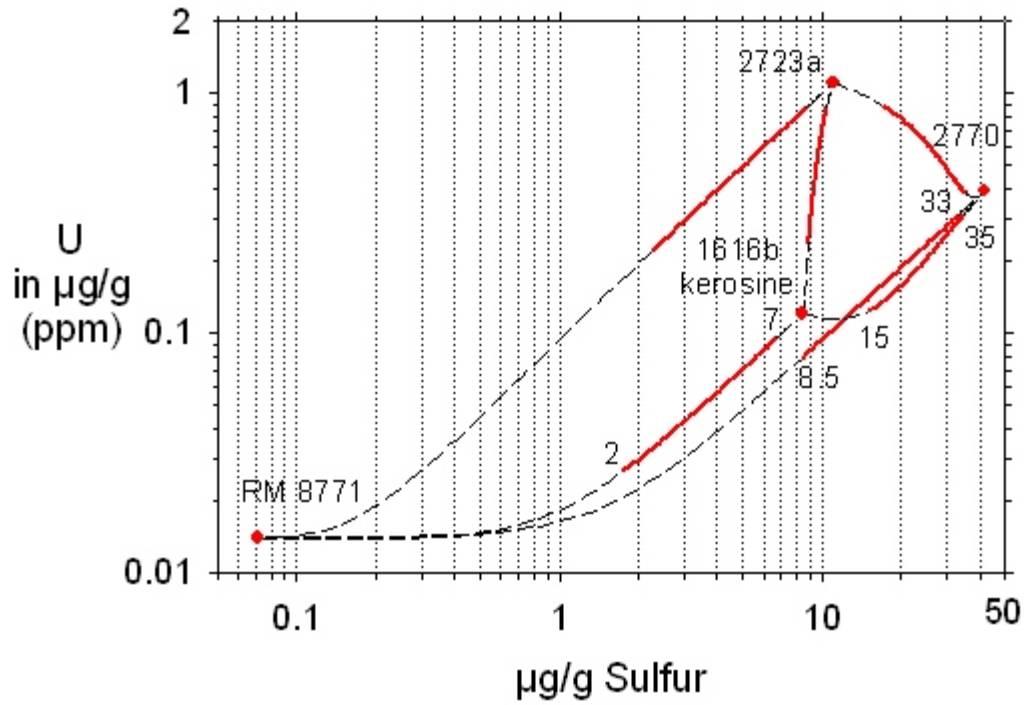


FIG. 3b. Low level distillate fuel Oils. Log-log graphical solution for mixing diesel fuel. The solutions are given by the solid red lines which terminate at mixing ratios of 4 to 1 and 1 to 4. The end member SRMs are represented by filled red circles. The number at the terminus of each red line is the approximate sulfur concentration for that mixture. There is complete and continuous coverage between 2 and 35 µg/g.

Uncertainty of All Possible Mixtures as a Function of Sulfur Concentration for Residual Fuel Oil SRMs

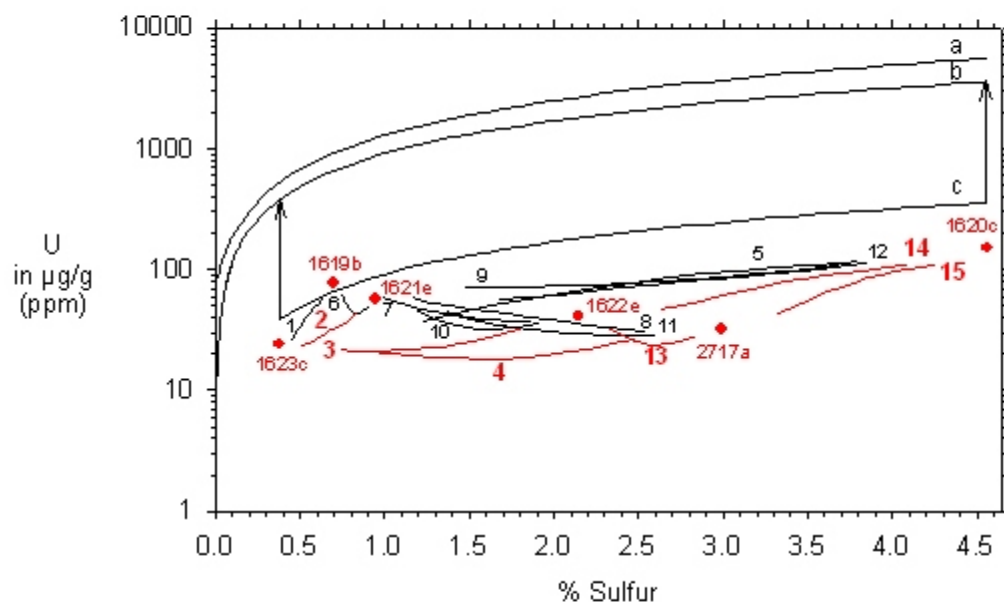


FIG. 4. Residual Fuel Oil. Semilog graphical solution to the mixing problem. The solutions are given by the bold lines and corresponds to mixes 2, 3, 4, 13, 14, and 15 listed in Table 4. Filled circles and alphanumeric denote SRM end members; see Tables 4 and 5. Lines a and b are the reproducibility values for ASTM D2622-03 (WDXRF) and D4294-02 (EDXRF). Line c is a construct that is a decade smaller than line b as indicated by the two vertical arrows.

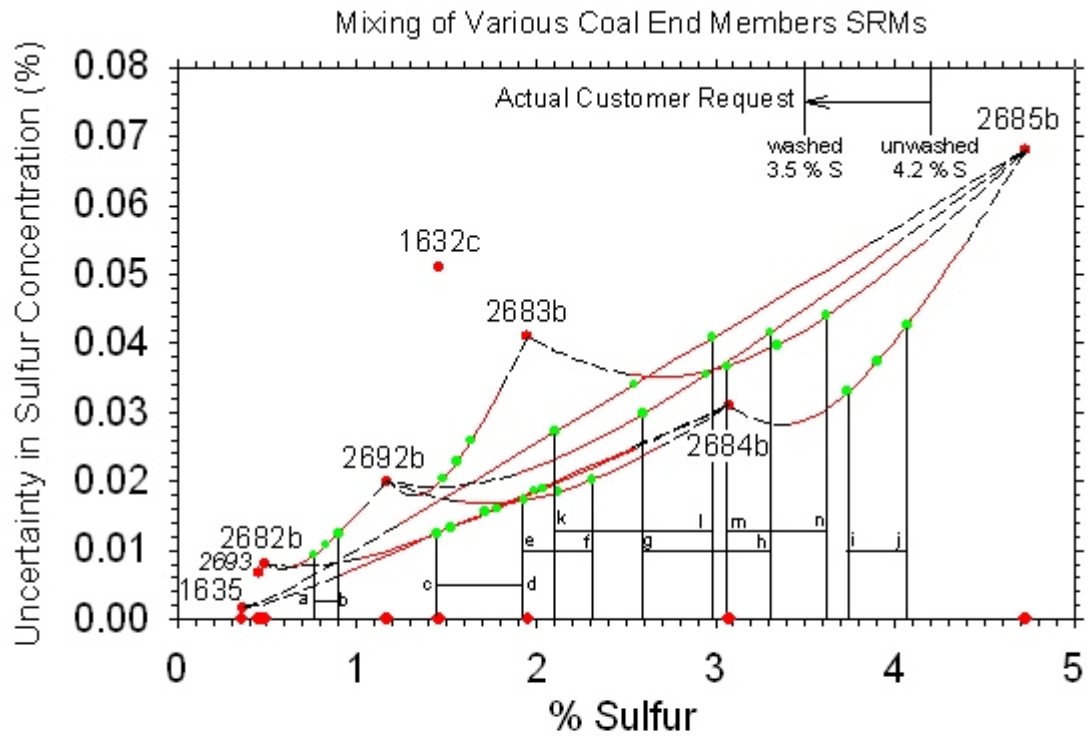


FIG. 5. Possible coverage of sulfur concentration in the 1 % to 4 % range using binary mixtures. The 8 solid circles within the graph and along the abscissa represent the SRM concentrations. The horizontal lines labeled ab...j and outer green circles represent ranges of 40-60 to 60-40 mixtures. The middle green circles represent 50-50 mixtures. No tie lines were calculated for SRM 2693.

Appendix A

The Effect of Weighing Accuracy on the Uncertainty

To approximate the affect of weighing uncertainty on the uncertainty of the resulting mixture, the mass fractions of equation (1) are written in terms of the measured quantities, the masses m_1 and m_2 :

$$M = \frac{m_1}{m_1 + m_2} X + \frac{m_2}{m_1 + m_2} Y \quad (\text{A-1})$$

If one assumes that X and Y are constants, then $M = f(m_1, m_2)$. Taking the total differential or increment of M with respect to the masses, m_1 and m_2 , as shown in A-2:

$$dM = \frac{\partial f}{\partial m_1} dm_1 + \frac{\partial f}{\partial m_2} dm_2 \quad (\text{A-2})$$

and then dividing by M and squaring gives the relative variance in M which can be written in terms of the relative standard deviation as in A-3:

$$\frac{\sigma_M}{M} = \frac{[|X - Y|] [m_1^2 + m_2^2]^{1/2}}{(m_1 X + m_2 Y) (m_1 + m_2)} \sigma_b \quad (\text{A-3})$$

where it is assumed that one uses the same balance to determine the masses, m_1 and m_2 permitting the following approximation in equation (A-3):

$$\sigma_1 \approx \sigma_2 \approx \sigma_b = 0.0005 \quad (\text{A-4})$$

where σ_b is the standard deviation for the uncertainty of the balance which for a four place balance is assumed to be 0.0005 g. Equation (A-3) is plotted in FIG. A-1 for the hypothetical end members of concentration 10 and 100 $\mu\text{g/g}$. It is obvious that if one weighs as least 1 gram of each end member then the uncertainty expressed as a standard deviation from this source is less than 0.05 % which is negligible for most applications.

The accuracy of equation (A-3) was checked by Monte Carlo simulation using equation (A-1). Random numbers were generated assuming a normal distribution with a standard deviation of 0.0005 g for different values of m_1 and m_2 . The results from the Monte Carlo simulation were in excellent agreement with those calculated by equation (A-3). Equation (A-3) was also checked assuming a uniform distribution with standard deviation equal to $0.0005/\sqrt{3}$ and this showed good agreement also.

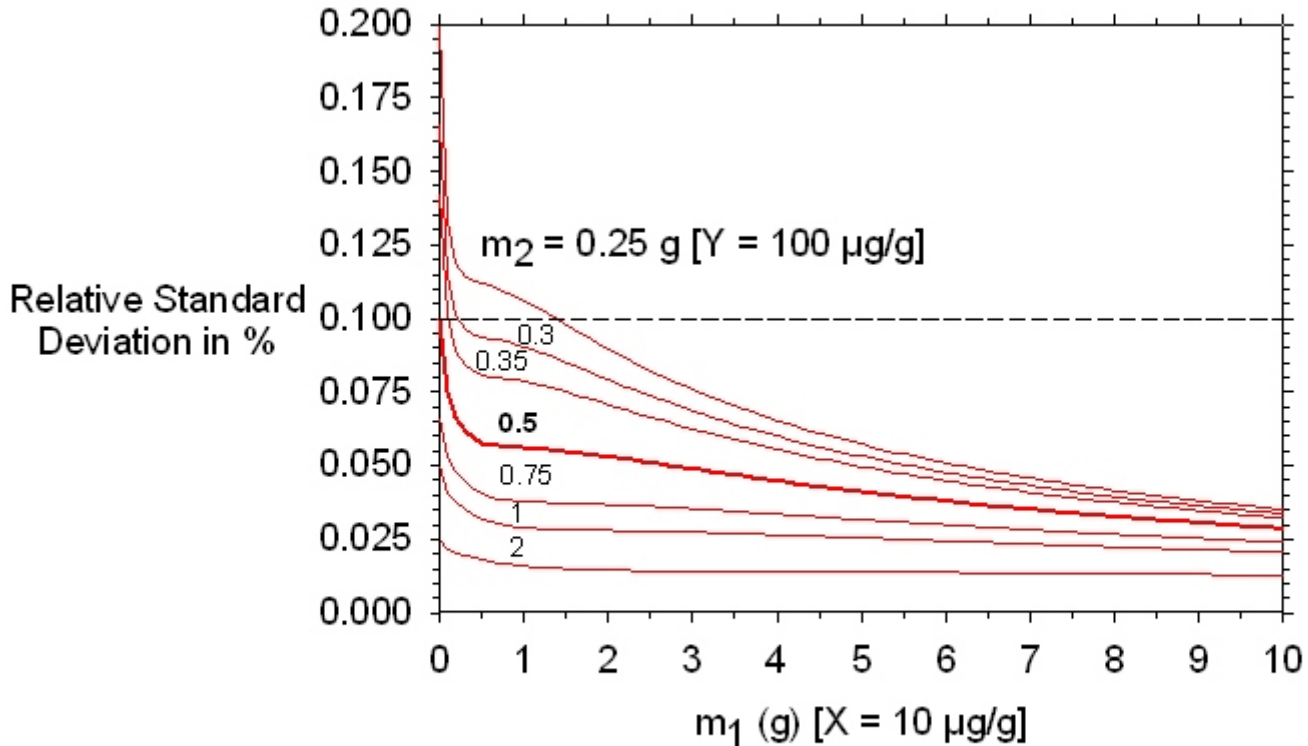


FIG. A-1. Relative Standard Deviation from Weighing Uncertainty of ± 0.0005 g for end members of 10 and 100 $\mu\text{g/g}$. Curves were calculated from equation (A-3). The horizontal dashed line delineates the 0.1 % relative uncertainty domain.

Appendix B

Calculation of the Minima in the Uncertainty for a Binary System

We wish to calculate the minimum in the uncertainty for a given binary mixture. The variance is given by equation (B-1):

$$\text{Var (M)} = f_1^2 s_1^2 + f_2^2 s_2^2 \quad [\text{B-1}]$$

Using the constraint that the sum of f_1 and f_2 must equal unity, the above can be written in the following form:

$$\text{Var (M)} = f_1^2 s_1^2 + (1-f_1)^2 s_2^2 \quad [\text{B-2}]$$

Taking the derivative of the variance with respect to f_1 and setting equal to zero gives the value of f_1 that minimizes the variance:

$$\frac{d\text{Var(M)}}{df_1} = 2f_1 s_1^2 - 2(1-f_1)s_2^2 = 0 \quad [\text{B-3}]$$

f_2 can be calculated from the difference in f_1 from unity to give the following relations:

$$f_1 = \frac{s_2^2}{s_1^2 + s_2^2} ; \quad f_2 = \frac{s_1^2}{s_1^2 + s_2^2} \quad [\text{B-4}]$$

It is obvious from these equations that if the uncertainties are equal then the minimum in the uncertainty is located at $f_1 = f_2 = 0.5$. The location of the minimum is highly sensitive to the differences in s_1 and s_2 because they are squared quantities. This can best be seen by rewriting the expression for f_1 in the following manner:

$$f_1 = \frac{1}{\left(\frac{s_1}{s_2}\right)^2 + 1} , \quad f_1 = \frac{1}{\left(\frac{s_1}{s_2} \frac{\bar{x}_2}{\bar{x}_1}\right)^2 + 1} \quad [\text{B-5}]$$

where the first expression is for the absolute uncertainty and the second expression is the for the relative uncertainty. As the second expression shows, the minimum occurs at $f_1 = 0.5$ if the relative uncertainties are equal.

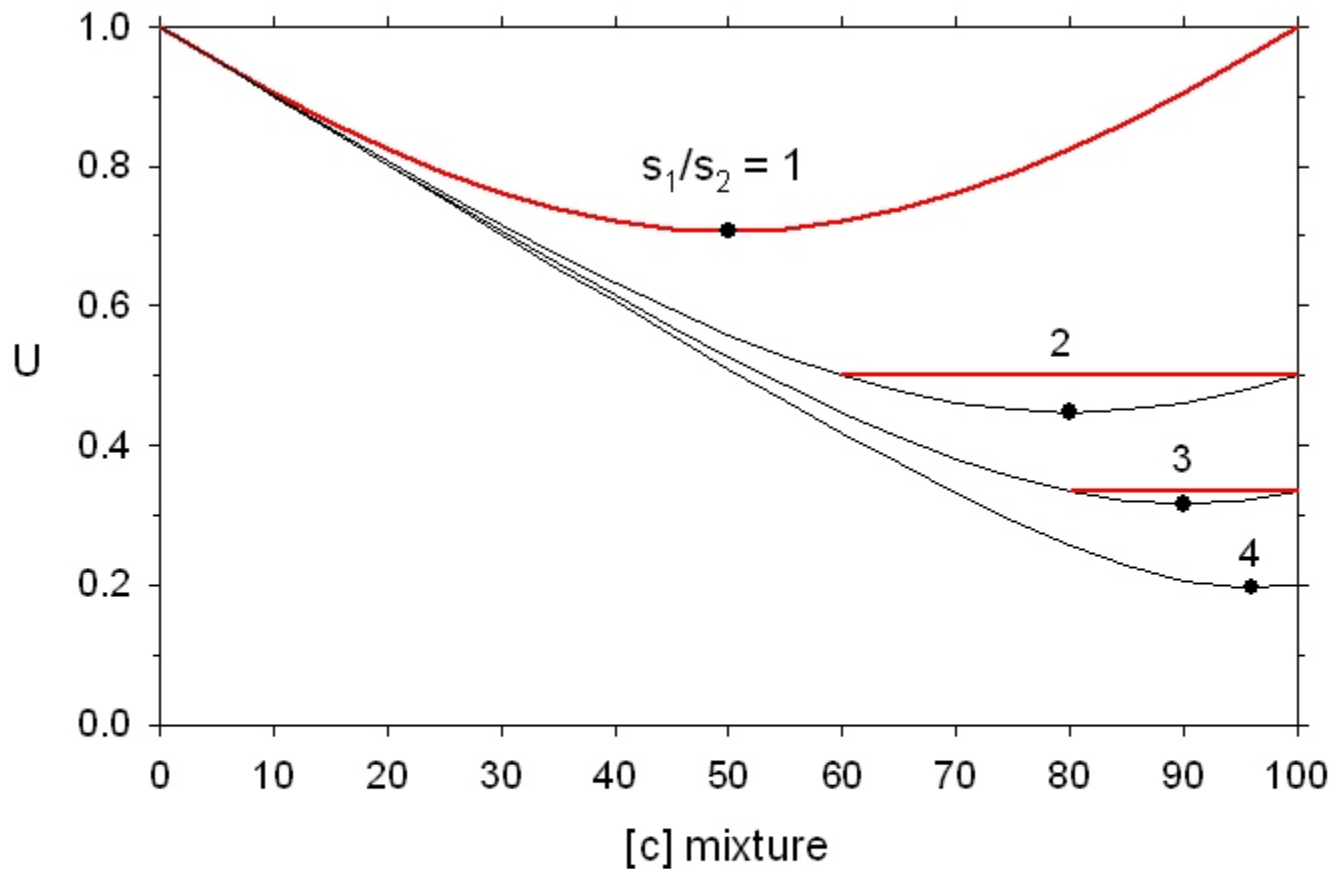


FIG. B-1. The effect of asymmetry in standard deviations on the minima in the uncertainty, U , of the binary mixtures. The end members have concentrations of 0 and 100 units. The red lines give the optimum range for different ratios of the standard deviations, s_1 and s_2 . Cases represented by lines labeled 3 and 4 are the most probable from statistical considerations.