

## Software Package To Facilitate the Preparation of Intermediate-Range Fossil Fuel Standards from Certified Reference Materials<sup>†</sup>

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A PC software package has been developed in Visual Basic for Applications to assist analysts in mixing fossil fuel reference materials to produce standards of intermediate concentrations. Mixing appropriate reference materials of similar matrices permits the analyst to produce needed standards over a continuous concentration range for analytes of interest. The program automates selection of optimum mixtures and calculates the concentrations and associated uncertainties of analytes in the blends. A graphical interface depicting all possible blends and an automated quality control test to monitor the process for potential problems are included.

### Introduction

Continually changing regulation of fossil fuel constituents, such as S, Cl, and Hg, has caused difficulties in obtaining appropriate reference materials needed to ensure compliance at pertinent concentration levels. The National Institute of Standards and Technology (NIST) has produced a variety of standard reference materials (SRMs) for this purpose, with concentration levels relevant to regulatory limits of S, Hg, and Cl in fossil fuel materials at the time of production. However, the wide variety and volatility of such regulations throughout the world<sup>1</sup> ensures that concentration regimes important in the present may not be sufficiently served by the current suite of reference materials in the future.

Similar to other national metrology institutes, NIST frequently receives requests for additional reference materials at concentrations specific to the needs of the user. The existing suite of SRMs for fossil fuels includes coal, metallurgical coke, petroleum coke, crude oil, residual fuel oil, middle distillate, and gasoline standards. To augment this suite with additional reference materials at all concentrations needed by the user community would require a major effort. The “designer method” presented in a previous paper<sup>2</sup> is intended to address this problem. It permits the user to design and prepare standards at any concentration desired by blending pairs of SRMs. These blends have concentrations and uncertainties that can be calculated and are traceable to NIST SRM certified values. This methodology permits the transfer of the high accuracy capability of isotope dilution thermal ionization mass spectrometry (ID–TIMS) and isotope dilution inductively coupled plasma mass spectrometry (ID–ICP–MS), methods that require expensive instrumentation and are labor-intensive, to the user

community via SRMs. This approach can be implemented immediately with existing SRM stocks and coverage at intermediate concentrations can be maintained in the future with fewer SRMs. Additionally, calibration with blended standards closely matched to the expected concentration of a sample improves the quality of the measurements.

The concentration (dry basis for solids) of a binary mixture ( $C$ ) is calculated using the equation

$$C = \frac{f_1 c_1 (1 - x_1/100) + f_2 c_2 (1 - x_2/100)}{f_1 (1 - x_1/100) + f_2 (1 - x_2/100)} \quad (1)$$

where  $f_1$  and  $f_2$  are the mass fractions of each component in the mixture,  $c_1$  and  $c_2$  are their concentrations (% , mg/kg, or  $\mu\text{g/kg}$ ), and  $x_1$  and  $x_2$  are their moisture contents (%). The associated expanded uncertainty ( $U$ ) for the mixture may be calculated by

$$U = \sqrt{(f_1 U_1)^2 + (f_2 U_2)^2} \quad (2)$$

where the quantities  $U_1$  and  $U_2$  are the expanded uncertainties associated with each component. The units used in eq 2 are the same as the concentrations in eq 1. Equation 2 is an approximation to the results that would be obtained from the Welch–Satterthwaite equation used and discussed by Kelly et al.<sup>2</sup> Recommended practice consists of propagating standard ( $1\sigma$ ) uncertainties through the analytic formula, reserving multiplication by the coverage factor ( $k$ ) for the end. Equation 2 gives results that vary less than 10% in most cases from this more complex method but has the advantage of ease of use when working directly from certificates. However, in some rare cases, the deviation from the Welch–Satterthwaite results is considerably larger, particularly when a small amount of one of the components is used. For this reason, it is recommended (but not required) that each component make up at least 20% of the overall blend.

Moisture content can be an important parameter when using solid reference materials, such as coals and cokes, because knowing the moisture content is critical for an accurate measurement of the mass of a standard.<sup>3</sup> Uncertainty

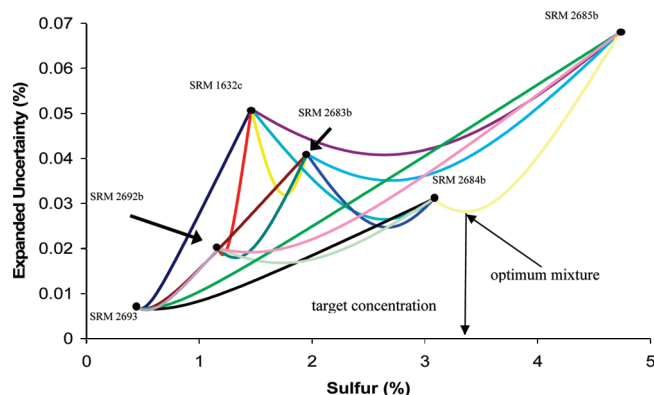
<sup>†</sup> Disclaimer: The full description of the procedures used in this paper requires the identification of certain commercial products and their suppliers. The inclusion of such information should in no way be construed as indicating that such products or suppliers are endorsed by NIST or are recommended by NIST or that they are necessarily the best materials, instruments, software, or suppliers for the purposes described.

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(2) Kelly, W. R.; MacDonald, B. S.; Leigh, S. D. *J. ASTM Int.* **2007**, *4*, 1–14.

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**Figure 1.** Example of mixing curves using the designer method for varying mass fractions of S in coal SRMs. The mixing software circumvents generation of this and similar charts, automatically choosing the blend with the lowest uncertainty at a given concentration.

in moisture content is not specifically denoted within the equations, and if the uncertainty of the moisture content is large, this uncertainty can be treated as additional uncertainty in mass, as shown elsewhere.<sup>2</sup> Using eqs 1 and 2, the concentration and uncertainty of any binary mixture (as shown in Figure 1 for a collection of coal SRMs) can be calculated. The results of the curves shown are similar to the concentration versus uncertainty curves produced by spiking different amounts of isotope into a sample in isotope dilution mass spectrometry.<sup>4,5</sup> Equations 1 and 2 assume that the components have been well-mixed to give a homogeneous mixture in terms of the technique used. With any SRM produced, a minimum sample mass is listed on the accompanying certificate that specifies the minimum amount of material an analyst should use. The minimum sample mass does not restrict the ratio of components in a given mixture if the mixture is large enough but can become a consideration given that the minimum mass listed for many solid powder reference materials is typically on the order of 150 mg.

Almost all methods used for S, Hg, and Cl in fossil fuels must be externally calibrated, and in many cases, employing stable homogeneous standards with similar matrices can minimize bias associated with differences in organic and mineral morphology. This can be important for the determination of the elemental content in fossil fuels by both the buyer and seller of such materials to ensure compliance with contract specifications. Additionally, the Environmental Protection Agency (EPA) has moved toward a performance-based quality system approach for the determination of sulfur in diesel fuel.<sup>6</sup> 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 for the material of interest. If these methods are sufficiently well-calibrated, then the methods are considered to demonstrate the requisite accuracy.

Instrumental chemical determinations in fossil fuels are commonly performed by measuring the response of an unknown and comparing that response to a calibration curve constructed using several standards that cover the concentration range of the unknowns. A first-order polynomial

function is frequently used to interpolate between the calibration points. The accuracy and precision of the results depend upon the accuracy of the standards, the precision of the method, and any systematic errors. One source of systematic error results from any difference in response of the analyte in the sample from that in the standard. This difference in response can result from attenuation of the signal emitted or, in the case where there is a sample preparation step, the yields being different for the sample and standard. For example, in the determination of sulfur in liquid fossil fuels by X-ray fluorescence spectrometry (XRF), it is well-established that the emission of the K-L<sub>2,3</sub> line is dependent upon the carbon and oxygen contents 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<sub>2</sub> may be different. Both of these systematic uncertainties, which are difficult to quantify, can be minimized as the difference between the matrix of the standard and sample are made identical.

The calculation software described in this paper coupled with fossil fuel SRMs will permit matrix matching of the sample and standard for any element at almost any concentration desired. This capability will permit the analyst to eliminate numeric interpolation with a concomitant reduction in uncertainty. The program permits the S, Hg, and Cl concentrations and their associated uncertainties to be calculated in blends of currently available fossil fuel SRMs without the added effort of a manual treatment of the uncertainty present in each standard.

## Experimental Section

At this time, a select group of NIST SRMs have been tested for mixing to generate standards with known S, Cl, and Hg concentrations. These SRMs and their associated concentrations/mass fractions are listed in Table 1. The software used for mixing was written in Visual Basic for Applications in Microsoft Excel 2003 on a personal computer (PC). An example screenshot of the starting or “Home” page of the program is shown in Figure 2.

Detailed descriptions of the blending and analysis of SRMs can be found in the literature,<sup>7</sup> as well as in a video demonstration.<sup>8</sup> After the software is used to calculate the amounts of each reference material required to reach a desired target concentration, each component must be weighed by difference into a container. Components for the mixture are assumed to be weighed on a single balance, which introduces no more than 0.2% uncertainty to the weighing process (e.g.,  $\geq 0.2500 \pm 0.0005$  g or  $\geq 0.02500 \pm 0.00005$  g). The procedure differs depending upon whether solid powders or liquid matrices are being used. Before weighing, solid mixtures require the amount of moisture in each component of the mixture to be determined after each solid component is allowed to equilibrate with the laboratory atmosphere before weighing. The solid component with the least mass should be added to the mixing vessel first. For solid samples, after adding both components to a single container, no physical mixing should be performed. Liquid components are mechanically mixed together. The size of the mixing container for liquid blends must be carefully chosen, so that after both components are added, a large enough volume remains for mixing to occur. The type of container and cap must prevent contamination and must not allow parts of a component or blend to be trapped behind or

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**START HERE**

**I** Matrix: Solid

coal metallurgical coke petroleum coke

**II** Select Analyte

**III** Set Target Concentration and Mass

**IV** Make Standards

**HOME PAGE**

**NIST**  
National Institute of Standards and Technology  
U.S. Department of Commerce

**Tools**

Help

Add/Change/Delete Standards

Start over/Erase sheets

**GUIDE FOR BLENDING**

**Instructions for Solid SRMs:**

1. Use one balance for all weighings ( $\geq 0.2500 \text{ g} \pm 0.0005 \text{ g}$ , or  $\geq 0.02500 \text{ g} \pm 0.00005 \text{ g}$ ).
2. Mix each CRM bottle by holding the top and bottom of the bottle in opposite hands, and rolling each hand over the other.
3. CRMs in powder form are to be equilibrated to the laboratory's atmosphere before weighing. Constant mass can be verified on a separate balance with a sensitivity of at least  $\pm 0.001$ . The test portions and their corresponding moisture samples are to be weighed contemporaneously.
4. Weigh a sample for determination of residual moisture in order to correct the certified value of each component from a dry basis to an "as run" (i.e., as weighed basis).
5. Record the mass of the sample combustion crucible, boat or digestion bomb (alternatively tare the balance and zero the mass of the crucible). Note: To minimize potential weighing errors with a five place balance, DO NOT handle the crucible once it has been placed on the balance, until all components have been weighed.
6. Add the CRM component of lesser mass directly into the sample boat. To minimize deviation from the target mass, the CRM material can be placed on an auxiliary balance and tared, so that the mass of the material captured on the spatula can be seen as a negative number on this auxiliary balance and, before transfer, its mass adjusted until very near the target mass.
7. Record the combined mass of the crucible plus first component. Then calculate the mass of the lesser component by difference. Now, if desired, recalculate an updated target mass of the greater component based on the actual mass of the lesser component to better hit the desired target value of the blend. After recording the combined mass of the crucible plus first CRM component, add the second CRM component on top of first component in the crucible (Alternatively, re-tare and zero the mass of the crucible plus first CRM component). Record total mass and calculate the mass of the second component by difference.
8. Lightly tap the sample crucible to level the CRM materials in the container. DO NOT stir or otherwise touch the actual sample.
9. Now combust or digest the sample and measure each blend and parent CRM for the analyte of interest. Combining multiple measurements (n) into a single result provides a practical means of increasing the sample mass of each replicate and in improving the efficacy of the QC Test.
10. Proceed to the QC Test for Blends.

Figure 2. Home page of the standard mixing program.

Table 1. List of NIST SRMs Tested for Mixing<sup>9</sup>

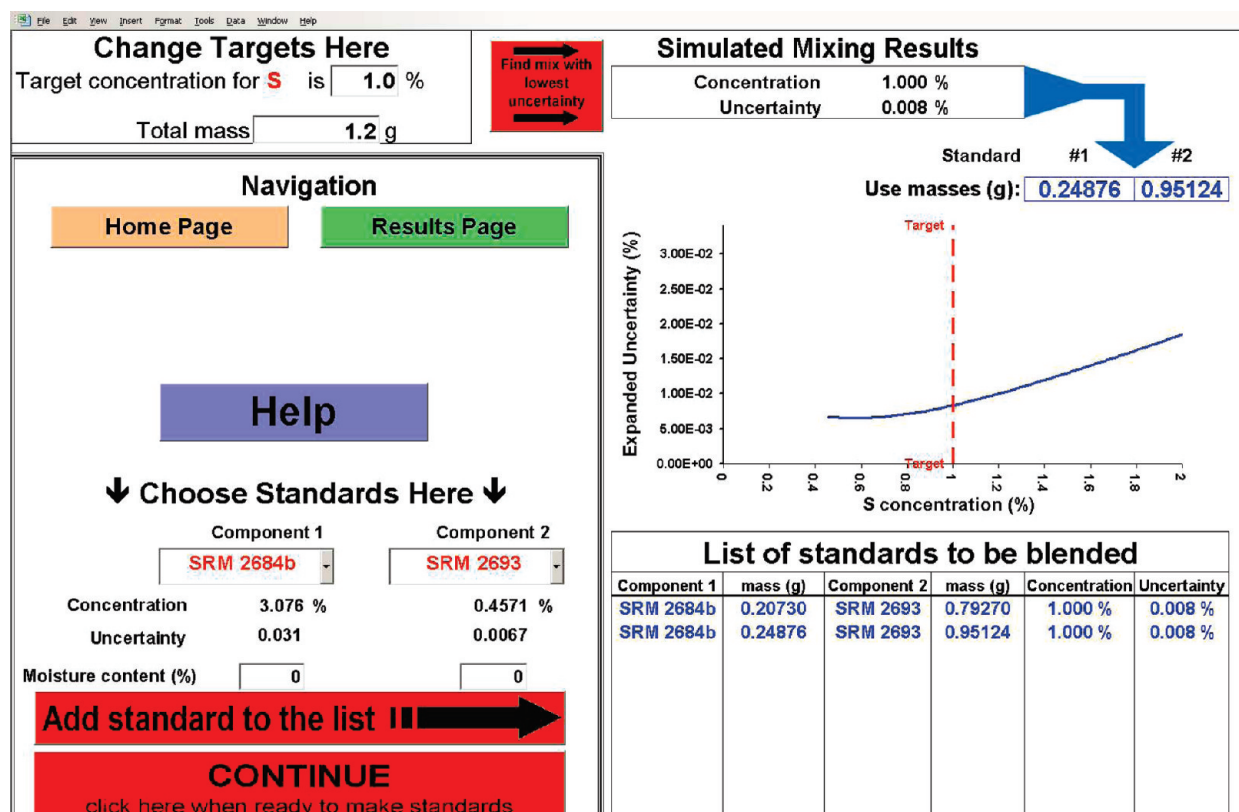
matrix	SRM	material type	S (%)	Cl (mg/kg)	Hg ( $\mu\text{g/kg}$ )
solid	2683b	bituminous coal	1.955		90.0
	2684b	bituminous coal	3.076		97.4
	2685b	bituminous coal	4.730	517	146.2
	2692b	bituminous coal	1.170	1651	133.3
	2693	bituminous coal	0.4571	369.6	37.3
	2775	foundry coke	0.5816		
	2776	foundry coke	0.825		
	2718	trace elements in green petroleum coke	4.703		
	2719	trace elements in calcined petroleum coke	0.8877		
	1616b	sulfur in kerosene	0.000841		
	1617a	sulfur in kerosene	0.17307		
	1624d	sulfur in diesel fuel oil	0.3882		
	2723a	sulfur in diesel fuel oil	0.00110		
	2724b	sulfur in diesel fuel oil	0.04265		0.034
liquid	2770	sulfur in diesel fuel oil	0.004157		
	2771	sulfur in diesel fuel blend stock	0.0000102		

within a cap seal. Mixing of the liquid blend must be performed by carefully holding the capped container sideways with hands parallel. Slowly mix the liquid contents by alternating the height of the hands and rolling the container slowly as the hands change position. Care must be taken to minimize the introduction of entrapped air into the sample whenever liquids are being mixed. Only total combustion methods can be used for solid mixtures,<sup>2</sup> but liquid mixtures can be measured using the same analytical techniques appropriate for nonblended standards. Lastly, after analysis, the quality of the measurements must be assessed through quality control (QC) procedures and by checking the interval repeatability ( $I_r$ ).<sup>7</sup> Whenever using the mixing program discussed here, it is still important that each analyst must ensure that the measurements conform to the quality system of their organization. The  $I_r$  QC test described is not a substitute for QC procedures already present in a laboratory.

## Results and Discussion

The mixing software is split into four subunits: (i) setting the target blend concentration and mass, (ii) choosing standards, (iii) making the blended standards, and (iv) the  $I_r$  QC test. Whenever the program is started, the user must have an idea of the approximate target concentration for the desired analyte (S, Cl, or Hg). The user must also know what type of matrix is being analyzed, so that appropriate reference materials can be selected (e.g., coal or petroleum coke). Once these conditions have been ascertained, the user starts on the home page (shown in Figure 2) by selecting a mass of the

(9) National Institute of Standards and Technology (NIST). SRM Order Request System, 2010, <http://www.nist.gov/srm>.



**Figure 3.** Screenshot of mixing program output after optimal mix of standards has been selected. The graph shown illustrates the relationship between uncertainty and final mixture concentration for a selected analyte.

mixture that the user would like to make, being cognizant of the method being used and physical constraints. Once these parameters are set, the first phase of the program is complete.

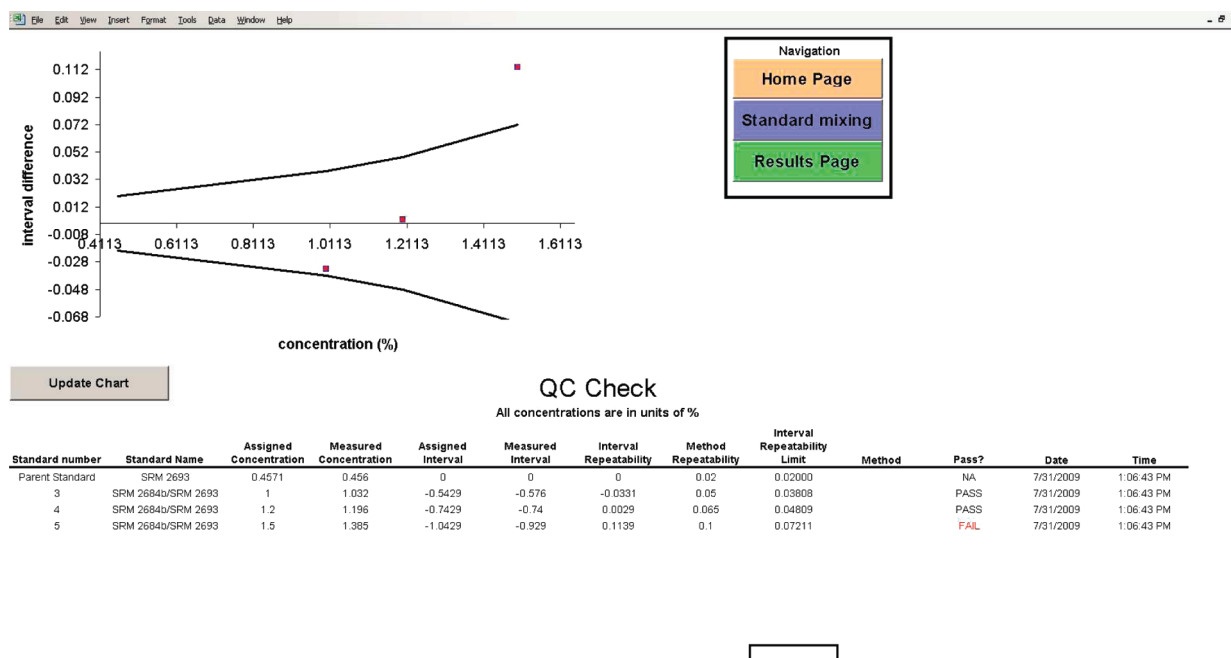
The second part of the program simulates the mixing of all available standards that conform to the user's settings. The calculations are used to choose the optimal mix at the target concentration of the analyte. The optimal mix is the mix that arrives at the target concentration with the lowest uncertainty in the concentration of the mixture. By default, the program contains a library of NIST fossil fuel SRM values, uncertainties, and minimum sample mass requirements. Because the user may not possess the entire library or may choose to overrule the automated selection of the optimal mix, other reference materials that conform to the user's initial material constraints can be selected instead. These other choices are available in a drop down menu on the second page of the program, the mixing page. This page permits the user to view a curve of uncertainty versus concentration (Figures 1 and 3) produced by the program, so that the target concentration and mixture mass can be adjusted, if necessary. The estimated mass required of each component is added to a list that the user can then use to prepare the mixtures.

The third phase of the program comes into play after each two-component mixture standard is prepared. Because the amount of each component weighed for mixing will differ from the targeted component masses, the actual masses used as well as the measured moisture contents for each solid component are entered. In this way, the actual concentration of a given mixture is calculated and added to the results page along with a date and time stamp, which can be easily printed for review. After this calculation, the user can analyze the prepared blend and samples.

The last section of the program performs a QC test of the standards prepared. The QC test requires the user to enter the measured concentrations for each standard analyzed and the repeatability limit ( $r$ ) of the method used. This measured concentration is compared to the concentration calculated for the blend and the interval repeatability limit of the measurement method, as described previously.<sup>7</sup> At least one blended standard and one of the unblended certified parent standards must be prepared and measured for a QC test to be performed. An example (using simulated data) of the output received from the QC test is shown in Figure 4. This example shows simulated data for all of the standards mixed as well as one of the unblended parent SRMs. In this example, the interval between SRM 2693 and the highest concentration blended standard falls outside the interval-repeatability limit<sup>7</sup> of the method used and fails the  $I_r$  QC test. This failure could be due to several causes, such as material heterogeneity, operator error, or the standard concentration being outside of the linear range of the instrument. Multiple replicates can be prepared for a given blend to address material heterogeneity.

The mixing program developed is a tool for analysts seeking standards at concentrations intermediate to those produced by NIST (or other national metrology institutes). However, there are a few potential pitfalls in the mixing procedure that must be discussed to ensure that additional uncertainty is not introduced into the process. A detailed example of the blending process is reported by MacDonald et al., and this software is intended to be used in conjunction with related resources.<sup>2,7,8</sup>

While the results that the mixing software provides are based on only explored mixing ranges that ensured at least 20% of the overall mass of the final mixture would be



**Figure 4.** QC results for the simulated measurement of a mixture of SRM 2684b and SRM 2693 coals. The highest concentration blended standard is outside the allowed limits, failing the QC test.

contributed by one standard, it is conceivable that this mixing range could be expanded if the minimum sample mass of each component is taken into account. Using masses below the minimum sample mass of a reference material can cause erroneous results, but in many cases, the minimum sample mass is too large to be practical for use with some current analytical instrumentation. This can be remedied by preparation of multiple replicates of a standard and verification of results with the  $I_r$  QC test.<sup>7</sup>

### Conclusion

The mixing software presented here facilitates the preparation of standards at a continuum of concentration ranges by analysts of fossil fuel materials. Because the mathematical calculation of the uncertainty is independent of the identities of the components blended, the provided software contains

the capabilities for expansion to any element or matrix. However, the physical act of mixing each component would be different for each case, and many typical methods for measurement might not be as robust for blends of reference materials with sufficiently different matrices. Other reference materials outside the lists provided in this paper may produce blends that can be used without problems, but their use together as blend components must be verified through investigation. For this reason, expansion of this software beyond the SRMs listed is not advocated without caution, careful review, and testing by the user.

**Supporting Information Available:** Standard mixing program. This material is available free of charge via the Internet at <http://pubs.acs.org>. Latest version of Standard Mixing Program also available at: <https://www-s.nist.gov/srmors/viewTable.cfm?tableid=64>.