Improving the High-Performance Inductively Coupled Plasma Optical Emission Spectrometry Methodology through Exact Matching

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Exact matching is investigated as a means of improving high-performance inductively coupled plasma optical emission spectrometry (HP-ICP-OES), a technique developed at the National Institute of Standards and Technology (NIST) to enable elemental determinations with relative expanded uncertainty of approximately 0.2% expressed at 95% confidence. “Exact matching” refers to the very careful matching of analyte mass fractions, internal standard mass fractions, and matrix compositions among the calibration and unknown sample solutions prepared for an analysis. Computer spreadsheet modeling results and laboratory data involving 16 pairs of analyte and internal standard wavelengths show that exact matching of analyte and internal standard mass fractions, and internal standard wavelengths, results in a significant reduction in relative expanded uncertainties, expressed at 95% confidence. Exact matching is investigated as a means of improving high-performance inductively coupled plasma optical emission spectrometry (ICP-OES) to enable elemental determinations with extraordinary low uncertainty. Often called “high-performance” (HP) ICP-OES, this methodology is capable of routinely providing relative expanded uncertainties on the order of 0.2%, expressed as 95% confidence intervals and accounting for all significant components of uncertainty, in samples lacking a significantly interfering matrix. HP-ICP-OES, which has been described in detail in previous publications,1−3 incorporates a judiciously chosen internal standard, an efficient drift-correction methodology, and gravimetric solution preparation, all within a robust experimental design. The technique is based on a single-point calibration. To perform an HP-ICP-OES analysis, a set of calibration standards and a set of sample solutions of the unknown are gravimetrically prepared so that all standards and samples are nominally the same with regard to the analyte mass fractions, the internal standard mass fractions, and the matrix compositions. The sample solutions and calibration standards are run on the ICP-OES instrument in a randomized complete block sequence. In other words, the sample solutions and standards are run once each in a randomized sequence, again in a randomized sequence, and so on, until each solution has been run the desired number of times (usually five). The ratios of the analyte intensities to the internal standard intensities are calculated, and the resulting ratios are corrected for drift using a unique drift-correction approach.4 The analyte mass fraction in the unknown sample is computed from the known mass fraction of the calibration standards and any observed difference between the means of the drift-corrected intensity ratios for the sample solutions and the calibration standards. Measurements involving ICP-OES procedures that are similar to the high-performance protocol have been reported by other laboratories.5−9

The HP-ICP-OES technique has become a method of choice for many NIST measurements.10−13 These include certification measurements for NIST reference materials (RMs) and Standard Reference Materials (SRMs). For example, the technique has been used recently for the certification of the Be mass fraction in SRM 1877 Beryllium Oxide Powder.14 Also, the elemental mass fractions of the single-element standard solutions in the SRM 3100 series are routinely determined using this approach. The SRMs in the 3100 series are important, because they are used by many certified reference material (CRM) manufacturers to establish meaningful

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traceability links from the certified values of their single-element CRMs to the International System of Units (SI). As an aid to performing HP-ICP-OES analyses for such applications, NIST has made available a “traceability tool” spreadsheet that guides the user through the measurement process. The traceability tool is now being used by many commercial CRM producers, as well as other laboratories needing the low uncertainties HP-ICP-OES can provide. The traceability tool can be downloaded from the NIST Web site free of charge.

HP-ICP-OES was originally developed primarily for relatively “clean” samples (i.e., samples lacking a significantly interfering matrix). At the time of development, the assumption was made that ICP-OES is sufficiently immune to matrix effects and small variations in analyte and internal standard mass fractions to negate requirements for very careful matching of standards to samples. Approximate matching was thought to be adequate, especially regarding analyte and internal standard mass fractions. However, we have discovered through long experience that this is often untrue. For some combinations of analyte and internal standard lines, the analytical performance of HP-ICP-OES can be improved by very carefully matching the matrix characteristics and analyte and internal standard mass fractions among the solutions prepared for an analysis. Consequently, in the majority of HP-ICP-OES analyses performed currently at NIST, this “exact matching” approach is employed.

Other laboratories have reported use of this sort of exact matching with ICP-OES methodologies that are similar to the high-performance protocol. In a determination of minor elements in steel, Merson and Evans obtained relative expanded uncertainties \( (k = 2) \) on the order of 0.5% by matching analyte concentrations to within 5% relative and matrix Fe concentrations to within 3% relative between samples and calibration standards. The effect of a 3% change in the Fe concentration on the ratio of the analyte intensity to the internal standard element intensity was observed to be on the order of the 0.1% measurement precision. On this basis, the authors concluded that matching the matrix Fe concentrations to better than 3% relative would not be beneficial. In other published work, Simpson et al. applied the same approach to the determination of Ca in human serum, obtaining a relative expanded uncertainty \( (k = 2) \) of 1.2%.

More recently, Rabb and Olesik studied the use of HP-ICP-OES for analyses of samples having complex matrices. To reduce matrix effects, they coupled the use of matrix matching, standard addition, and the common analyte internal standard (CAIS) technique with HP-ICP-OES. They found that even a small amount of an element that is present in samples but absent in calibration standards can induce an unacceptable bias in the analytical results. Specifically, while studying the determination of Cu using Mn as the internal standard, they found that mass fractions of Zn as small as 25 mg kg\(^{-1}\) resulted in a 0.56% change in the ratio of the Cu intensity to the Mn intensity. This matrix effect may seem small. However, it would induce a bias in the determined Cu concentration of approximately 0.5% relative, far exceeding the typical 0.2% relative uncertainty attained with HP-ICP-OES. This example illustrates the need for careful matrix matching.

NIST has recently completed detailed studies of the benefits afforded through the implementation of exact matching with HP-ICP-OES. The studies involved both exact matching of analyte and internal standard mass fractions and exact matching of matrix compositions among the solutions prepared for analysis. The results are reported in this paper.

**EXPERIMENTAL SECTION**

All laboratory experiments were performed using a Perkin-Elmer (Waltham, MA) model 3300DV ICP-OES instrument, equipped with a cross-flow nebulizer, a Scott double-pass spray chamber fabricated from Pyton, an alumina injector with an inner diameter of 2.0 mm, and a quartz torch. (Identification of commercial products in this paper was done in order to specify the experimental procedure. In no case does this imply endorsement or recommendation by the National Institute of Standards and Technology.) The plasma was operated using standard settings of 1300 W rf power, and plasma, auxiliary, and nebulizer gas flow rates of 15, 0.5, and 0.80 L min\(^{-1}\), respectively. These parameters produced robust plasma giving Mg (II) 280.270 nm to Mg (I) 285.213 nm intensity ratios consistently >8. The values were corrected for the differing Echelle grating diffraction efficiencies at the two wavelengths by multiplying the observed ratios by 1.85. Solutions were delivered to the nebulizer by a peristaltic pump at a flow rate of 1.50 mL min\(^{-1}\). All spectra were acquired in axial viewing mode unless otherwise stated. Spectra were quantified as peak areas with two-point background correction.

All solutions were prepared using Fisher trace metal grade acids and deionized water. The SRMs in the NIST SRM 3100 series standard solutions were used as sources of the analyte and internal standard elements.

**RESULTS AND DISCUSSION**

The benefits of exactly matching the analyte and internal standard mass fractions and of exactly matching the matrix compositions among the solutions prepared for HP-ICP-OES analysis were studied in two separate sets of experiments. To be clear, exact matching of the analyte and internal standard mass fraction does not mean that the mass fractions of the analyte are equal to those of the internal standard. Rather, it means that the mass fractions of the analyte are the same among all prepared solutions (calibrants and unknown solutions), and likewise, the mass fractions of the internal standard are the same among all prepared solutions (calibrants and unknown solutions), even though the analyte mass fractions may be different from the internal standard mass fractions.

Exact Matching of Analyte and Internal Standard Mass Fractions. Laboratory Experiments. The effects of exactly matching the analyte and internal standard mass fractions among solutions were investigated as follows. For each of 16 different combinations of analyte and internal standard lines, a set of eight solutions, each 50 mL in volume, was prepared using approximate

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15 Available at https://www-s.nist.gov/srmors/tables/viewTableH.cfm?tableid=39.
match the analyte and internal standard element mass fractions among solutions. The points for each set of eight solutions are normalized to the mean. The analytical and internal standard wavelengths were Cs (I) 455.528 nm and In (I) 325.609 nm, respectively. The Cs and In mass fractions in the solutions were 440 and 6 mg kg⁻¹, respectively.

Figure 1. ICP-OES relative sensitivity values observed for sets of eight solutions prepared with (closed symbols) and without (open symbols) exact matching of analyte and internal standard mass fractions. The two sets of solutions were run in two separate experiments on the ICP-OES instrument. In each experiment, a set of solutions was run in a randomized complete block sequence, and the ratios of the analyte intensities to the internal standard intensities were calculated and drift-corrected. A separate value of the ICP-OES instrument sensitivity, defined as the drift-corrected analyte to internal standard intensity ratio divided by the ratio of the analyte mass fraction to the internal standard mass fraction (hereafter called the analyte to internal standard mass fraction ratio), was calculated for each of the eight solutions. The relative standard deviation (RSD) of the eight sensitivity values computed in this way was employed as a quantitative measure of the variability of those values. Comparisons of the variability of the sensitivity values observed for the two sets of solutions provided a means of assessing the benefits of exact matching.

As an example, the data for the combination of the Cs (I) 455.528 nm analytical wavelength and the In (I) 325.609 nm internal standard wavelength is presented in Figure 1. The values of ICP-OES instrument sensitivity observed for the approximately matched (i.e., without exact matching) and exactly matched sets of solutions are plotted, with the eight points in each set normalized to their respective mean (hereafter called relative sensitivity values). For this case, exactly matching the analyte and internal standard mass fractions dramatically improved the precision of the relative sensitivity values.

The data for all 16 combinations of analyte and internal standard wavelengths are given in Table 1. There are 17 rows of data in the table because data for the combination of Mo as the analyte and Y as the internal standard were acquired with both axial and radial viewing using the same sets of approximately and exactly matched solutions. The three analytical lines for S, which form a multiplet, were observed simultaneously. The third and fourth columns in the table give the RSDs of the sets of relative sensitivity values observed for the approximately and exactly matched solutions. The fifth column provides the “improvement factors” obtained through exact matching, calculated in each case as the RSD of the relative sensitivity values for the approximately matched solutions divided by that for the exactly matched solutions. The observed improvement factors range from 0.64 to 51. The RSDs of the nominal analyte and internal standard element mass fraction ratios for the approximately matched solution sets ranged from about 2% to about 9%, and the analyte and internal standard element mass fractions among the solutions in a given set were uncorrelated. This is the way solutions for HP-ICP-OES have traditionally been prepared at NIST.

The F-distribution can be used to evaluate the statistical significance of the improvement factors, because these factors are

Table 1. Improvements in the Precision of ICP-OES Relative Sensitivity Values Obtained by Exactly Matching the Analyte and Internal Standard Element Mass Fractions among Solutions

<table>
<thead>
<tr>
<th>analyte line</th>
<th>internal standard line</th>
<th>RSD of relative sensitivity values, %</th>
<th>improvement factor&lt;sup&gt;a&lt;/sup&gt;</th>
<th>α&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (I) 396.152 nm</td>
<td>Mn (I) 279.482 nm</td>
<td>0.116 approximate matching</td>
<td>exact matching</td>
<td>2.8</td>
</tr>
<tr>
<td>Be (I) 265.045 nm</td>
<td>Mn (I) 279.482 nm</td>
<td>0.029</td>
<td>0.045</td>
<td>0.64</td>
</tr>
<tr>
<td>Ca (II) 393.366 nm</td>
<td>Sc (II) 424.682 nm</td>
<td>0.38</td>
<td>0.53</td>
<td>0.72</td>
</tr>
<tr>
<td>Co (II) 238.892 nm</td>
<td>Y (II) 371.030 nm</td>
<td>0.015</td>
<td>0.010</td>
<td>1.5</td>
</tr>
<tr>
<td>Cs (I) 455.528 nm</td>
<td>In (I) 325.609 nm</td>
<td>0.697</td>
<td>0.035</td>
<td>20</td>
</tr>
<tr>
<td>Cu (I) 324.754 nm</td>
<td>Mn (I) 279.482 nm</td>
<td>0.087</td>
<td>0.016</td>
<td>5.3</td>
</tr>
<tr>
<td>Ge (I) 265.117 nm</td>
<td>In (I) 325.609 nm</td>
<td>0.371</td>
<td>0.033</td>
<td>11</td>
</tr>
<tr>
<td>Mg (II) 279.555 nm</td>
<td>Y (II) 371.030 nm</td>
<td>0.171</td>
<td>0.047</td>
<td>3.6</td>
</tr>
<tr>
<td>Mn (II) 257.610 nm</td>
<td>Y (II) 371.030 nm</td>
<td>0.166</td>
<td>0.051</td>
<td>3.3</td>
</tr>
<tr>
<td>Mo (II) 204.598 nm</td>
<td>Y (II) 371.030 nm</td>
<td>1.184</td>
<td>0.047</td>
<td>25</td>
</tr>
<tr>
<td>Mo (II) 204.598 nm&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Y (II) 371.030 nm&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.059</td>
<td>0.059</td>
<td>1.0</td>
</tr>
<tr>
<td>Na (I) 589.592 nm</td>
<td>Sr (I) 460.733 nm</td>
<td>0.069</td>
<td>0.061</td>
<td>1.1</td>
</tr>
<tr>
<td>P (I) 213.618 nm</td>
<td>Ge (I) 265.117 nm</td>
<td>0.097</td>
<td>0.020</td>
<td>4.8</td>
</tr>
<tr>
<td>S (I) 180.731 nm&lt;sup&gt;c&lt;/sup&gt;</td>
<td>P (I) 213.618 nm</td>
<td>2.028</td>
<td>0.040</td>
<td>51</td>
</tr>
<tr>
<td>S (I) 182.034 nm&lt;sup&gt;c&lt;/sup&gt;</td>
<td>P (I) 213.618 nm</td>
<td>1.047</td>
<td>0.047</td>
<td>22</td>
</tr>
<tr>
<td>S (I) 182.625 nm&lt;sup&gt;c&lt;/sup&gt;</td>
<td>P (I) 213.618 nm</td>
<td>0.084</td>
<td>0.041</td>
<td>2.1</td>
</tr>
<tr>
<td>Se (I) 196.026 nm</td>
<td>In (I) 325.609 nm</td>
<td>1.761</td>
<td>0.069</td>
<td>26</td>
</tr>
</tbody>
</table>

<sup>a</sup> See text for further details. <sup>b</sup> Column 3 divided by column 4. <sup>c</sup> α gives the probability that the observed improvement factor can be attributed to random noise, based on the F-distribution. <sup>d</sup> Radial viewing at 15 mm above the load coil. <sup>e</sup> Wavelength in vacuum.
ratio of standard deviations. There are seven degrees of freedom associated with both the numerator and denominator in each ratio. The final column in Table 1 gives the value of \( \alpha \) corresponding to each improvement factor, where \( \alpha \) states the probability that the observed improvement factor can be attributed to random noise. From this assessment, 8 of the 17 improvement factors have \( \alpha \)-values of less than 0.05. This means that half of the improvement factors can be attributed to actual benefits of exact matching with a statistically confidence level of 0.95 or greater. Moreover, several of the improvement factors are very statistically significant. The most extreme example was found when S (I) 180.731 nm was used as the analytical line and P (I) 213.618 nm was used as the internal standard line.

Close examination of some of the approximately matched data sets showed that the relative sensitivity values were sometimes dependent on the nominal analyte to internal standard mass fraction ratios. The data for the approximately matched solution set using P (I) 213.618 nm as the analytical line and Ge (I) 265.117 nm as the internal standard line are plotted in Figure 2 as an example. In this case, increases in the nominal mass fraction ratio resulted in decreases in the relative sensitivity. The dependence was reversed for some other combinations of analyte and internal standard wavelengths. Given that HP-ICP-OES is essentially based on a single-point calibration, this behavior implies nonlinearity in the instrument response for the analytical line, the internal standard line, or both. Whether the dependence of sensitivity on mass fraction ratio is direct or inverse would depend upon the directions and magnitudes of the instrument response curvature for both lines. Curvatures in both directions have been observed in our laboratory.

To investigate this further, calibration curves were measured for each analytical and internal standard wavelength, and the degree of nonlinearity, expressed as a percentage, in each curve was quantified as

\[
\text{nonlinearity} = 100 \left( \frac{m_{\text{tan}} - m_{\text{lin}}}{m_{\text{lin}}} \right)
\]  

(1)

where \( m_{\text{lin}} \) is the slope of the tangent to the curve at the analyte to internal standard mass fraction ratio used during the exact matching experiments and \( m_{\text{lin}} \) is the slope of a hypothetical line defined by the point on the curve pertaining to this ratio and the origin. In essence, the tangent is a realization of the actual ICP-OES instrument response, whereas the hypothetical line represents the ideal, unrealized instrument response. A composite nonlinearity score was then calculated for each exact matching experiment by taking the square root of the sum of the squares of the nonlinearity scores for the analyte and internal standard wavelengths.

A quantitative measure of the effect of ICP-OES instrument response nonlinearity on the improvement factor is illustrated by Figure 3. In this graph, the improvement factors from the exact matching experiments are plotted against the composite nonlinearity scores computed as described above. The improvement factors have been “standardized” by dividing the values in Table 1 by the corresponding RSDs of the nominal analyte to internal standard mass fraction ratios of the solutions in the approximately matched sets. This standardization of the improvement factors is necessary to plot meaningfully the data from the different experiments on the same ordinate scale. This is because the benefit of exact matching should increase as the degree of matching utilized in the preparations of the approximately matched sets of solutions deteriorates.

The graph in Figure 3 demonstrates an approximately linear relationship between the standardized improvement factors and the composite nonlinearity scores. This relationship shows that nonlinearity in the instrument response to the analyte and/or internal standard can induce solution-to-solution imprecision when solutions in a set are only approximately matched. The data for the three S analytical wavelengths, which are marked in Figure 3, are especially illuminating in this regard, since they were acquired simultaneously from the same approximately and exactly matched solution sets. Similarly, the data for Mo viewed axially and radially, also marked in Figure 3, are illustrative, because they too were acquired using the same solution sets.

These laboratory experiments indicate that, for many combinations of analyte and internal standard wavelengths, the quality of
HP-ICP-OES analysis depends upon the degree of matching of the analyte and internal standard mass fractions among the solutions prepared for the analysis. The data show that exact matching among the solutions within a given set of calibration standards or unknown samples in many cases improves solution-to-solution precision. Variability observed among the data obtained from such solution sets that was previously attributed to real irreproducibility in solution preparation (e.g., see Figure 2 and related discussion in ref 2) is now seen to have been more likely due to the deleterious effects of inexact matching. More important, the data discussed here imply that exact matching between the set of calibration standards and the set of unknown samples may mitigate a potential bias that would otherwise be undetected and not reflected in the uncertainty budget.

**Spreadsheet Modeling.** Further investigations of the effects of ICP-OES instrument response nonlinearity were conducted through computer spreadsheet modeling. As an example, consider the case in which the instrument response to both the analyte and internal standard wavelengths is characterized by the quadratic equation intensity = $-50 \text{(mass fraction)}^2 + 100 \text{000(mass fraction)}$. This case was selected as the example because it is particularly instructive. The nonlinearity is visually undetectable, and the coefficient of determination, $R^2$, for a linear least-squares fit [intensity = $99 \text{000(mass fraction)} + 3000$] is 0.999 992. Without plotting the residuals associated with the linear fit, a reasonable analyst would conclude that the instrument response is highly linear. The nonlinearity might not even be apparent in the residual plot when random noise is also present. The composite nonlinearity score for analyte and internal standard lines having this degree of curvature is 0.71%. Sets of analyte and internal standard mass fractions were generated randomly, all having mean values of 10 mg kg$^{-1}$, and with the absence of correlation between the analyte and internal standard mass fractions within a given set. With the use of the hypothetical instrument response, plots like that in Figure 2 were generated for the various sets. The plot for a set in which the RSD of the analyte to internal standard mass fraction ratios was 0.6% is given in Figure 4. As shown, the plot has the same form as the plot in Figure 2. The range of relative sensitivity values observed is 0.10%, which is half the expanded uncertainties often attained using HP-ICP-OES analysis.

The degree of exact matching required for a specific analysis depends upon the precise instrument nonlinearity associated with the analytical and internal standard wavelengths being employed. Given the wide range of possibilities, it is impractical to attempt to provide guidance pertaining to each possible situation. Instead, consider the case in which the instrument response to both the analyte and internal standard wavelengths is characterized by the quadratic equation intensity = $-300 \text{(mass fraction)}^2 + 100 \text{000(mass fraction)}$. This can be considered a worst case scenario, in the sense that the apparent linearity is still high. The curve is visually linear, and the coefficient of determination, $R^2$, resulting from a linear least-squares fit is 0.9997. Therefore, even a prudent analyst might incorrectly assume that the instrument response is actually linear.

The dependence of the RSD of the relative sensitivity values, RSD$_{RSV}$, on the RSD of the analyte to internal standard mass fraction ratios, RSD$_{MFR}$, generated using this model is described by the equation RSD$_{RSV} = 0.026(\text{RSD}_{MFR})^2 + 0.031(\text{RSD}_{MFR}) + 0.000 \text{002}$. This equation is useful for quantifying, in this particular case, the degree of exact matching of the analyte to internal standard mass fraction ratios among the solutions in a given set (e.g., a set of calibration standards) necessary to avoid significant solution-to-solution imprecision induced by the underlying nonlinearity in the instrument response. As stated earlier, the expanded uncertainties attained using HP-ICP-OES analysis are generally on the order of 0.2%. Given a coverage factor, $k$, of 2, the combined standard uncertainty is normally on the order of 0.1%. As a rule of thumb, it may be assumed that RSD$_{RSV}$ should be kept below approximately one-fifth of this value, or 0.02%, to avoid significant solution-to-solution imprecision. For this particular case, this means that the solutions must be prepared such that RSD$_{MFR}$ is less than or equal to about 0.6%.

The dependence of the relative range of relative sensitivity values, RANGE$_{RSV}$, on the relative range of the analyte to internal standard mass fraction ratios, RANGE$_{MFR}$, generated using this model is given by the equation RANGE$_{RSV} = 0.0087(\text{RANGE}_{MFR})^2 + 0.031(\text{RANGE}_{MFR}) + 0.000 \text{002}$. This equation can be used to quantify, for this particular case, the degree of exact matching between the mean analyte to internal standard mass fraction ratio of the calibration standards and that of the unknown sample solutions required to avoid significant analytical bias in the HP-ICP-OES analysis. It may be assumed that RANGE$_{RSV}$ should be kept below 0.02% relative to avoid such bias. This means that the solutions must be prepared such that the relative difference in the mean analyte to internal standard mass fraction ratio for the calibration standards and that for the unknown solutions is less than or equal to about 0.6%.

It should be emphasized that, from an analytical viewpoint, exactly matching the mean analyte to internal standard mass fraction ratio of the calibration standards to that of the unknown solutions is generally more important than exactly matching the analyte to internal standard mass fraction ratios among a set of either the calibration standards or the unknown solutions. This is because the analytical bias induced by a mismatch between the mean ratios might be undetected and not reflected in the
uncertainty budget for the HP-ICP-OES analysis. In contrast, the solution-to-solution imprecision induced by mismatching the ratios among a set of solutions will naturally be reflected in the data and, therefore, inherently included in the uncertainty estimation.

As another point, exactly matching only the ratios of the analyte mass fractions to the internal standard mass fractions while allowing these mass fractions to vary on an absolute scale would be an inadequate approach. This is because the instrument responses to the analytical and internal standard wavelengths will almost certainly be different.

Use of Blanks. To this point in the discussion, the use of blanks in HP-ICP-OES analysis has not been mentioned. The high-performance protocol, as described in previous publications, does not include blanks. However, nonzero blank intensity associated with the analyte and/or internal standard wavelength could theoretically have similar effects to those caused by instrument response nonlinearity. This is due to the fact that when one or more nonzero blank intensities apply, the actual slope of the instrument response function is necessarily different from the slope assumed in the analysis. Preliminary spreadsheet modeling confirmed this, but also pointed out that, given even the highest blank intensities commonly observed in our laboratory, the severity of the problem seems to be much less than that associated with even subtle instrument nonlinearity.

The potential for analytically deleterious effects of nonzero blanks in HP-ICP-OES analysis was investigated in the laboratory. Experiments were conducted by running sets of eight exactly matched solutions and four blanks in a randomized complete block sequence on the ICP-OES instrument, calculating and drift-correcting the analyte to internal standard intensity ratios, and computing the relative sensitivity values for each solution, both with and without taking the blank intensities into account. This was done for each of the 16 combinations of analyte and internal standard wavelengths listed in Table 1. An improvement factor, defined as the RSD of the relative sensitivity values obtained using the blanks divided by that obtained without using the blanks, was calculated for each combination. The mean and median improvement factors were 0.96 and 0.98, respectively, and the largest value was only 1.05. These results confirm that the effects of nonzero blanks on HP-ICP-OES analysis are usually negligible.

Implications. The results presented here show that exact matching of analyte mass fractions and internal standard mass fractions among the solutions within a given solution set (e.g., a set of calibration standards) and between the set of calibration standards and the set of unknown sample solutions can mitigate analytically deleterious effects induced by nonlinearity in the ICP-OES instrument response associated with the analyte and/or internal standard. It is advisable to check experimentally the linearity of instrument response at both wavelengths prior to HP-ICP-OES analysis. Visual examination of a plot of the residuals resulting from a linear fit to the data is one effective approach. Simply relying upon the value of the correlation coefficient or coefficient of determination should be avoided, due to insensitivity to small degrees of curvature. If nonlinearity is found at either wavelength, another wavelength should be selected. Alternatively, solutions may be prepared at lower analyte and internal standard mass fractions to shift the working ranges into more linear regions. Taking such precautions reduces the degree of exact matching required.

HP-ICP-OES analysis requires an initial guess at what the analyte mass fraction in the unknown sample is likely to be so that matching calibration standards can be prepared. If the analyte mass fraction determined through the analysis is too different from the initial guess, it may be advisable to perform a subsequent HP-ICP-OES analysis using the determined analyte mass fraction in place of the initial value. It is difficult to give specific guidance regarding the magnitude of difference that should trigger a subsequent analysis. As a rule of thumb, it is suggested that a subsequent analysis should be performed when the initial value falls outside the expanded uncertainty interval, expressed at a level of confidence of 95%, associated with the determined value.

Exact Matching of Solution Matrix Compositions. The presence of matrix effects in ICP-OES has been recognized almost since the time the method was first introduced to the analytical community. It is well-known that analytical accuracy can be degraded by these matrix effects and that the conscientious analyst may need to take steps to mitigate the consequences. The approaches to reducing these consequences that are most often used include standard addition calibration and matrix matching between calibration standards and unknown samples. For a large majority of analytical applications of ICP-OES, percent level or poorer uncertainty is acceptable. In these cases, the degree of matrix matching required for adequate mitigation of matrix effects is usually not high. However, this may not be the case for applications of HP-ICP-OES, owing to the fact that target relative uncertainties are on the order of 0.2% or better.

Matrix effects and the benefits of exactly matching matrix compositions among the solutions prepared for HP-ICP-OES analysis were studied as follows. For several combinations of analyte and internal standard wavelengths, sets of solutions were prepared having nominally identical analyte and internal standard mass fractions but with systematically varied matrix compositions. The solutions in each set were run on the ICP-OES instrument in a randomized complete block sequence for a total of five runs per sample. The analyte to internal standard intensity ratios were calculated and corrected for drift, and the relative sensitivity values observed for each solution were computed. Experiments were performed in this way for the two major categories of ICP-OES matrix effects that are most relevant to HP-ICP-OES analysis. The categories of interest are acid effects and concomitant element effects, specifically those of easily ionized elements (EIEs), such as Na.

Acid Effects. A representative example of data obtained while investigating the influence of acid effects on HP-ICP-OES is shown in Figure 5. This graph illustrates the inverse linear dependence of the instrument sensitivity on the mass fraction of nitric acid observed for sample solutions prepared to contain nominally identical mass fractions of analyte (115 mg kg\(^{-1}\) P) and internal standard (18 mg kg\(^{-1}\) Ge). The magnitude of the slope of the line implies that to mitigate significant solution-to-solution imprecision, again taken to be represented by an RSD of 0.02%, the standard deviation of the nitric acid mass fractions among the solutions in a given set of solutions (e.g., a set of calibration standards) should not exceed approximately 0.0007. At a mean nitric acid mass fraction of 0.02, this equates to an RSD of about
Figure 5. Dependence of the observed relative sensitivity of the ICP-OES instrument on the mass fraction of nitric acid for a set of solutions prepared to contain identical mass fractions of analyte (115 mg kg\(^{-1}\) P) and internal standard (18 mg kg\(^{-1}\) Ge). Error bars represent 95% confidence intervals calculated from the responses for replicate solutions at each nitric acid mass fraction: analytical wavelength, P (l) 213.618 nm; internal standard wavelength, Ge (l) 265.117 nm.

Figure 6. Dependence of the observed relative sensitivity of the ICP-OES instrument on the nitric and hydrochloric acid mass fractions for a set of solutions prepared to contain identical total acid (nitric plus hydrochloric) mass fractions of 0.02 and identical mass fractions of analyte (115 mg kg\(^{-1}\) P) and internal standard (18 mg kg\(^{-1}\) Ge). The line was fitted to the data using the hydrochloric acid mass fraction values. The equation for a regressed line fitted using the nitric acid mass fractions would be identical, except that the sign of the slope would be negative. The magnitude of the slope of the line implies that keeping solution-to-solution imprecision below 0.02% RSD requires that the standard deviation of the nitric and hydrochloric acid mass fractions among the solutions in a given set be kept below about 0.0002. The RSD equivalents will, of course, depend upon the mean nitric and hydrochloric acid mass fraction values. The magnitude of the slope also implies that keeping analytical bias below 0.02% relative requires that the absolute difference between the mean mass fractions of either acid for the set of calibration standards and the set of unknown solutions be kept below approximately 0.0002.

**EIE Effects.** The results of studies concerning the effects of EIEs on HP-ICP-OES analysis are presented in Figure 7. For these studies, sets of solutions were prepared to contain identical analyte and internal standard mass fractions and acid compositions but with varying mass fractions of Na. The source of Na used was SRM 3152a sodium standard solution, lot no. 010728. Importantly, this SRM does not contain any of the analytes or internal standards at mass fractions that could significantly perturb the analyte or internal standard compositions of the prepared solutions. The plots for the analyte P and internal standard Ge in Figure 7a and for the analyte Cu and internal standard Mn in Figure 7b clearly indicate linear dependences of ICP-OES instrument sensitivity on Na mass fractions varying between 0 and 4.0 mg kg\(^{-1}\). The two sets of data plotted in Figure 7b, which were acquired on two separate days using two separate sets of solutions, show that this dependence is reproducible. To the authors’ knowledge, EIE effects at such small mass fractions of an easily ionized element have never before been demonstrated. However, these results are consistent with the extreme sensitivity of Cu analysis to the presence of Zn mass fractions as small as 25 mg kg\(^{-1}\) reported by Rabb and Olesik.\(^7\) Given the magnitudes of the slopes of the fitted lines in these two plots, maintaining 0.02% or lower RSDs arising from solution-to-solution imprecision would require that the solutions within a given set be prepared such that the standard deviations of the Na mass fractions do not exceed 0.4 and 0.2 mg kg\(^{-1}\) for the P/Ge and Cu/Mn pairs, respectively. Also, avoiding analytical bias larger than 0.02% relative would require that the mean Na mass fraction of the calibration standards differ from that of the unknown solutions by less than 0.4 and 0.2 mg kg\(^{-1}\) for the P/Ge and Cu/Mn pairs, respectively. It is possible that the necessity of matching the Na mass fractions so closely might be somewhat alleviated through “buffering”, whereby a large amount of Na would be intentionally and precisely added to all solutions.

In contrast to the plots in panels a and b of Figure 7, the data for the Ca/Sc pair in Figure 7c do not demonstrate a dependence of the ICP-OES instrument sensitivity on Na mass fraction at a statistical significance level of \(P = 0.05\), as indicated by the fact that the 95% confidence interval for the slope of the fitted line, 0.00018 ± 0.00021 kg mg\(^{-1}\), overlaps zero. This is probably due to the fact that, unlike P (IP = 10.5 eV) and Cu (IP = 7.7 eV), the plot in Figure 6 illustrates a linear dependence of the instrument sensitivity on the acid composition. The regressed line in the plot was fitted to the data using the hydrochloric acid mass fractions as the abscissa values. The equation for a regressed line fitted using the nitric acid mass fractions would be identical, except that the sign of the slope would be negative. The magnitude of the slope of the line implies that keeping solution-to-solution imprecision below 0.02% RSD requires that the standard deviation of the nitric and hydrochloric acid mass fractions among the solutions in a given set be kept below about 0.0002. The RSD equivalents will, of course, depend upon the mean nitric and hydrochloric acid mass fraction values. The magnitude of the slope also implies that keeping analytical bias below 0.02% relative requires that the absolute difference between the mean mass fractions of either acid for the set of calibration standards and the set of unknown solutions be kept below approximately 0.0002.

For a set of solutions prepared to contain identical analyte and internal standard wavelengths, though the dependences were observed for other combinations of analyte and internal standard wavelengths, though the dependence was in some cases direct, rather than inverse.

Another representative example of acid effect data obtained in this work is given in Figure 6. In this case, all solutions were again prepared to contain 115 mg kg\(^{-1}\) P as the analyte and 18 mg kg\(^{-1}\) Ge as the internal standard. The sum of the mass fractions of nitric acid and hydrochloric acid in each solution was 0.02, though the portion that was nitric acid was varied.

3.5%. The magnitude of the slope of the line also implies that avoidance of significant analytical bias, again taken to be 0.02% relative, would require that the absolute difference between the mean nitric acid mass fractions of the set of calibration standards and the set of unknown solutions not exceed 0.0007. Similar dependences were observed for other combinations of analyte and internal standard wavelengths, though the dependence was in some cases direct, rather than inverse.
Ca (IP = 6.1 eV) can be considered an EIE, with an ionization potential that is not very different from that of Na (IP = 5.1 eV).

**Implications.** These data show that HP-ICP-OES analysis may be improved by employing exact matrix matching among the solutions within a given solution set, as well as between the set of calibration standards and the set of unknown sample solutions. No attempt was made in this work to reduce matrix effects through judicious selections of sample introduction components or other experimental parameters. It is possible that sensitivity to matrix effects can be reduced through such selections, thereby alleviating to some extent the need for exact matrix matching. It may also be possible to employ the crossover point concept recently described by Chan and Hieftje to help overcome this issue.

**Improvements in Analytical Performance of HP-ICP-OES with Exact Matching.** The final question to be addressed in this paper regards the amounts by which HP-ICP-OES precision and bias are improved through the use of exact matching. The answer to this question will vary with the particular analysis. However, a consideration of the certifications of the SRMs in the NIST SRM 3100 series is instructive. This SRM series consists of single-element solutions for each of 67 elements. HP-ICP-OES has been used by NIST as a major component of the certification strategy for a large majority of these SRMs for over a decade, with well over 100 analyses having been performed. The development and implementation of exact matching began in late 2005. To assess improvements in the results of HP-ICP-OES analyses of these SRMs afforded by exact matching, a survey was performed of historical data for the period from 1999 through the present. The mean and median of the set of relative expanded uncertainties, expressed at a level of confidence of 95%, obtained prior to the implementation of exact matching are 0.23% and 0.19%, respectively (n = 65). The corresponding statistics for results obtained afterward are 0.11% and 0.08%, respectively (n = 49). Therefore, the use of exact matching has resulted in a general decrease in the relative expanded uncertainties associated with the HP-ICP-OES analyses by approximately a factor of 2.

In some cases, the expanded uncertainty associated with a given HP-ICP-OES analysis may not be significantly affected by the use of exact matching. This is because the uncertainty budget can be dominated by components of uncertainty that are unaffected by exact matching, such as the uncertainty associated with the purity assay of the source material used to prepare calibration standards. Even in such cases, exact matching is advisable, because of the possibility of avoiding an otherwise undetected bias.

Finally, it should be mentioned that an additional component of uncertainty might be required in the uncertainty budget in the event that adequate exact matching cannot be assured. This situation is more likely to arise in terms of exact matrix matching than exact matching of analyte and internal standard mass fractions.

**CONCLUSIONS**

The results reported in this paper show that optimal implementation of HP-ICP-OES requires careful attention to certain aspects of the preparation of calibration standards and unknown sample solutions. Specifically, the analyte mass fractions, internal standard mass fractions, and matrix compositions of the solutions
within a given set (e.g., a set of calibration standards) and between
the set of calibration standards and the set of unknown sample
solutions should be exactly matched. The exactness of matching
needed can be reduced somewhat by ensuring that the instrument
response to the analyte and internal standard wavelengths are as
linear as possible and by taking steps to reduce matrix effects.
When properly implemented, exact matching enables the routine
attainment of 0.1% relative expanded uncertainties, expressed at
a level of confidence of 95%, for HP-ICP-OES analysis. This
represents an improvement of a factor of 2 compared to HP-ICP-
OES analysis performed without exact matching.

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