

**Achieving 0.2 % Relative Expanded Uncertainty in Ion Chromatography Analysis using a High-Performance Methodology**

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## **ABSTRACT**

A high-performance (HP) technique that was originally developed for inductively coupled plasma optical emission spectrometry (ICP-OES) has been successfully translated to ion chromatography (IC) to enable analyses with extremely low uncertainty. As an example application of the HP-IC methodology, analyses of several National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) in the SRM 3180 series of anion standard solutions are reported. The relative expanded uncertainty values expressed at 95 % confidence for these analyses range from 0.087 % to 0.27 % and average 0.18 %. Strong correlation between analyte and internal standard anion peak heights or peak areas, as well as the use of a unique drift-correction approach, is shown to be important for attaining such low uncertainty.

## INTRODUCTION

Ion chromatography (IC) is a well established analytical method for the determination of ionic species in solution, with detection limits down to  $\text{pg g}^{-1}$ .<sup>1-3</sup> When IC is used to perform quantitative determinations, measurement uncertainties are typically greater than 1 % relative and may be higher than several percent, even when the ions of interest are present at greater than trace levels. At the National Institute of Standards and Technology (NIST), we are developing methodologies that can be used to improve the measurement uncertainties associated with IC analysis. One motivation is development of metrologically sound analytical techniques that may be useful to laboratories outside of NIST. Another is improvement of NIST Standard Reference Material<sup>®</sup> (SRM) certification. The SRM 3180 series of anion standard solutions, consisting of aqueous, high-purity solutions of fluoride, nitrate, phosphate, bromide, sulfate and chloride ions, are of interest in this context. The certified mass fractions for these anion solution SRMs are directly traceable to the International System of Units (SI), allowing their use as a link to provide traceability to the SI for assigned values of commercially produced reference materials.

A high-performance (HP) technique<sup>4-7</sup> developed at NIST for inductively coupled plasma optical emission spectrometry (ICP-OES) has been successfully translated to ion chromatography (IC) to achieve improved IC uncertainties. The methodology comprises the following: internal standardization to compensate for short-term noise, use of a unique drift-correction approach<sup>5</sup> to compensate for long-term instrument drift, careful gravimetric preparations of the calibration standard and the unknown sample, and a robust experimental design that minimizes the important components of uncertainty and allows straightforward evaluation of a meaningful uncertainty budget. When applied to ICP-OES, the HP technique provides relative expanded uncertainties expressed at a 95 % confidence level on the order of 0.2 % for determinations of elemental mass fractions for the SRM 3100 series of single-element solution standards. These uncertainties can be halved by implementing “exact matching” with the HP-ICP-OES method.<sup>8</sup> “Exact matching” refers to very careful matching of matrix compositions and analyte and internal standard element mass fractions among the calibrant and unknown sample solutions prepared for an analysis.

In this paper, successful application of the HP approach to IC is reported. The methodology is explained, and typical analysis results are presented. Also, data are presented to demonstrate the effectiveness of internal standardization for compensation of short-term noise and of the drift-correction procedure for reducing variability

associated with replicate peak area and peak height measurements. The analytical benefits of employing exact matching in the HP-IC protocol are briefly examined.

Certification and stability evaluation analyses of four of the SRMs in the 3180 series are used as examples. Certification analysis refers to the HP-IC analysis of the candidate SRM performed at the time the certified anion mass fraction is assigned. Stability evaluation analysis refers to a subsequent determination of anion mass fraction in the SRM performed to ensure the long-term stability of the mass fraction relative to the certified value and assigned uncertainty. Stability evaluations of the SRMs in the 3180 series are usually performed approximately 5 y after certification, as well as on an as-needed basis. All of these SRMs are packaged in borosilicate glass ampoules, except for SRM 3183 Fluoride Anion Standard Solution, which is packaged in high-density polyethylene (HDPE) bottles that are sealed inside aluminized polyester pouches. Even though HP-IC analyses of the SRM 3180 series are utilized in this paper as examples, it should be emphasized that the applicability of HP-IC is not limited to analyses of reference materials, but can be extended to other IC analyses requiring exceptionally low uncertainty.

The success of HP-IC demonstrates that the HP approach can be readily adapted to analytical techniques other than ICP-OES. A previous publication has already demonstrated its application to ICP-MS.<sup>9</sup> In principle, the HP protocol should be adaptable to most, if not all, analytical techniques that rely upon comparison of calibration materials to unknown solutions for quantification.

## **EXPERIMENTAL**

### *Ion Chromatography (IC)*

Chromatographic analyses were performed on a Dionex DX-500 IC system (Dionex Corp., Sunnyvale, CA) equipped with a GP50 gradient pump, an LC30 chromatography oven, an EG40 eluent generator, an AS40 autosampler, and a CD20 conductivity detector with suppressor (ASRS-300 4mm, Dionex Corp.).<sup>i</sup> The detailed chromatographic conditions for each analysis are listed in Table 1.

For the  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  SRM certification analyses and the  $\text{F}^-$  stability check analysis, the gradient pump was set to deliver deionized (DI) water (minimum resistivity = 18  $\text{M}\Omega$  cm) at a flow rate of 1  $\text{mL min}^{-1}$  to the eluent generator, which converted the DI water to a high-purity potassium hydroxide (KOH) eluent by means of an applied

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<sup>i</sup> 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.

direct current. An isocratic KOH eluent concentration was optimized for each analyte anion, as well as for the respective internal standard anion. For the  $F^-$  and  $NO_3^-$  SRM certification analyses, the eluent generator was not used. Instead, an isocratic elution of  $2.0 \text{ mmol L}^{-1} \text{ Na}_2\text{CO}_3$  (ACS Grade, Fisher Scientific) +  $0.75 \text{ mmol L}^{-1} \text{ NaHCO}_3$  (Analytical Reagent Grade, Mallinckrodt Baker) was utilized. After separation, the column effluent was passed through the suppressor unit operated at an established optimum suppression current. The suppressor neutralized the eluent, reduced the background conductance, removed the counter-ions from the sample, and converted the analyte ions to a single highly conductive form. In combination, all these factors lead to enhanced sensitivity and lower detection limits. The chromatography oven was utilized to help prevent significant baseline drift caused by temperature variation. The Chromeleon Client software (v. 6.70, Build 1820, Dionex Corp.) provided control of the DX-500 IC system and all the components listed above, allowing the user to automate the chromatography analysis, in addition to providing a data analysis tool for quantitative results.

#### *Sample and Calibrant Preparations*

All sample and calibrant preparations were performed using water with a minimum resistivity of  $18.2 \text{ M}\Omega \text{ cm}$  that was passed through a  $0.22 \mu\text{m}$  filter. Each preparation was performed gravimetrically on a 4-place analytical balance (AB304-S/FACT, Mettler-Toledo Inc., Columbus, OH) interfaced to a laptop computer for recording mass values. To ensure SI traceability, balance calibration was verified using a 50 g standard mass that is traceable to the SI through a standard mass set maintained at NIST.

Calibrants were prepared from NIST Primary Solution Aliquots, the concept of which requires explanation. For certification and stability evaluation analyses associated with both the SRM 3100 series elemental solutions using HP-ICP-OES and the SRM 3180 series anion solutions using HP-IC, replicate preparations of the calibrant begins with a NIST Primary (NP) material. This is a high-purity metal or salt on which NIST has performed an assay and a verification of stoichiometry (if it is a compound) culminating in assignment of an assay value with an estimation of uncertainty. A series of NIST Primary Solutions (NPSs) are gravimetrically prepared by dissolution of the NP material, and the analyte mass fraction of each NPS and an associated uncertainty are assigned. Each NPS is then divided into a series of NPS Aliquots by weighing into separate low-density polyethylene (LDPE) bottles. The mass of analyte present in each bottle is assigned by multiplication of the aliquot mass by the known mass fraction

of the corresponding NPS. The uncertainty in the mass of analyte in each bottle is also estimated. These NPS Aliquots are then used to make multiple preparations of the calibrant for either HP-ICP-OES or HP-IC analysis. This calibration scheme provides traceability to the SI, because the known analyte mass values associated with the replicate preparations of the calibrant are directly traceable to a high-purity, assayed material weighed on a calibrated balance, and because all significant components of uncertainty are appropriately propagated. More than a decade of experience at NIST has shown that NPS Aliquots can be stored for years without detectable changes in the mass of analyte present in each NPS Aliquot bottle, permitting their use for calibration years after preparation.

For HP-IC certification and stability analyses of the SRMs in the 3180 series, a judiciously chosen internal standard stock solution was prepared by dissolution in water for each anion. Each chosen internal standard is listed in Table 1. Eight preparations of the calibrant were prepared from eight NPS Aliquots, one pair of NPS Aliquots originating from each of four NPS solutions, all of which were prepared from the same NP material. Two aliquots from each of three ampoules or bottles of the SRM were weighed into LDPE bottles. An aliquot of the internal standard solution was then weighed into each of these bottles, as well as into each of the bottles containing an NPS Aliquot. All bottles were vigorously mixed and diluted appropriately for IC analysis.

The  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  SRM certification analyses and the  $\text{F}^-$  stability analysis were performed using exact matching along with the HP protocol, while the  $\text{F}^-$  and  $\text{NO}_3^-$  certification analyses were performed without exact matching. When exact matching was employed, the solutions were prepared having nominally identical analyte mass fractions, internal standard mass fractions, and matrix compositions. Note that this does not mean that the analyte mass fractions for a set of solutions were equivalent to the internal standard mass fractions. Rather, it means that the analyte mass fractions among the calibration and unknown solutions prepared for an analysis were very closely matched, and that the internal standard mass fractions among those solutions were also very closely matched, even though the analyte and internal standard mass fractions might have been different. When exact matching was employed, the relative standard deviation (RSD) values for the nominal analyte mass fractions and internal standard mass fractions across the set of solutions were on the order of 0.06 % or less. In comparison, when exact matching was not used, the RSD values were on the order of 3 %.

### *Experimental Design and Measurement Uncertainty*

As stated earlier, HP-IC follows the protocol that is used routinely in HP-ICP-OES. That protocol has been described in detail in several previous publications.<sup>4-7</sup> HP-IC does not employ a calibration curve. It can be conceptualized as a chromatographic double-pan balance. Replicate preparations of the unknown sample are compared chromatographically to replicate preparations of the calibration standard, where the preparations of the calibrant are made up to mimic the expected characteristics of the preparations of the unknown sample in terms of matrix composition and analyte and internal standard mass fractions. As explained above, the degree of matching of these characteristics among the preparations of the calibrant and unknown sample depends on whether or not exact matching is being implemented, with the degree of matching being much higher when exact matching is employed. The HP-IC methodology does not include blanks. Previous research has shown that blanks are unnecessary in HP-ICP-OES analysis.<sup>8</sup> Quality assurance samples are used in all HP-IC analyses performed at NIST, but will not be discussed.

For an HP-IC analysis, the prepared calibration and unknown solutions are run on the IC instrument in a randomized complete block sequence. In other words, each solution is injected once in a randomized sequence, then again in a randomized sequence, and so forth, until each sample has been injected the desired number of times (usually five). The randomized complete block sequence is necessary for implementation of the drift-correction routine.<sup>5</sup> It also ensures that injections of the preparations of the calibration standard are not separated temporally from injections of the preparations of the unknown, further helping to mitigate analytical bias that might otherwise be caused by instrumental drift. After the solutions are run in this way, the ratios of the analyte peak heights or areas to the internal standard peak heights or areas, depending on whether peak height or area is chosen as the signal parameter, are calculated and corrected for drift.<sup>5</sup> The average analyte mass fraction of the preparations of the calibration standard, which is known from the gravimetric data for those preparations, and the magnitude of the difference between the average analyte mass fractions of the preparations of the calibration standard and the preparations of the unknown observed chromatographically are used to calculate the anion mass fraction in the unknown sample.

As described earlier, analyses of the SRMs in the 3180 series are reported in this paper as an example HP-IC application. The calculations pertaining to these analyses are now given, with the understanding that very similar, if not identical, calculations will apply when HP-IC is utilized for other analyses. The analytical equation is

$$w_x = \frac{QC}{S} \quad (1)$$

where  $w_x$  is the mass fraction of the analyte anion,  $X$ , in the SRM being analyzed,  $S$  is the IC instrument sensitivity measured with the calibrant solutions, and  $Q$  is the IC response to the unknown sample solutions. The parameter,  $C$ , defined to be unity with uncertainty, accounts for uncertainty in the known analyte anion mass values associated with the calibration solutions. Such a parameter is necessary because this component of uncertainty is unaccounted for by the replication that is inherent within the HP-IC experimental design. The uncertainty in  $w_x$  is estimated by propagating the individual components of uncertainty on the right-hand side of the equation.

To perform the calculations, a separate value of  $S$  is calculated for each of the  $i$  calibration solutions prepared from the NPS Aliquots ( $i = 8$  for all analyses reported here), according to

$$S_i = \frac{R_i m_i^{IS}}{m_i^A} \quad (2)$$

where  $R_i$  is the observed analyte to internal standard peak height or area ratio,  $m_i^{IS}$  is the mass of internal standard stock solution added, and  $m_i^A$  is the mass of analyte present. A single-factor analysis of variance (ANOVA) is conducted on the set of  $S_i$  values. If the null hypothesis is accepted at the  $P = 0.05$  level of significance, the  $S_i$  values are treated as being statistically independent samples from a single, normally distributed, population, and  $S$  is taken to be the average of the  $S_i$  values. The standard uncertainty associated with  $S$  is simply the standard deviation of the mean of the  $S_i$  values, and the degrees of freedom equal  $i$  minus 1. If the null hypothesis is rejected at the  $P = 0.05$  level of significance, the  $S_i$  values for the calibrant solutions made from each pair of NPS Aliquots that originated from a single NPS solution are first averaged. Then,  $S$  is taken to be the average of these averages. In this case, the standard uncertainty for  $S$  is the standard deviation of the mean of the averages, and the degrees of freedom equal one-half  $i$  minus 1. While the statistical treatment does not affect the value of  $S$ , and therefore does not affect the value of  $w_x$ , it can become important when computing the uncertainty budget for the analysis, especially with regard to the effect on degrees of freedom.

A separate value of  $Q$  is computed for each of the  $j$  preparations of the SRM ( $j = 6$  for all analyses reported here) according to

$$Q_j = \frac{R_j m_j^{IS}}{m_j} \quad (3)$$

where  $R_j$  is the observed analyte to internal standard peak height or peak area ratio,  $m_j^{IS}$  is the mass of internal standard stock solution added, and  $m_j$  is the mass of SRM present. The value of  $w_x$  is calculated using Eq. 1 and the average of the  $Q_j$  values as  $Q$ . The standard uncertainty associated with  $Q$  is simply the standard deviation of the mean, with the degrees of freedom being one less than  $j$ .

## RESULTS AND DISCUSSION

The anion mass fractions determined in the  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  SRM certification analyses and in the F SRM stability evaluation analysis are presented in Table 2 along with the combined standard uncertainties, degrees of freedom, expansion factors, expanded uncertainties, and relative expanded uncertainties. The HP-IC method provided expanded uncertainties ranging from  $0.00087 \text{ mg g}^{-1}$  (0.087 % relative) to  $0.0027 \text{ mg g}^{-1}$  (0.27 % relative), expressed at a level of confidence of 95 %, calculated according to the *ISO Guide to the Expression of Uncertainty in Measurement (GUM)*.<sup>10</sup> The average of the five relative expanded uncertainty values is 0.18 %. Similar analytical performance is expected when HP-IC is applied to other IC analyses, provided that the solutions prepared for analysis lack a significantly interfering matrix. Uncertainty may rise when such a matrix is present. The uncertainty budget from the  $\text{SO}_4^{2-}$  SRM certification analysis is given in Table 3 as an example of how the uncertainty is calculated for all analyses. The components of uncertainty are derived directly from Eq. 1.

As shown in Table 1, three of the five HP-IC analyses were performed using exact matching in the preparations of the solutions for analysis, while two were not. Comparison of the relative expanded uncertainty values for the analyses performed with and without exact matching fails to demonstrate any significant reduction of uncertainty when exact matching is employed. A recently published paper on the use of exact matching in HP-ICP-OES analysis showed an improvement in relative expanded uncertainty of a factor of two when exact matching was implemented. However, those results were based on a comparison of 49 HP-ICP-OES analyses performed with exact matching and 65 analyses performed without it. In comparison, the number of HP-IC analyses

currently available is very small. A more in-depth investigation will be required to study the potential analytical benefits of incorporating exact matching into the HP-IC protocol.

The internal standard for each SRM analysis was selected to compensate for short-term noise and to help mitigate, at least to a first approximation, the effects of long-term IC instrument drift. It is important that the selected internal standard provide a sufficiently high signal-to-noise ratio, but also allow the analyte peak and internal standard peak to be completely resolved in a reasonable amount of time. All IC runs for the analyses of the SRM 3180 series were completed in less than 8 min. Figs. 1A and 1B are examples showing that the correlation between the analyte and internal standard signals can be excellent, leading to very effective noise cancellation. Perfect correlation is indicated by all points lying along a line with positive unity slope and zero intercept.

The drift-correction procedure that is part of the HP protocol has been described in detail in a previous publication.<sup>5</sup> Briefly, the observed analyte to internal standard peak height or peak area ratios for all injections are plotted against the solution run sequence. The replicate signal ratios pertaining to each solution are normalized to their mean value in this plot to allow the data for all solutions to be plotted on a common ordinate scale. A polynomial of up to sixth order is fitted to the plotted data. The equation for the fitted polynomial is then used to correct the signal ratios for the drift. Two examples of the IC instrumental drift are shown in Figs. 2A and 2B, where the drift can be small as in the case of the  $\text{NO}_3^-$  SRM certification analysis or large as in the case of the  $\text{F}^-$  SRM certification analysis. The numerical models fitted to the data are also depicted in the figures.

To illustrate the effectiveness of the drift-correction method, the RSD values for the replicate peak height measurements for the  $\text{F}^-$  SRM solutions and NPS solutions (calibration solutions) obtained during the  $\text{F}^-$  SRM certification analysis are listed in Table 4 with and without the drift-correction applied. Given the randomized complete block run sequence, replicate injections of each solution are separated widely in time. Therefore, these RSD values are a measure of instrumental drift. Referring to Table 4, the drift-correction method for the  $\text{F}^-$  analysis reduced the average RSD associated with the SRM and calibrant solutions from 0.11 % to 0.07 %. Moreover, the RSD with drift-correction is smaller than the corresponding RSD without drift-correction for 14 of the 16 pairs.

## CONCLUSIONS

HP-IC provides relative expanded uncertainty expressed at 95 % confidence on the order of two parts per thousand. Such low uncertainty is much better than what can be obtained when IC is employed conventionally. Drift-correction and a strong correlation between analyte and internal standard peak heights or areas, depending on the quantification parameter selected, are important for attaining low HP-IC uncertainties. It is unclear at this point whether incorporation of exact matching into the HP protocol provides additional analytical benefit.

The development of HP-IC is valuable to NIST in terms of improved analyses of SRMs, but the methodology may also find usefulness outside NIST for other IC analyses requiring exceptionally low uncertainty. The application of the HP protocol to IC demonstrates that the HP approach, originally developed at NIST for low-uncertainty ICP-OES analysis, can be readily adapted to other analytical techniques that rely upon comparisons between calibration materials and unknown samples for quantification.

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**Table 1.** Ion chromatography operating conditions

Standard Reference Material <sup>®</sup> (SRM)	SRM 3181 SO <sub>4</sub> <sup>2-</sup> (Lot No. 080603)	SRM 3183 F <sup>-</sup> (Lot No. 050721)	SRM 3183 F <sup>-</sup> (Lot No. 050721)	SRM 3185 NO <sub>3</sub> <sup>-</sup> (Lot No. 050517)	SRM 3186 PO <sub>4</sub> <sup>3-</sup> (Lot No. 090723)
Type of Analysis	Certification	Stability evaluation	Certification	Certification	Certification
Guard column	Ion-Pac AG11-HC 4 mm x 50 mm	Ion-Pac AG11-HC 4 mm x 50 mm	Ion-Pac AG9-SC 4 mm x 50 mm	Ion-Pac AG9-SC 4 mm x 50 mm	Ion-Pac AG11-HC 4 mm x 50 mm
Analytical column	Ion-Pac AS11-HC 4 mm x 250 mm	Ion-Pac AS11-HC 4 mm x 250 mm	Ion-Pac AS9-SC 4 mm x 250 mm	Ion-Pac AS9-SC 4 mm x 250 mm	Ion-Pac AS11-HC 4 mm x 250 mm
Detection	Suppressed conductivity	Suppressed conductivity	Suppressed conductivity	Suppressed conductivity	Suppressed conductivity
Suppressor	ASRS-300 (4 mm)	ASRS-300 (4 mm)	ASRS-300 (4 mm)	ASRS-300 (4 mm)	ASRS-300 (4 mm)
Suppression current	100 mA	100 mA	50 mA	50 mA	100 mA
Injection loop volume	25.0 µL	25.0 µL	25.0 µL	25.0 µL	25.0 µL
Eluent generator cartridge	EG40 (4 mol L <sup>-1</sup> KOH)	EG40 (4 mol L <sup>-1</sup> KOH)	N/A	N/A	EG40 (4 mol L <sup>-1</sup> KOH)
Eluent concentration	3.0 mmol L <sup>-1</sup> [KOH]	10.0 mmol L <sup>-1</sup> [KOH]	2.0 mmol L <sup>-1</sup> Na <sub>2</sub> CO <sub>3</sub> + 0.75 mmol L <sup>-1</sup> NaHCO <sub>3</sub>	2.0 mmol L <sup>-1</sup> Na <sub>2</sub> CO <sub>3</sub> + 0.75 mmol L <sup>-1</sup> NaHCO <sub>3</sub>	30.0 mmol L <sup>-1</sup> [KOH]
GP50 gradient pump	1.00 mL min <sup>-1</sup>	1.00 mL min <sup>-1</sup>	2.00 mL min <sup>-1</sup>	2.00 mL min <sup>-1</sup>	1.00 mL min <sup>-1</sup>
LC30 chromatography oven temperature	30 °C	30 °C	23 °C	23 °C	30 °C
Pressure	2300 psig	2000 psig	N/A	N/A	2300 psig
Quantification	Peak area	Peak area	Peak height	Peak height	Peak height
Data collection rate	5.0 Hz	5.0 Hz	5.0 Hz	5.0 Hz	5.0 Hz
Internal standard (IS)	NO <sub>3</sub> <sup>-</sup> (KNO <sub>3</sub> ) <sup>(a)</sup>	SRM 3182 Cl <sup>-</sup> (Lot No. 060925)	Cl <sup>-</sup> (KCl) <sup>(b)</sup>	ClO <sub>3</sub> <sup>-</sup> (KClO <sub>3</sub> ) <sup>(b)</sup>	SRM 3184 Br <sup>-</sup> (Lot No. 020701)
SRM retention time	4.5 min	3.2 min	1.0 min	3.3 min	6.4 min
IS retention time	6.7 min	5.0 min	1.6 min	3.0 min	4.7 min

<sup>(a)</sup> Certified ACS Grade, Fisher Scientific (Pittsburgh, PA).<sup>(b)</sup> Baker & Adamson (New York, NY).

**Table 2.** HP-IC analysis results for SRMs in the 3180 series

Standard Reference Material <sup>®</sup> (SRM)	SRM 3181 SO <sub>4</sub> <sup>2-</sup> (Lot No. 080603)	SRM 3183 F <sup>-</sup> (Lot No. 050721)	SRM 3183 F <sup>-</sup> (Lot No. 050721)	SRM 3185 NO <sub>3</sub> <sup>-</sup> (Lot No. 050517)	SRM 3186 PO <sub>4</sub> <sup>3-</sup> (Lot No. 090723)
Type of Analysis	Certification	Stability evaluation	Certification	Certification	Certification
Determined Mass Fraction	0.99986 mg g <sup>-1</sup>	1.0040 mg g <sup>-1</sup>	1.0022 mg g <sup>-1</sup>	0.9996 mg g <sup>-1</sup>	1.0007 mg g <sup>-1</sup>
Combined Standard Uncertainty, $u_c$	0.00040 mg g <sup>-1</sup>	0.0012 mg g <sup>-1</sup>	0.0014 mg g <sup>-1</sup>	0.0009 mg g <sup>-1</sup>	0.0004 mg g <sup>-1</sup>
Degrees of Freedom	12	211	53	12	6
Expansion Factor, $k$ , for a Level of Confidence of 95%	2.179	1.971	2.006	2.179	2.447
Expanded Uncertainty, $U$	0.00087 mg g <sup>-1</sup>	0.0023 mg g <sup>-1</sup>	0.0027 mg g <sup>-1</sup>	0.0019 mg g <sup>-1</sup>	0.0010 mg g <sup>-1</sup>
Relative Expanded Uncertainty, $U_{rel}$	0.087 %	0.23 %	0.27 %	0.19 %	0.10 %
Exact Matching Applied	Yes	Yes	No	No	Yes

**Table 3.** Determined SO<sub>4</sub><sup>2</sup> mass fraction value and uncertainty budget for the certification analysis of SRM 3181 (Lot No. 080603)

Uncertainty Component <sup>(a)</sup>	$c_i$ <sup>(b)</sup>	$u_i$ <sup>(c)</sup>	$c_i u_i$	Degrees of Freedom
$Q$	0.80 mg g <sup>-1</sup>	0.00035	0.00028 mg g <sup>-1</sup>	5
$S$	-0.80 mg <sup>2</sup> g <sup>-2</sup>	0.00035 g mg <sup>-1</sup>	-0.00028 mg g <sup>-1</sup>	7
$C$	0.99986 mg g <sup>-1</sup>	0.000061	0.000061 mg g <sup>-1</sup>	103
Combined Uncertainty				
Combined Standard Uncertainty, $u_c$			0.00040 mg g <sup>-1</sup>	
Expansion Factor, $k$ , for a Level of Confidence of 95 %			2.179	
Expanded Uncertainty, $U$			0.00087 mg g <sup>-1</sup>	12.2
Relative Expanded Uncertainty, $U_{rel}$			0.087 %	

**Determined Mass Fraction = 0.99986 mg g<sup>-1</sup>**

<sup>(a)</sup> Components of uncertainty defined by Eq. 1 and associated text.

<sup>(b)</sup> Sensitivity factor as defined in the ISO *Guide to the Expression of Uncertainty in Measurement (GUM)*.<sup>10</sup>

<sup>(c)</sup> Standard uncertainty as defined in the ISO *Guide to the Expression of Uncertainty in Measurement (GUM)*.<sup>10</sup>

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**Table 4.** Effect of drift-correction on RSD values for replicate solution injections during the F<sup>-</sup> SRM stability check analysis. Given the randomized complete block run sequence, the replicate injections are widely separated temporally, meaning that these RSD values are a measure of instrument drift.

Sample ID	Without Drift-Correction	With Drift-Correction
NPS – 1	0.13	0.07
NPS – 2	0.10	0.08
NPS – 3	0.17	0.12
NPS – 4	0.06	0.07
NPS – 5	0.12	0.09
NPS – 6	0.14	0.08
NPS – 7	0.10	0.06
NPS – 8	0.07	0.03
SRM – A1	0.09	0.02
SRM – A2	0.07	0.05
SRM – B1	0.11	0.07
SRM – B2	0.11	0.06
SRM – C1	0.19	0.11
SRM – C2	0.09	0.03
SRM – D1	0.11	0.12
SRM – D2	0.06	0.03

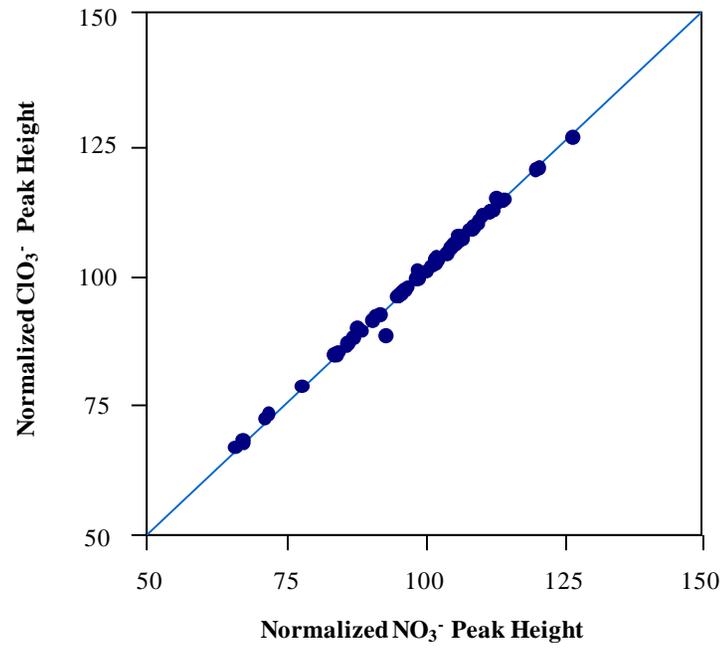
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## Figure Captions

**Figure 1.** An internal standard for each SRM analysis was selected to compensate for short-term noise and to help diminish the effects of IC instrument drift. Perfect correlation between the analyte and internal standard is indicated by all points lying along a line with positive unity slope and zero intercept, leading to very effective noise cancellation. Two examples of excellent correlation are given in A.)  $\text{NO}_3^-$  candidate SRM and the  $\text{ClO}_3^-$  internal standard; and B.)  $\text{SO}_4^{2-}$  candidate SRM and the  $\text{NO}_3^-$  internal standard.

**Figure 2.** Two examples of the IC instrumental drift are shown in A.)  $\text{NO}_3^-$  candidate SRM analysis with  $\text{ClO}_3^-$  as the internal standard using mean centered peak height for each sample; and B.)  $\text{F}^-$  candidate SRM analysis with  $\text{Cl}^-$  as the internal standard using mean centered peak area for each sample. A polynomial of up to sixth order is fitted to the plotted data; this equation (depicted in each figure) is then used to correct the signal ratios for the drift. The drift can be small as in the case of the  $\text{NO}_3^-$  SRM certification analysis or large as in the case of the  $\text{F}^-$  SRM certification analysis.

A.



B.

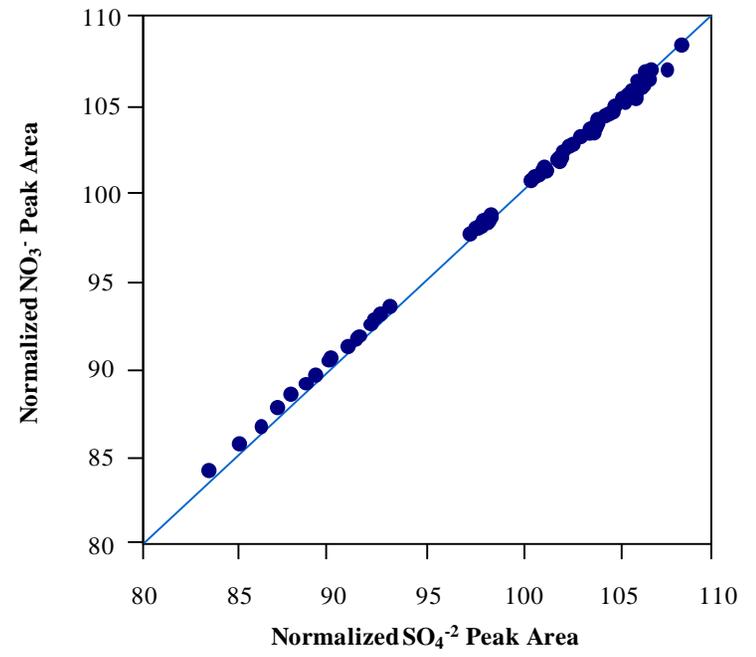
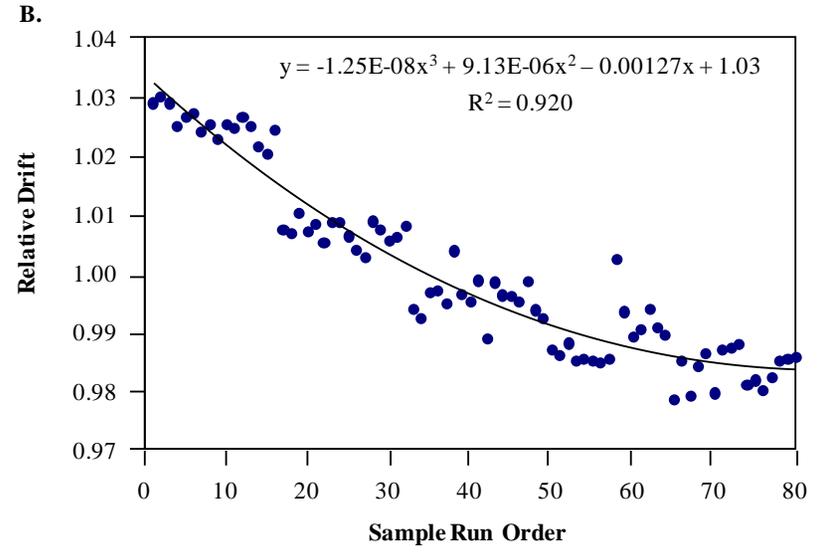
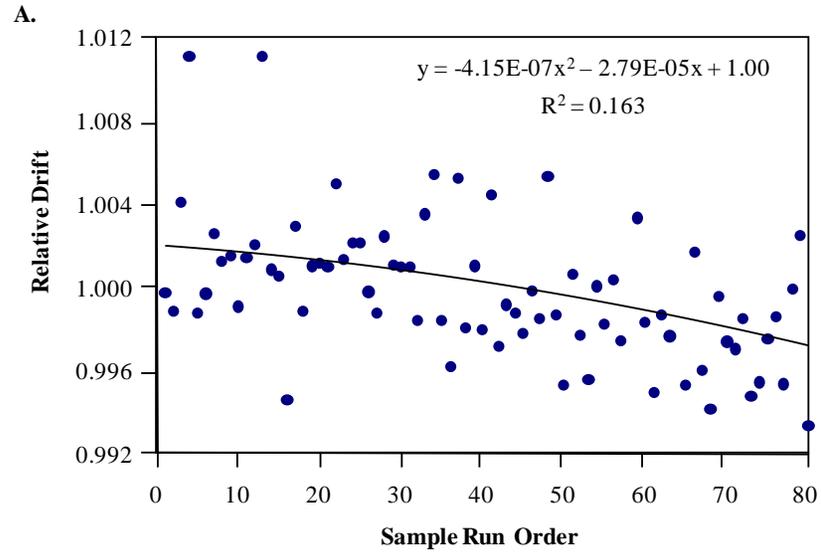


Figure 1



**Figure 2**