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**Certification of 3180 Series  
Standard Reference Materials®  
Anions in Solution**

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Thomas W. Vetter  
John L. Molloy  
Antonio Possolo

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# **Certification of 3180 series Standard Reference Materials<sup>®</sup> Anions in Solution**

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## **Abstract**

The 3180 series Standard Reference Materials (SRMs) are single anion solutions intended for use as primary calibration standards for the quantitative determination of a single anion and are a key link in the traceability chain for analysis measurements of those anions made world-wide. The mass fraction of the anions in these materials are traceable to the International System of Units (SI). The 3180 series SRMs are calibration standards gravimetrically prepared from carefully assayed, high-purity materials dissolved in a water-based matrix with nominal mass fractions of 1 mg/g. The certified values and expanded uncertainties of these SRMs are determined by combining a gravimetric preparation value and a carefully measured ion chromatography instrumental value, taking their associated uncertainties into account. Over the course of its shelf life, an anion solution standard undergoes stability testing to monitor the continued validity of its certified value. Currently, NIST offers seven anion standard solutions: bromide, chloride, fluoride, iodide, nitrate, phosphate, and sulfate. New lots of these SRMs are produced continuously to meet demand and certificates of analysis are issued for each new lot to accurately reflect the anion mass fraction and associated uncertainty.

## **Keywords**

Anions; Certified Value; Gravimetric Preparation; Ion Chromatography; Primary Standard (PS); Primary Standard Solution (PSS); Single Anion Standard Solution; Stability; Standard Reference Material (SRM); Traceability; Uncertainty.

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## 1. Introduction

The anion standard solution Standard Reference Materials (SRMs), also known as the 3180 series SRMs, are calibration standards gravimetrically prepared from carefully assayed, high-purity materials. Currently, these SRMs are certified using a combination of the gravimetrically prepared (GP) values and ion chromatography (IC). A NIST certified value is a value for which NIST has the highest confidence in that all known or suspected sources of bias and imprecision have been considered and any contributions they may make to measurement uncertainty have been quantified and are expressed in the reported uncertainty [1]. The uncertainty of each certified value is determined using a careful evaluation of the sources of uncertainty, leveraging knowledge of critically evaluated measurement procedures, as well as the historical performance of those procedures over time. The preparation of a calibration standard from a primary material is a relatively straightforward, fundamental procedure in analytical chemistry, but executing it to achieve a high degree of confidence in the mass fraction of the analyte in the resulting material can be difficult in practice. The questions that follow must be addressed for NIST to assign a certified value and appropriate uncertainty for each 3180 series SRM anion solution. How can a standard solution be tested in a traceable manner with a high degree of accuracy? How can the source material and calibrants be assayed with sufficiently high accuracy. What can be used as a calibrant or validation sample during this process? What is an appropriate estimate of uncertainty for the mass fraction value, and how can that uncertainty be minimized?

### 1.1. Program History

The 3180 series SRMs are an offshoot of the 3100 series SRM program of single-element solutions. Beginning in the early 1990s, NIST began production of the anion solution SRMs as a complement to the 3100 series SRM program. When the 3100 series SRMs were first produced, they were intended to be produced regularly; therefore, NIST adopted the protocol for these SRMs of using a lot number system to avoid changing the SRM number each time a new solution was produced and certified. The 3180 series SRMs follow this same practice.

All the anion solutions are prepared starting with an assay of a high-purity source material, either a sodium or potassium salt of the anion of interest. These source materials, which are homogeneous and stable for long periods of time, are assayed using highly accurate titrimetric and gravimetric techniques. The assayed salts are dissolved and diluted to a bulk solution that is transferred to multiple ampoules or bottles. The resulting anion solutions are stable and traceable to the SI with relatively small uncertainties. Initially, the shelf life of the anion solutions was set around 5 years based on limited knowledge about how the SRM solutions would behave over time. Currently most of the 3180 series SRMs have an expiration date of 8 years, after which time they are tested against NIST primary standard solutions (PSS), described in Sec. 2.4. If no statistically significant difference is detected between the certified value and the value measured to verify stability, then the expiration date for the SRM is extended. If a particular lot of a 3180 series SRM has changed significantly from the certified value, the lot will no longer be sold and a new lot of the SRM is produced. The long-term

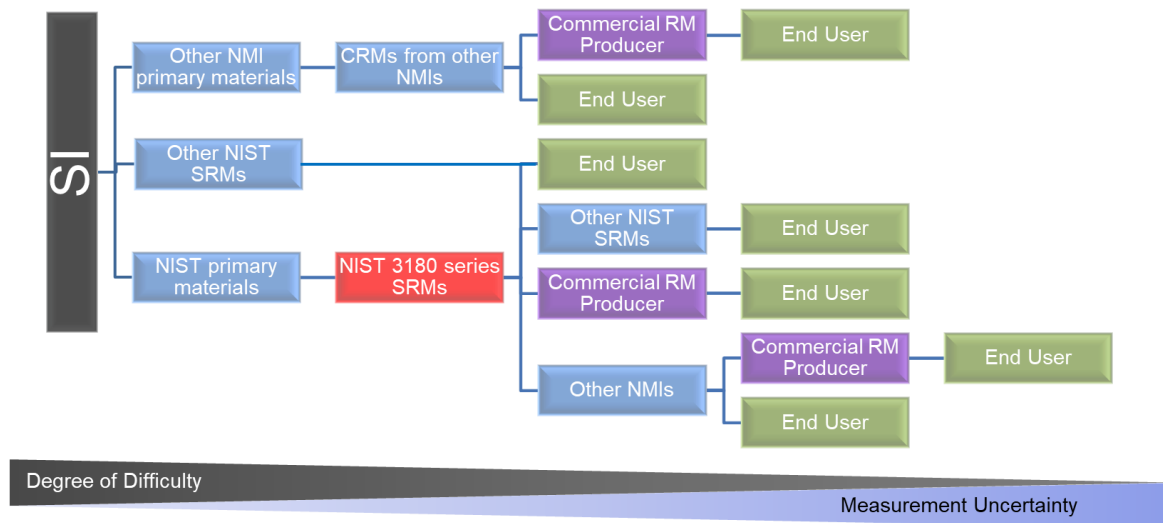
stability of the 3180 series SRMs is dependent on the given anion, but most have been shown to be stable for 8 years to 10 years.

Currently, the 3180 series SRMs consists of seven anion solutions, but other anions may be added to the 3180 series SRM program in the future. These solutions typically have a nominal mass fraction of 1 mg/g in water. All the 3180 series SRMs are stored in 10 mL clear borosilicate glass ampoules with two exceptions: SRM 3183 Fluoride Anion (F<sup>-</sup>) Standard Solution, which is stored in 60 mL high density polyethylene (HDPE) bottles, and SRM 3180 Iodide Anion (I<sup>-</sup>) Standard Solution, which is stored in 5 ml amber borosilicate glass ampoules.

The remainder of this document will describe the 3180 series SRM program as it developed and currently stands, with a sample calculation of how anion mass fractions and their associated uncertainties are assigned.

## 1.2. The Position and Role for the 3180 Series SRMs in the Metrological Ecosystem

Figure 1, which shows the position and role of the 3180 series SRMs in the “metrological ecosystem”, displays multiple pathways for traceability chains and for uses of NIST SRMs discussed in this work. Figure 1 has a horizontal scale along the bottom that captures the idea that measurements closer to a direct realization of the SI tend to be more difficult, using more complex/expensive/time consuming techniques, specialized calibration schemes or higher amounts of operator expertise. At the same time, as one progresses down a traceability chain, away from the SI, each successive measurement adds to the achievable minimum measurement uncertainty, a concept that has been explored in more detail elsewhere [2–4].



**Fig. 1. The metrology ecosystem surrounding the 3180 series SRMs.**

The 3180 series SRM solutions are not unique in this sense; many certified reference materials (CRMs) could serve the purpose of establishing traceability to the International System of Units (SI). However, most users of the 3180 series SRMs choose to establish traceability for elemental analysis using this route because it provides a short, valid chain of traceability back to the SI in a form that is ready to use, typically only requiring a straightforward dilution.

There are four categories of users of the 3180 series SRMs: internal NIST users, other National Metrology Institutes (NMIs) (or similarly Designated Institutes), commercial reference material producers, and end users of the materials. The specific need for users of SRMs is not always obvious, but the above categorization does provide a hierarchy of the uncertainty demands for each user. A key element of the program is that expanded uncertainties of the certified values are kept relatively low to serve all users shown in Fig. 1.

Internally, the 3180 series SRMs are used as calibration materials to provide SI traceability of certification measurements of other SRMs provided by NIST. This is especially evident when looking at the Consultative Committee for Amount of Substance (CCQM) Key Comparison Database (KCDB) list of calibration and measurement capabilities (CMCs) claimed by NIST [4, 5]. Category 2 of the CMCs is “Inorganic Solutions” and NIST has CMC claims covering many of the materials in the 3180 series.

Other NMIs and commercial reference material producers use the NIST 3180 series SRM solutions as a traceability source as well. Because of the CMC claims supporting the 3180 series materials, other NMIs that participate in CCQM find the materials attractive as easily defensible and recognized sources of traceability supported by CMCs [5].

Commercial reference material producers, especially in the United States, often care about accurate values, long shelf lives, and small uncertainties. Small uncertainties are of paramount importance to these customers as it establishes a minimum uncertainty that a commercial reference material producer can assign to their own material.

### 1.3. General Overview of 3180 Series SRM Life Cycle

Figure 2 shows a generalized lifecycle of the 3180 series SRMs. These materials are in continuous production, as shown by the circular nature of Fig. 2, rather than a more typical linear timeline for most SRMs produced by NIST. This diagram should be considered an outline for the remainder of this document.

### 1.4. Planning a New Lot of SRM

Because the 3180 series SRMs are in continuous production, planning each new lot is a critical part of the process. The planning of a new lot usually starts 18 months prior to the end of the period of validity or the date the stock of the SRM is expected to run out. When making a new lot, the sales rate and the expected stability of the SRM are considered. Typically, a twelve-year supply is made.



**Fig. 2. The lifecycle of the 3180 series SRMs.**

## 2. Gravimetric Preparation

Production of the 3180 series SRMs begins with the gravimetric preparation of the anion solutions so that an initial mass fraction of the anion in solution can be calculated. Details of the gravimetric preparation for current and previous production lots of 3180 series SRMs are given below. Any departures in the production and certification of 3180 series SRMs are noted in the text.

Historically, in the oldest preparations of 3180 series (and 3100 series) SRMs, the certified value was assigned using only a gravimetric value for the mass fraction of the analyte based on the gravimetric preparation of the solution by dissolution of an assayed high-purity material. Later, the results of a second determination of the mass fraction of the analyte based on instrumental analysis was combined with the gravimetric value. The addition of the instrumentally determined value helps to account for variations in the analyte mass fraction that might arise during the ampouling/packaging process. The instrumental analysis is as equally important as the gravimetric preparation in the calculation of the value of the anion mass fraction in the SRM. In addition, it can serve as a cross check to ensure that any problems in the gravimetric preparation are not overlooked.

### 2.1. Labware

Prior to use, all labware used in the preparation of the 3180 series SRMs is cleaned by soaking in 10 % volume fraction nitric acid ( $\text{HNO}_3$ ) (10 % volume fraction hydrochloric acid,  $\text{HCl}$ , for SRM 3185) for several days, followed by rinsing with copious amounts of high-purity water (Sec. 2.2), and air-drying in an ISO Class 5 clean area/laminar flow hood [6] in the advanced chemical sciences laboratory building. For large labware such as carboys, the containers are also filled with high-purity or ultra-high-purity water (Sec. 2.2) and allowed to stand for several days. The carboys are then rinsed again with copious amounts of ultra-high-purity water and allowed to dry in the ISO Class 5 clean area.

### 2.2. Materials

The source material for the 3180 series SRMs are high-purity sodium or potassium salts that have been accurately assayed for the anion of interest and well-characterized for impurities and sources of uncertainty. The principal assays of the source materials are performed internally at NIST by the Inorganic Chemical Metrology Group using methods such as gravimetry or titrimetry whose results are traceable to the SI. Secondary analysis, such as for trace metal or anion contaminants, may be done at NIST or by outside laboratories. For some of the 3180 series SRMs, the anion salts that are used in the solution preparation are other NIST SRMs. For other anions, the materials used have been independently assayed and characterized and are used only internally at NIST and this material is referred to as a primary standard (PS). Table 1 lists the anion salts used in the 3180 series SRMs. The anion salts that are SRMs are handled in accordance with the SRM certificate of analysis (COA), which calls for a drying step prior to use. Each PS has its own handling instruction, which also requires a drying step prior to SRM preparation.

**Table 1. Anion salts used in the production of 3180 series SRMs.**

SRM	Anion	Salt	Source
3180	Iodide ( $I^-$ )	KI (potassium iodide)	PS
3181	Sulfate ( $SO_4^{2-}$ )	$K_2SO_4$ (potassium sulfate)	PS
3182	Chloride ( $Cl^-$ )	KCl (potassium chloride)	SRM 999c
3183	Fluoride ( $F^-$ )	NaF (sodium fluoride)	PS
3184	Bromide ( $Br^-$ )	KBr (potassium bromide)	PS
3185	Nitrate ( $NO_3^-$ )	$NaNO_3$ (sodium nitrate)	PS
3186	Phosphate ( $PO_4^{3-}$ )	$KH_2PO_4$ (potassium dihydrogen phosphate)	SRM 200b
3188 <sup>a</sup>	Perchlorate ( $ClO_4^-$ )	$KClO_4$ (potassium perchlorate)	PS

a SRM 3188 is not a current SRM, but at the time of this publication the candidate SRM 3188 is in preparation and will be available by 2026.

Historically, high-purity water was used as the primary solvent for the 3180 series SRMs. The high-purity water in past preparations of the 3180 series SRMs has been College of American Pathologists (CAP) Type III grade or better water [7], generated on site at the NIST Advanced Chemical Sciences Laboratory building. For more recent 3180 series SRM preparations, ultra-high-purity water has been used as the solvent. This ultra-high-purity water is comparable to ASTM Type I water [8] and is prepared in-house by sub-boiling distillation using a conditioned, quartz still with deionized water as feedstock. Prior to use in the SRM preparation, the ultra-high-purity water is analyzed by IC to ensure that the anions of interest in a particular SRM preparation are below the limits of detection.

For some of the 3180 series SRMs, additives may be added to the ultra-high-purity water to promote stability. Any additives and their respective amount concentrations used in a particular SRM preparation are discussed below.

### 2.3. Solution Preparation

After the desired mass of the anion salt for the respective SRM (see Table 1) is determined on an analytical balance<sup>1</sup>, to the nearest 0.01 mg, the sample is transferred to a 1 L Teflon perfluoroalkoxy (PFA) beaker. Approximately 200 mL of ultra-high-purity water is added to the beaker, which is covered with a Teflon polytetrafluoroethylene (PTFE) lid and then placed on a hotplate with a surface temperature setting of approximately 200 °C. The solution is heated until complete dissolution of the anion salt has been attained (usually 5 minutes to 10 minutes).

The mass of an empty, clean, and dry carboy (typically 10 L or 20 L capacity, depending on the total solution needed) is determined to the nearest 0.1 g. The anion solution in the PFA beaker is quantitatively transferred to the carboy and is diluted with enough ultra-high-purity water to reach the desired anion mass fraction. The carboy is returned to the balance, its mass is determined, the solution mass is determined by difference, and the anion mass fraction in the solution is calculated. The calculated mass fraction based on the gravimetric preparation is assigned as the gravimetric preparation result.

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1 Balances are serviced and their calibration is checked annually.

### 2.3.1. Packaging

Packaging of the 3180 series SRMs is performed by the NIST Office of Reference Materials (ORM). Prior to being dispensed, the solutions in the carboy are mixed by hand shaking the carboy. For most of the 3180 series SRMs, nominal 10 mL aliquots of the SRM are dispensed into ten-milliliter, clear, borosilicate glass ampoules that are flame-sealed under nitrogen gas. Any potential bias due to evaporation during the flame-sealing is insignificant relative to other components of the uncertainty budget, as confirmed by a comparison of the calculated mass fraction from gravimetric preparation and the IC measurement of the packaged solution. Prior to being filled, each ampoule is cleaned in high-purity water and oven dried. Five ampoules of the SRM are packaged together as one unit.

### 2.3.2. Packaging of SRM 3180

For SRM 3180 Iodide Anion ( $I^-$ ) Standard Solution, nominal 5 mL aliquots are dispensed into 5 mL amber glass ampoules that are flame-sealed under nitrogen gas. Amber ampoules are used for SRM 3180 to minimize photodegradation of iodide in the SRM during storage.

### 2.3.3. Packaging of SRM 3183

SRM 3183 Fluoride Anion ( $F^-$ ) Standard Solution is packaged in plastic because the fluoride ion is known to interact with glass over time, thus shortening the period of validity of the SRM. For SRM 3183, nominal 50 mL aliquots are dispensed into 60 mL HDPE bottles and sealed in aluminized plastic bags. Prior to it being filled, each bottle is cleaned by soaking in 20 % volume fraction  $HNO_3$  for 24 h, followed by soaking in high-purity water for 24 h. Each bottle is rinsed with a copious amount of high-purity water and air-dried in an ISO Class 5 clean area [6]. A unit of SRM 3183 is one bottle of the SRM.

## 2.4. NIST Primary Standard Solutions

Prior to certification measurement, NIST primary standard solutions (PSSs) are prepared and validated (Sec. 2.4.2) as part of the certification program for the 3180 series SRMs. The PSSs are intended for use as calibration standards for the IC in the certification of 3180 series SRMs. For all the SRMs in this series, multiple sets of PSSs are prepared and, where possible, more than one anion salt is used for the various preparations. Use of more than one type of salt is advantageous because differences in results between the salts can be used to quantify measurement bias. Some of the high-purity salts used to prepare the PSS calibration standards are also used in the gravimetric preparation of the SRMs (Sec. 2.2).

### 2.4.1. Preparation of NIST Primary Standard Solutions

NIST Primary standard solutions (PSSs) are made as nominally 1 kg solutions with anion mass fractions of 1 mg/g and are prepared in a similar manner to the procedures listed in Sec. 2.3. After the nominal 1 kg solutions are mixed and allowed to equilibrate to room temperature,

aliquots of the same nominal mass (typically between 30 g and 34 g, depending on the analyte) are each transferred to separate 60 mL low-density polyethylene (LDPE) bottles, and the mass of the aliquot determined to the nearest 0.01 mg. The total mass of anion contained in each bottle is calculated from the anion mass fraction in the solution and the mass of solution delivered. Regardless of future transpiration from the bottles, the total anion mass is believed to remain constant. Fresh standard solutions are prepared by diluting the entire contents of a bottle to a known mass. Biases due to stability of the PSS over time are eliminated, but each aliquot can only be used once.

#### 2.4.2. Gravimetric Preparation of Samples for IC

The gravimetric preparation procedure follows an exact matching protocol that has been described previously [9]. The purpose of the protocol is to prepare samples in a way that the analyte mass fraction, internal standard (IS) mass fraction, and matrix are exactly the same in prepared samples of the calibrants, validation material(s), and test samples [9]. Gravimetric preparation and exact matching result in smaller uncertainties in the IC measurement and eliminate errors due to volume variability. They also provide more accurate, precise, and manageable data. Most importantly, gravimetric preparation establishes traceability of the anion mass fraction to the SI. The procedure follows the same general steps for a majority of the 3180 series SRMs.

#### 2.4.3. Validation of NIST Primary Standard Solutions

All newly prepared PSS aliquots for a given anion are validated against one another and against previous preparations of PSS aliquots of that anion, when available. This comparison of new and old preparations is, in part, to ensure the continuity of the PSSs over the course of the 3180 series SRM program and also serves as a check on the stability of the older preparations. The validation method uses at least two randomly selected aliquots from each PSS preparation. For new PSS preparations, the two aliquots are selected randomly using a stratified-random approach.

The validation of the PSSs uses IC to detect and quantify the anion mass fraction of the PSS using an IS. The IS is a second anion that has complete separation from the primary anion of interest. The experimental design for the IC comparisons follows the protocol used routinely in high-performance ICP-OES comparisons [10, 11]. To each PSS aliquot bottle, a known mass of a predetermined nominal aliquot of the IS stock solution is added. Each solution is then diluted with ultra-high-purity water to attain analyte and internal mass fractions appropriate for introduction into the IC instrument, based on the predetermined behavior of each anion. The solutions are run on the IC instrument according to the high-performance protocol [10, 11]. Solution preparation is also described in Sec. 3.1.

After the IC measurements are completed, the anion mass fraction for each of PSS aliquots is determined. The anion mass fraction for each PSS is compared using one-way analysis of variance (ANOVA) to determine whether there is a statistically significant difference between the aliquots at the 95 % confidence level [12]. This analysis is especially important for PSS

preparations made from different anion salts because it can reveal unknown biases in the NIST primary materials used in the PSS preparations. Once the PSSs are validated, the individual PSS aliquots are fit for use as primary calibration materials for certification and stability measurement of anions in the SRM program.

### 3. Analytical Methods for the Determination of Anion Mass Fraction

The use of a second method to determine the anion mass fraction in the 3180 series SRMs is complementary to gravimetric preparation and of equal importance to the value assignment of the anion mass fraction. Additionally, having an analytical method to determine the mass fraction is useful to quantify potential biases in the SRM solutions in conditions similar to those in which they may be used. For the 3180 series SRMs, ion chromatography is used as the analytical method because any anions present can be separated and effectively identified, and the method is insensitive to the counter-ion (potassium or sodium).

After the SRM solution is packaged (in ampoules or HDPE bottles), a subset of the units is used in the analytical determination. Analytical samples of the candidate SRM are selected at random from across the entire production lot, ideally near the first, last, and middle based on the order in which the SRM ampoules or bottles were filled. Although the carboy containing the candidate SRM solution is mixed thoroughly before the filling process, there is still the potential for heterogeneity across an SRM production lot due to a variety of factors (e.g., evaporation, concentration gradients, residual solvent in the ampouling machine, or contaminants in the ampoules). The largest differences observed in the case of heterogeneity are expected to be between the first and last ampoules made in the production process.

#### 3.1. Solution Preparation for IC Analysis

Initial preparation begins with the creation of an IS solution with an anion that can be easily separated from the target anion in the IC analysis. Generally, the IS solutions are prepared by dissolving the sodium or potassium salt of the anion in ultra-high-purity water so that the resulting IS anion mass fraction is between 2.5 mg/g and 10 mg/g. For the IS solutions, the exact mass fraction is unimportant for use as an IS because only a consistent stock material for all samples is needed. Care is taken with the preparation, and the IS anion mass fraction is generally known to better than  $\pm 0.5\%$ , relative.

Prior to analysis, test portions of the target anion and the IS anion are analyzed on the IC to ensure proper separation and to determine the response factor/instrument sensitivity ratio for each anion. The response factor is the ratio of the area of the peak in the chromatogram whose retention time corresponds to the anion of interest, to the anion mass fraction. The response factor of each anion is used in the solution preparation calculation so that the final mass fractions of the target anion and the IS will ideally have the same peak areas.

For the analysis, SRM sample solutions and controls are prepared by transferring nominal equivalent aliquots of the candidate SRM into separate, new, LDPE bottles. Control solutions are prepared from previous lots of the newly prepared SRM that are still within specification. Based on the response factors, a predetermined mass of the IS solution is added to each bottle. All bottles are mixed vigorously. All spiked solutions are serially diluted with ultra-high-purity water to yield nominal 50 g samples for analysis at mass fractions appropriate for introduction into the IC instrument. The masses of all added solutions are determined to the nearest 0.1 mg.

Validated PSSs (Sec. 5.2.1) that are used as calibrant solutions are spiked with a portion of IS such that the resulting mass ratio of the analyte and the IS is the same as the mass ratio to the IS in the SRM sample solutions. The spiked solutions and SRM solutions are prepared such that the mass ratios of the SRM to the IS for all solutions are generally within less than 0.5 %, relative, of the value of the ratio. The PSSs are then diluted with ultra-high purity water to same nominal mass fraction as the SRM solutions.

### 3.2. SRM Mass Fraction Determination by IC

The certification of anion mass fractions for the 3180 series SRMs uses IC for the quantitation of the anions. The IC experimental design follows the “high-performance calibration” protocol used routinely in high-performance ICP-OES [2, 10, 11]. The prepared solutions are injected into the IC in random order, and this order is repeated four times, for a total of five injections per prepared solution. The same drift correction procedure used in high-performance ICP-OES is employed to correct for long-term instrumental drift [10]. A secondary anion that has complete chromatographic separation from the primary anion is used as an IS. Ratioing the anion to the IS helps compensate for noise because it minimizes any fluctuations due to the measurement process rather than fluctuations due to the sample. [10].

#### 3.2.1. Primary Analysis

For this analysis, the analytical equation is:

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

where  $w_A$  is the analyte anion (A) mass fraction determined in the candidate SRM or control,  $S$  is the IC instrument sensitivity, and  $Q$  is the IC response to the candidate SRM or control. The parameter  $C$ , defined to have a value of unity, is used to account for uncertainty in the purity of the PS calibration materials used to prepare the calibration solutions, as well as the uncertainty associated with the gravimetric method used to prepare them. These two uncertainties are unaccounted for in the replication uncertainty that is inherent within the high-performance calibration experimental design.

The  $S_i$ , which are values of  $S$  are first calculated separately for each of the  $i$  calibration solutions prepared from the selected PSS aliquots, according to the equation:

$$S_i = \frac{R_i m_{IS,i}}{m_{A,i}} \quad (2)$$

where  $R_i$  is the observed analyte to IS peak area ratio,  $m_{IS,i}$  is the mass of IS stock solution added, and  $m_{A,i}$  is the mass of analyte anion believed to be present. After the set of  $i$   $S_i$  values are calculated, the set is evaluated in a manner that is consistent with procedures that have been established elsewhere [11, 13]. This procedure includes an evaluation of the homogeneity of the sensitivity values,  $S_i$ , which are combined into a consensus value with an associated effective degrees of freedom.

Next, the  $Q_j$ , which are values of  $Q$ , are calculated separately for each of the  $j$  control sample preparations (when available), according to:

$$Q_j = \frac{R_j m_{IS,j}}{m_{A,j}} \quad (3)$$

where  $R_j$  is the observed analyte to IS peak area ratio,  $m_{IS,j}$  is the mass of IS stock solution added, and  $m_{A,j}$  is the total mass of the control sample solution used in the analysis. The two values of  $Q_j$  are averaged, and the analyte mass fraction for the given control is computed according to Eq. 1 using the resulting value of  $Q$ . The control result is considered in agreement with the known value whenever the mean value falls within the interval defined by the assigned value of the control and its expanded uncertainty. If the mean value falls outside this interval, the  $t$ -test described in NIST Special Publication 829 [14] is used to determine whether the result is in agreement. Specifically, the absolute value of the observed difference between the determined and assigned values,  $\Delta$ , is compared to a critical difference,  $\Delta_c$ , defined by:

$$\Delta_c = t_{1-\alpha/2} \frac{s}{\sqrt{n}} + U \quad (4)$$

where  $\frac{s}{\sqrt{n}}$  is the standard uncertainty of the mean for the determined value,  $t_{1-\alpha/2}$  is the double-sided student's  $t$  for probability  $\alpha$  and the appropriate effective degrees of freedom, and  $U$  is the expanded uncertainty associated with the assigned value. The null hypothesis (i.e., there is a bias between the determined and assigned values) is rejected at a given value of  $\alpha$  when  $\Delta > \Delta_c$ .

When the experiment is assumed to be under control, a separate value of  $Q_j$  is computed using Eq. 3 for each aliquot of the candidate SRM solution used in the IC measurement. Also, a separate value of the analyte anion mass fraction,  $w_{A,j}$ , is calculated for each preparation using:

$$w_{A,j} = \frac{Q_j}{S} \quad (5)$$

A one way ANOVA is conducted on the set of  $w_{A,j}$  values to evaluate the presence or absence of statistically significant heterogeneity among the candidate SRM sample portions. If the  $p$ -value of the test is greater than 0.05, then no statistically significant heterogeneity is detected. If the test's  $p$ -value is smaller than 0.05 (meaning that there are significant differences in the set of  $w_{A,j}$ ), then the heterogeneity is evaluated further to determine whether the candidate SRM is suitable for sale.

### 3.2.2. IC Mass Fraction and Uncertainty

For a given IC analysis, the anion mass fraction,  $w_A$ , is essentially the average of all the  $w_{A,j}$  measured for the SRM. More precisely,  $w_A$  is calculated from the relationship:

$$w_{A,j} = \frac{\sum_{j=1}^n Q_j}{\sum_{i=1}^m S_i} \quad (6)$$

where  $n$  is number of SRM solution measurements and  $m$  is the number of calibration measurements. In terms of Eq. 2, the value of  $m = i/2$  with  $i/2 - 1$  degrees of freedom.

The combined standard uncertainty,  $u_c$ , for the anion mass fraction is calculated based on the expression:

$$u_c(y(x_1, x_2, \dots)) = \sqrt{\sum_{i=1}^n c_i^2 u(x_i)^2} \quad (7)$$

where  $y(x_1, x_2, \dots)$  is a function of the inputs  $x_1, x_2, \dots, x_n$  and  $c_i$  is a sensitivity coefficient defined as  $c_i = \partial y / \partial x_i$  [15]. From Eq. 1,  $w_A$  is a function of  $Q$ ,  $S$ , and  $C$  [i.e.,  $w_A = y(Q, S, C)$ ] and the combined standard uncertainty is:

$$u_v(w_A) = \sqrt{c_Q^2 u(Q)^2 + c_S^2 u(S)^2 + c_C^2 u(C)^2} \quad (8)$$

where  $c_Q$ ,  $c_S$ , and  $c_C$  are the corresponding derivatives of Eq. 1 with respect to  $Q$ ,  $S$ , and  $C$ , and  $u(Q)$ ,  $u(S)$ , and  $u(C)$  are the respective uncertainties of  $Q$ ,  $S$ , and  $C$ . In practice,  $u(Q)$  and  $u(S)$  are the standard deviations of the means of  $Q$  and  $S$ , and  $u(C)$  is the standard uncertainty of the calibration solutions (Sec. 3.2.1 and Eq. 1). The functional forms of the sensitivity coefficients are  $c_Q = C/S$ ,  $c_S = -C/S^2$ , and  $c_C = Q/S$ , but, because  $C$  is defined as 1, the coefficients  $c_Q$  and  $c_S$  reduce to  $c_Q = 1/S$  and  $c_S = -1/S^2$ .

Once the combined standard uncertainty has been determined, the expanded uncertainty,  $U$ , expressed at a level of confidence of 95 %, can be calculated. Along with the combined standard uncertainty, of equal importance to determining expanded uncertainty is the assessment of the effective degrees of freedom,  $\nu_{\text{eff}}$ , and the calculation of the coverage factor,  $k$ . The effective degrees of freedom and  $k$  are calculated in accordance with the Guide to the Expression of Uncertainty in Measurement (JCGM-GUM) [16].

## 4. Quantification of SRM Anion Mass Fraction and Uncertainty

The certification of anion mass fractions for the 3180 series SRMs uses the data from the gravimetric preparation and IC analysis (Sec. 2.4.3 and Sec. 3.2, respectively) to determine a consensus value. Each measurement method contributes a measurement result that comprises an estimate of the anion mass fraction, its associated standard uncertainty, and the number of degrees of freedom that this uncertainty is based on. The results from gravimetric preparation based on calculations of the mass fraction from the gravimetric preparation and from IC are combined to produce the certified anion mass fractions and their associated uncertainties for the 3180 series SRMs.

The following sections discuss the historical method for calculating the certified anion mass fractions for the 3180 series SRMs and the current method for calculating the certified values.

### 4.1. Historical Method for Certification

The calculation of the SRM mass fraction of the 3180 series SRMs and evaluation of the associated uncertainty has evolved over time. The changes represent a concerted, sustained effort to improve measurement rigor. Additionally, as more lots of the 3180 series SRMs have been produced, evaluation of the uncertainty sources has improved as a result of better characterization of the source materials and of the differences between the values obtained from the gravimetric preparation and instrumental measurement methods, and increased knowledge about the long-term stability of the anions solutions.

The 3180 series SRMs were developed in the mid-1990s as an offshoot of and sister program to the single-element solution SRM program (3100 series SRMs). During that early period, the certified value and associated uncertainty of the various SRM lots relied solely on the results of the gravimetric preparations. As the 3180 series SRM and 3100 series SRM programs evolved, an instrumental measurement of the analyte mass fraction in the SRM solutions was added to the certification process (IC for the anion solutions/3180 series SRMs and ICP-OES for the single-element solution/3100 series SRMs) [2, 11].

There have been several iterations of procedures for combining the results from gravimetric preparation with the results from instrumental methods (e.g., IC and ICP-OES) to determine the certified mass fraction and uncertainty. The characterization of the between-method differences is a critical aspect of the evaluation of the uncertainty associated with the blended results of the gravimetric preparation and ion chromatography.

Up until recently, a between-method uncertainty component,  $M$ , had been estimated based on the historical average difference between GP and ICP-OES for the single-element solution (3100 series) SRMs. Since there was only a small number of anion solutions, the between-method uncertainty was evaluated based on ICP-OES data, hence it did not capture specific features of the IC method. Also, instead of being taken into account as a separate uncertainty contribution, the uncertainty component  $M$  was split evenly and incorporated into the combined standard uncertainties of both the GP and of the IC method.

The results from GP and IC, each of which comprises a measured value, associated standard uncertainty, and the number of degrees of freedom supporting the uncertainty evaluation were then combined using the version of the DerSimonian-Laird [17] procedure described by Koepke et al. [18], whose shortcomings have been discussed in [19–21].

More recent approaches to incorporate the between-method uncertainty into the expanded uncertainty addressed some shortcomings and have attempted to account for an unknown or ‘dark’ uncertainty component (see section 4.2.1 below), especially when results from the gravimetric preparation and the instrumental methods are close [22, 23]. However, these methods have mostly remained working exercises in methodologies and have not been applied to the uncertainty evaluations of the 3100 and 3180 series SRMs [24].

The most recent method, which was developed by Lang et al. [24], is described below. It was first used to certify SRM 3182 Chloride Anion (Cl<sup>-</sup>) Standard Solution, Lot No. 190830 [25] and will be used to certify all future lots of anion solution SRMs.

It should be noted that these recent developments do not invalidate the certification of previous lots of series 3180 SRMs, which remain valid until the expiration of their stated periods of validity.

## 4.2. Statistical Measurement Model for Certification

Beginning in 2020 with SRM 3182, Lot No. 190830, the certified mass fraction and uncertainty evaluation of the 3180 series SRMs (anion solution SRMs) have been calculated using a new statistical model based on a blending procedure that exploits historical information about between-method differences accumulated over many years of developing SRMs in both the 3100 and 3180 series SRMs [24, 25]. The use of historical information is its main benefit, because it overcomes the limitation of traditional methods that aim to characterize between-method uncertainty contribution based on a single degree of freedom. The statistical model used to blend the results of the gravimetric and instrumental (ion chromatography) determinations of the mass fraction of the anions the 3180 series SRMs is a Bayesian model that Lang et al. [24] describe in great detail, and whose components are reviewed here and presented in the Stan and R codes listed in supplementary file 1 of Ref [24]. Meija et al. [26] provide an overview of Bayesian statistical models used in measurement science, and in particular explain the concepts of prior and posterior distributions, and of credible intervals, which are mentioned below.

### 4.2.1. Statistical Measurement Model

The statistical model represents the measured values as  $w_G = \omega + \lambda_G + \varepsilon_G$  and  $w_I = \omega + \lambda_I + \varepsilon_I$  where  $\omega$  denotes the true value of the measurand, the subscripts G and I refer to the gravimetric preparation and instrumental (IC) determination,  $\lambda_G$  and  $\lambda_I$  denote method effects, and  $\varepsilon_G$  and  $\varepsilon_I$  denote method-specific measurement errors.

The method effects are modeled as two independent drawings from a Gaussian distribution with mean 0 and standard deviation,  $\tau$ , which quantifies what is generally called *dark*

*uncertainty* [22, 23] but is attributed to between-method differences here. The measurement errors are modeled as two independent drawings from Gaussian distributions both with mean 0 but possibly different standard deviations,  $\sigma_G$  and  $\sigma_I$ .

#### 4.2.2. Historical Information

The following relationship captures the historical information about between method differences for single-element solutions and for anion solutions. It expresses the size of the dark uncertainty relative to the gravimetric value as a function of the absolute value of the difference between the values measured gravimetrically and instrumentally relative to the gravimetric value:

$$\ln\left(\frac{\tau}{w_G}\right) = \alpha + \beta \ln\left(\frac{|w_I - w_G|}{w_G}\right) \quad (9)$$

where  $\ln$  denotes the natural logarithm (base  $e$ ). The intercept  $\alpha$  and the slope  $\beta$  are estimated using historical data for all SRMs (both single-element and anion solutions) whose gravimetric and instrumental determinations yield mutually inconsistent results. The value of  $\tau$  produced by Eq. 9 is an *a priori* estimate of  $\tau$  that subsequently is updated considering the actual difference  $w_I - w_G$  observed with each new lot of the 3180 series SRMs. The current estimates of the intercept and slope are  $\hat{\alpha} = -0.06846$  and  $\hat{\beta} = 1.05309$ .

The dark uncertainty is what earlier was called “method uncertainty” and denoted using the letter  $M$  (which stood for between-method difference, or bias). Here it is represented by  $\tau$ , which is used as the standard deviation of the method effects,  $\lambda_G$  and  $\lambda_I$ .

#### 4.2.3. Solution Long-Term Instability

To account for the potential effect of long-term instability of the solution, we add yet another effect,  $\kappa$ , to the model:  $w_G = \omega + \kappa + \lambda_G + \varepsilon_G$  and  $w_I = \omega + \kappa + \lambda_I + \varepsilon_I$ .

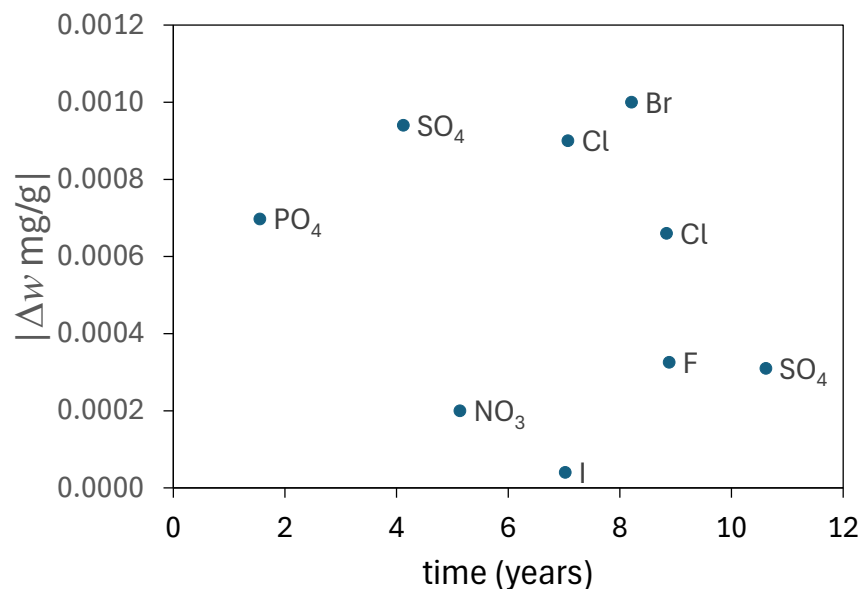
The non-observable quantity  $\kappa$  represents the contribution from long-term instability, so that one can interpret  $\gamma = \omega + \kappa$  as the value of the mass fraction in solution at any future time between when the SRM was first certified (and this mass fraction was  $\omega$ ), and when the SRM’s validity expires.

Since, in this case, there is no compelling reason to expect  $\kappa$  to be positive or negative, we model it as outcome of a non-observable random variable with a Student’s  $t$  distribution with  $\nu_s$  degrees of freedom, a mean of 0 mg/g, and standard deviation  $u_s$ , where the subscript “s” stands for “stability”.

The mean being 0 mg/g reflects the inability to state *a priori* whether long-term instability will cause the mass fraction to increase or decrease over time, while the uncertainty component  $u_s$  quantifies our estimate of the magnitude of the possible change, regardless of the direction, up or down.

The uncertainty component  $u_s$  has been estimated by incorporating some current and historical stability measurements made on the 3180 series SRMs [ $u_s = u(\kappa)$ ]. There have been numerous

stability measurements of the 3180 series SRMs over the course of the program. To capture the best picture of any change in the SRM solutions over time, stability measurements have been limited to SRM lots with an IC measurement used to calculate the certified values that can be compared with IC stability measurements. Comparing only IC measurements of the same lot of the same SRM, made at different times, eliminates between-method bias that might obfuscate the change in anion solution mass fraction. The change in anion mass fraction,  $\Delta w$ , is calculated as  $\Delta w = |w_t - w_0|$ , where  $w_0$  is the initial IC measurement and  $w_t$  is the second IC measurement made after  $t$  years. Since there is no known reason to expect the change over time to be positive or negative,  $\Delta w$  is taken as an absolute value of the measurement values. Figure 3 shows nine stability measurements of the 3180 series SRMs that are direct comparisons of IC mass fraction determination.



**Fig. 3. Change in anion mass fraction over time,  $\Delta w$  mg/g for 3180 series SRMs as measured by ion chromatography.**

Shown are the various anions represented in the stability measurements.

From the figure, the largest deviation of the anion mass fraction occurred in the bromine (Br) anion solution after a time of approximately 8 years. Thus, after eight years the maximum deviation due to solution instability might be expected to be 0.0010 mg/g. For many of the 3180 series SRMs, the practical shelf-life and initial expiration date is 10 years, and giving a 2-year buffer, the estimated end of life of the SRM solutions is 12 years. Since the end of life is 50 percent longer than the 8-year mark for the bromine measurement, the maximum deviation,  $\Delta w$ , is estimated to be 50 percent larger than the value at 8 years, or 0.0015 mg/g.

Using this maximum deviation, the uncertainty is then modeled as a Student's  $t$  distribution with 9 degrees of freedom,  $\nu_s = 9$ , (because the evaluation of  $u_s$  was based on observations of aging for 9 historical anion solution SRMs) and then rescaled so as to have standard deviation equal to the reported standard uncertainty attributable to instability. In this case, the standard uncertainty,  $u_s$ , is 0.000 75 mg/g, based on 9 degrees of freedom. At present, this represents a

reasonable estimate of long-term instability for a worst-case scenario in the anion solutions. This value can be refined in the future as the number of stability measurements increases.

#### 4.2.4. Specifications of the Bayesian Model

The Bayesian specification of the model defined in Sec. 4.2.1 and Sec. 4.2.2 involves the following choices, which are reflected in the Stan and R codes listed in supplementary file 1 of Ref [24] which were also the codes used in the certification of SRM 3182 Chloride Anion ( $\text{Cl}^-$ ) Standard Solution, Lot No. 190830 [25]:

- $\omega$  has a Gaussian prior distribution with mean equal to the restricted maximum likelihood (REML) [27] estimate of  $\omega$  based on the gravimetric and instrumental results, which is computed using R function `metagen` defined in package `meta` [28], and standard deviation that is twice the standard deviation of the REML estimate of  $\omega$ .
- $\mu_G = \omega + \lambda_G$  and  $\mu_I = \omega + \lambda_I$  both have Gaussian distributions with mean  $\omega$  and standard deviation  $\tau$ .
- $\kappa$  has a prior Student's  $t$  distribution with  $\nu_S$  degrees of freedom, rescaled to have standard deviation  $u_S$ . Since the measurement results provide no information about  $\kappa$ , both its prior and posterior means are 0 mg/g (up to the fluctuations resulting from the vagaries of Monte Carlo Markov Chain sampling mentioned below), and the sole consequence of including this term in the model is the effective propagation of the uncertainty associated with potential long-term instability of the solution.
- $\gamma = \omega + \kappa$ , where  $\gamma$  denotes the value of the mass fraction in solution at any future time between when the SRM was first certified, and when it reaches the end of its period of validity
- $\sigma_G$  and  $\sigma_I$  have prior gamma distributions with means  $u(w_G)$  and  $u(w_I)$  and coefficients of variation both equal to 0.1. The choice of 0.1 expresses the belief that the method-specific uncertainty evaluations are not grossly incorrect in the sense that  $\sigma_G$  and  $\sigma_I$  should be within 20 % of the corresponding evaluations of  $u_G$  and  $u_I$ .
- $u(w_G)$  has a gamma distribution with shape  $\nu_G/2$  and rate  $\nu_G/(2\sigma_G^2)$ , and similarly  $u(w_I)$  has a gamma distribution with shape  $\nu_I/2$  and rate  $\nu_I/(2\sigma_I^2)$ . This part of the model expresses the established fact that, under the Gaussian model, sample variances have rescaled chi-squared sampling distributions.
- $w_G$  has a Gaussian distribution with mean  $\mu_G$  and standard deviation  $\sigma_G$ , and similarly  $w_I$  has a Gaussian distribution with mean  $\mu_I$  and standard deviation  $\sigma_I$ .

## 5. Case Study for the Preparation and Certification of SRM 3180

Below is a sample calculation of how the 3180 series SRMs are now certified for the anion mass fraction. The process for certification will be similar for all the new lots of the 3180 series SRMs. The calculations below are for SRM 3180 Iodide Anion ( $I^-$ ) Standard Solution, Lot No. 230111.

### 5.1. Gravimetric Preparation

This section describes the gravimetric preparation of SRM 3180, Lot No. 230111.

#### 5.1.1. Materials

The source material for SRM 3180 is high-purity potassium iodide; it is designated as NP-I-1. The crushed and dried potassium iodide was assayed by the NIST Inorganic Chemical Metrology Group by gravimetric titration against coulometrically assayed ceric ammonium nitrate and the assigned assay mass fraction of KI was 0.999 20 with a standard uncertainty of 0.00017 and 13.7 effective degrees of freedom.

A solution containing sodium sulfite ( $Na_2SO_3$ ) and sodium hydroxide ( $NaOH$ ) at amount concentrations of 0.010 mol/L and 0.0052 mol/L, respectively, was prepared by dissolving 12.6 g  $Na_2SO_3$  and 4.2 g  $NaOH$  solution in ultra-high-purity water to a final mass of 10.002 kg (density is assumed to be 1 g/mL). This mixture serves as a stabilizing solution of the iodide ion as iodide is reactive and can oxidize over time. The addition of the sulfite ( $SO_3^{2-}$ ) ion in a basic solution in the final SRM preparation serves to prevent the iodide anion from oxidation.

#### 5.1.2. SRM Preparation

Approximately 14 g of the potassium iodide were placed in a platinum pan that had been previously cleaned by soaking in 10 % volume fraction  $HNO_3$  for several days, followed by rinsing with copious amounts of ultra-high-purity water, and then air-drying in an ISO class 5 clean area. The potassium iodide was crushed into a powder, using a borosilicate pestle to break up large crystals, dried for 3 h in an oven at 200 °C, and allowed to cool to ambient temperature in a desiccator containing  $MgClO_4$ . From the dried KI, the masses of two portions with nominal masses of 6.34 g and 3.72 g (for a total nominal mass of 10.06 g) were determined to the nearest 0.01 mg on balance and transferred into two separate clean 1 L PFA beakers. Nominally 200 mL and 100 mL of ultra-high-purity water was added to the beakers with the 6.34 g and 3.72 g samples, respectively. Each beaker was covered with a PTFE lid and placed on a hotplate with a surface temperature setting of approximately 200 °C. The solutions were heated until complete digestion had been attained. Two beakers of the KI solution were prepared instead of a single preparation because, after the first nominal 6.34 g portion was transferred to the PFA beaker, it was determined that more solution should be produced. For better control of the system, the second nominal 3.72 g KI portion was placed in a second clean beaker.

The mass of a clean, dry LDPE carboy having a capacity of 10 L was determined to the nearest 0.1 g. The solutions in each of the PFA beakers were quantitatively transferred into the carboy and diluted with stabilizing solution (Sec. 5.1.1) to almost 7 L. The carboy mass was re-determined on the balance, the solution mass was calculated by difference, and the solution  $I^-$  mass fraction was calculated. Stabilizing solution was added to adjust the  $I^-$  mass fraction to a target value of 1 mg/g. The carboy mass was re-determined and the final  $I^-$  mass fraction was calculated. Prior to its being dispensed, the solution in the carboy was mixed by hand-shaking of the carboy.

The total mass of  $I^-$  in the SRM solution was calculated from the total solution mass, the stoichiometric factor (ratio of I relative atomic mass to KI relative molecular mass) [29], and the assay value of KI (Sec 5.1.1). The  $I^-$  mass fraction was computed by dividing the total mass of  $I^-$  by the mass of solution. All masses were corrected for buoyancy.

The final mass fraction of the SRM solution is given in Fig. 4, together with each of the input values used to calculate the mass fraction. Each input value is accompanied by the standard uncertainty ( $u$ ), the relative standard uncertainty ( $u_{rel}$ ), and the effective degrees of freedom ( $\nu_{eff}$ ), where appropriate. The coverage factor ( $k$ ) for a 95 % level of confidence and the resulting expanded uncertainty ( $U$ ) and relative expanded uncertainty ( $U_{rel}$ ) are given for the final mass fraction.

Table 2 lists each of the components of uncertainty, with a short description of how each uncertainty is determined. All uncertainties are calculated according to the ISO and NIST Guides [16, 30].

Mass of NP-I-1 (mg)	10063.138	}	}	}	}	}	}	}	}
$u$ (mg)	0.109								
$u_{rel}$ (%)	0.0011								
Assay	0.999940	}	}	}	}	}	}	}	}
$u$	0.000222								
$u_{rel}$ (%)	0.022								
$\nu_{eff}$	4.4	}	}	}	}	}	}	}	}
Stoichiometric Factor	0.764472002								
$u$	0.000000297								
$u_{rel}$ (%)	0.000039	}	}	}	}	}	}	}	}
Mass of I (mg)	7692.53								
$u$ (mg)	1.71								
$u_{rel}$ (%)	0.022	}	}	}	}	}	}	}	}
$\nu_{eff}$	4.5								
Mass of Solution (g)	7686.562								
$u$ (g)	0.461	}	}	}	}	}	}	}	}
$u_{rel}$ (%)	0.0060								
<b>Mass Fraction (mg/g)</b>	<b>1.00078</b>								
$u$ (mg/g)	0.00023	}	}	}	}	}	}	}	}
$u_{rel}$ (%)	0.023								
$\nu_{eff}$	5.1								
$k$	2.571	}	}	}	}	}	}	}	}
$U$ (mg/g)	0.00059								
$U_{rel}$ (%)	0.059								

Fig. 4. Calculation of mass fraction and uncertainty for the gravimetric preparation of the SRM.

**Table 2. Standard uncertainty components for the gravimetric preparation of the SRM.**

Uncertainty	Basis	Type <sup>a</sup>	V <sub>eff</sub>
Mass of Primary Material	Calculated from the worst-case uncertainty from the past 3 balance service events for the MC210S semi-micro balance <sup>b</sup> , excluding values that were out-of-tolerance. The combined standard uncertainty, $u_c$ , calculated as the square root of the sum of the squares of the standard uncertainties of the 2 buoyancy-corrected masses, equals 0.109 mg.	B	$\infty$
Assay of Primary Material	Taken from the assay of potassium iodide.	combined standard	4.43
Stoichiometric Factor	Calculated from uncertainties of the relative atomic masses of the elements that were used in the titrimetric assay of KI [29]. The published uncertainties were assumed to be uniformly distributed expanded uncertainties ( $k = \sqrt{3}$ ) [31].	B	$\infty$
Mass of Analyte	Calculated as the square root of the sum of the squares of the relative standard uncertainties for the mass of the primary material and the assay.	combined standard	4.4
Mass of Solution	Calculated from the worst-case uncertainty from the past 3 balance service events for the Combics 1 digital weighing system <sup>c</sup> , excluding values that were out-of-tolerance. The combined standard uncertainty, $u_c$ , calculated as the square root of the sum of the squares of the standard uncertainties of the 2 buoyancy-corrected masses, equals 0.461 g.	B	$\infty$
Mass Fraction	Calculated as the square root of the sum of the squares of the relative standard uncertainties for the mass of I <sup>-</sup> and the mass of solution.	combined standard	39.6

- a A or B identifies whether a Type A or B approach is used to evaluate the standard uncertainty component.  
b The MC210S semi-micro balance used has a resolution of 0.01 mg and another balance with the appropriate resolution and specifications would be suitable and may be used for future gravimetric preparations.  
c The Combics 1 digital weighing system used has a resolution of 0.0001 kg and another system with the appropriate resolution and specifications would be suitable and may be used for future gravimetric preparations

As shown in Fig 4., the I<sup>-</sup> mass fraction as determined by gravimetric preparation in the SRM solution is (1.000 78 ± 0.000 59) mg/g, where the uncertainty is expanded to a level of confidence of approximately 95 %.

### 5.1.3. SRM Packaging

The contents of the carboy containing the gravimetrically prepared SRM 3180 solution was transferred to clean five-milliliter, amber, borosilicate glass ampoules and tip-sealed using an automated ampouling device. Prior to being filled, each ampoule had been cleaned in high-purity water and air dried in an ISO class 5 clean area. A small number of the ampoules filled initially were discarded to avoid introduction of potential contaminants and allow the ampouling process to reach a steady state. Sealed ampoules were placed in the boxes based on fill order. After analytical samples were removed (See Sec. 5.2.2), the ampoules were packaged as units consisting of five 10 mL ampoules. Ampouling and packaging was done by the NIST Office of Reference Materials (ORM).

## 5.2. Ion Chromatography Determination of the Iodide Mass Fraction

This section describes how the iodide mass fraction in SRM 3180, Lot No. 230111, was determined using IC as the measurement technique.

### 5.2.1. NIST Iodide Primary Standard Solutions

NIST Primary Standard Solutions (PSSs) were prepared using high-purity potassium iodide and sodium iodide (designated as NP-I-1 and NP-I-2, respectively) that had been assayed previously by the NIST Inorganic Chemical Metrology Group. The assay of iodide in potassium iodide is described in Sec. 5.1.1. The iodide in sodium iodide was assayed indirectly by the gravimetric assay of sodium, with corrections for impurities, and calculated based on the application of stoichiometric factors. Solutions were prepared as described in Sec. 2.4.1. Solutions made from potassium iodide (NP-I-1) had been previously prepared in 2011 and 2021 and solutions made from sodium iodide (NP-I-2) were prepared in 2024. The solutions were validated against one another using IC as described in Sec. 2.4.3. Single factor ANOVA of the resulting validation measurements did not detect a statistically significant difference between any of the aliquots at the 95 % confidence level ( $F = 1.024$ ,  $F_{critical} = 1.944$ ,  $p = 0.441$ ). Thus, because there was no observed difference between the freshly prepared PSSs made from NP-I-2 and older PSS preparations prepared from NP-I-1, the PSSs were fit for the certification measurements.

### 5.2.2. Analytical Samples

A set of 6 ampoules of the SRM, were randomly selected from the all the boxes of the SRM ampoules that were packed in approximate run order, taking two ampoules each from box.

There was no control sample for this certification. Normally, the control sample is the previous production lot of a given SRM. However, the previous lot of SRM 3180 (Lot No. 110530) was found to be out of specification during a stability assessment and the expiration date was not extended. Therefore, the previous lot could not be used as a control.

### 5.2.3. Sample, Calibrant, and Control Solution Preparations

Prior to analysis, an IS solution was prepared in the manner described in Sec. 3.1 by dissolving SRM 200b Potassium Dihydrogen Phosphate (Fertilizer Standard) [32] in ultra-high-purity water to contain a phosphate ( $\text{PO}_4^{3-}$ ) nominal mass fraction of 2.5 mg/g.

Six SRM sample solutions were prepared by transferring nominal 4.75 g aliquots of the SRM into separate, new, low-density polyethylene (LDPE) bottles and determining the aliquot mass to the nearest 0.1 mg. The ampoules for the samples were taken from the boxes of the SRM ampoules as described in Sec. 5.1.3. No control samples solutions were prepared because the previous lot was past its period of validation and determined to be unstable.

Validated NIST primary solutions (PSSs, Sec. 5.2.1), prepared to have the same nominal mass fraction as SRM 3180 ( $1 \text{ mg/g I}^-$ ), were used as calibrant solutions.

A nominal 1.89 g aliquot of IS solution (2.5 mg/g  $\text{PO}_4^{3-}$ ) whose mass was determined to the nearest 0.1 mg was transferred into each bottle containing the SRM, and a nominal 12.8 g aliquot of IS solution whose mass was determined to the nearest 0.1 mg was transferred into each bottle containing the PSS aliquots (nominally 32 g of solution), in a manner such that, in all of the solutions spiked with an IS, the ratio of  $\text{I}^-$  to  $\text{PO}_4^{3-}$  closely matched. All bottles were mixed vigorously. All spiked solutions underwent one subsequent dilution with ultra-high-purity water to yield nominal 50 g samples for analysis at mass fractions appropriate for introduction into the IC instrument ( $\approx 22.9 \text{ mg/kg I}^-$ ;  $\approx 22.7 \text{ mg/kg PO}_4^{3-}$ ). A nominal  $\text{I}^-$ :  $\text{PO}_4^{3-}$  ratio of 1.009:1, within a range of  $\pm 0.31 \%$ , relative (RSD,  $1 s$ , = 0.13 %) was obtained.

#### 5.2.4. Analytical Method

Ion chromatography (IC) was used to determine the mass fraction of  $\text{I}^-$  in the SRM 3180. The IC experimental design followed the “high-performance calibration” protocol as described in Sec. 3.2.

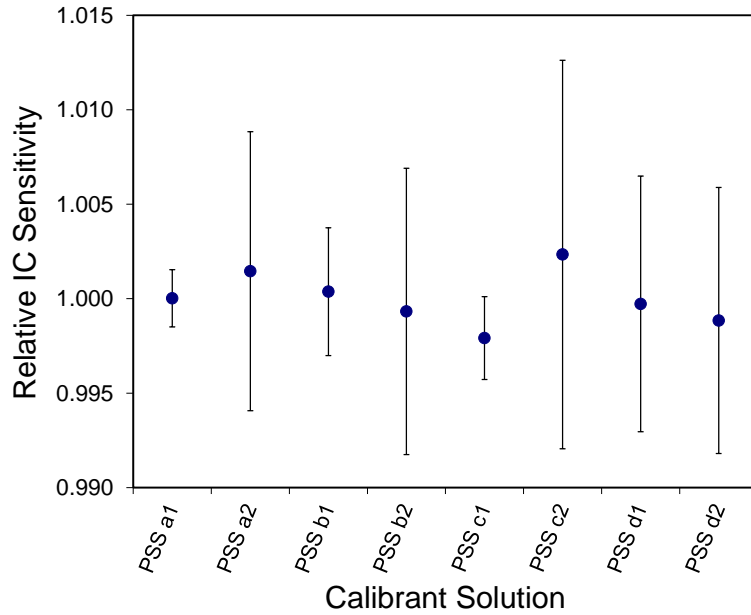
Briefly, the analysis of iodide was performed on a Dionex ICS-5000 (ThermoFisher Scientific, Waltham, MA)<sup>2</sup> using an Ion-Pac AS18 analytical column (2 mm  $\times$  250 mm) with an Ion-Pac AG18 guard column (2 mm  $\times$  50 mm). The chromatography was run isocratically at 0.45 mL/min with a 34 mmol/L KOH mobile phase produced using an in-line Dionex EGC III KOH Eluent generator cartridge. After exiting the analytical column, the mobile phase was passed through a ADRS 600 2 mm electrochemical suppressor with a current of 38 mA and then passed through a conductivity detector. Each analysis on the IC was run for 20 minutes. This analytical method allowed for the complete separation of the main analyte (iodide) from the IS (phosphate) and the sulfite stabilizer in the SRM 3180 solution. The retention times of iodide, phosphate, and sulfite using this method were 17.9 min., 3.7 min., and 6.6 min., respectively.

#### 5.2.5. Results of IC Analysis of SRM 3180

As described in Sec. 3.2, the results from the IC analysis of the prepared solutions (Sec. 5.2.3) were used to calculate a set of IC instrument sensitivities,  $S_i$ , for iodide using the PSS calibration solutions (Eq. 2). Figure 5 shows the set of  $S_i$ , that were used in the certification measurement of the SRM. One-way ANOVA was conducted on the set of  $S_i$  values of the PSS aliquots to evaluate the presence or absence of a statistically significant difference between the PSS aliquots used to calculate  $S_i$ . The  $p$ -value of the test was greater than 0.05 ( $F = 1.312$ ,  $F_{\text{critical}} = 2.313$ ,  $p = 0.11$ ), indicating no statistically significant difference between the calculated sensitivities was detected.

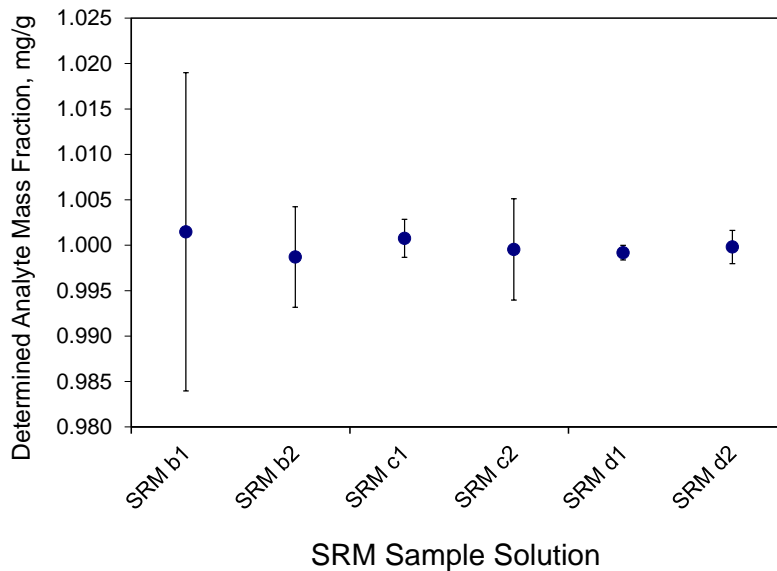
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<sup>2</sup> Certain commercial entities, equipment, or materials may be identified in this document in order to describe an experimental procedure or concept adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the entities, materials, or equipment are necessarily the best available for the purpose.



**Fig. 5. Comparison of normalized  $S_i$  values for iodide calibration solutions.**  
Uncertainty bars represent 95 % levels of confidence.

The iodide mass fraction  $w_{I,j}$  for each SRM aliquot was calculated using Eq. 5, where  $w_{A,jj} = w_{A,j}$  since iodide,  $I^-$ , is the anion, A. Figure 3 shows the set of  $w_{I,j}$  values of the SRM aliquots that are used to calculate the average iodide mass fraction of the SRM. One-way ANOVA was conducted on the set of  $w_{I,j}$  to evaluate the presence or absence of a statistically significant difference between the iodide mass fractions. The  $p$ -value of the test was greater than 0.05 ( $F = 0.590$ ,  $F_{critical} = 2.621$ ,  $p = 0.71$ ), indicating that no statistically significant difference between the values of  $w_{I,j}$  for each SRM aliquot was detected.



**Fig. 6. Comparison of iodide mass fractions,  $w_{I,j}$ , for SRM 3180 sample solutions.**  
Uncertainty bars represent 95 % levels of confidence.

The  $I^-$  mass fraction for the SRM, was calculated as the average of the six ampoule mass fractions  $w_{I_j}$  to yield an IC-determined value of 0.999 91 mg/g. The uncertainty budget along with the combined standard uncertainty,  $u_c$ , the coverage factor,  $k$ , and the expanded uncertainty,  $U$ , expressed at a level of confidence of 95 %, as calculated according to the ISO and NIST Guides, are presented in Table 3 [16, 30]. A description of each component of uncertainty is presented in Table 4. The calculated combined standard uncertainty, coverage factor, and the expanded uncertainty, for the mass fraction of iodide are  $u_c = 0.000\ 678$  mg/g,  $k = 2.145$ , and  $U = 0.001\ 45$  mg/g. From the IC measurements, the determined value and expanded uncertainty,  $U$ , expressed at a level of confidence of 95 %, is  $(0.999\ 91 \pm 0.001\ 45)$  mg/g. The mass fraction of  $I^-$  derived from the IC determination will be combined with a value derived from the gravimetric preparation for the SRM to produce a recommended certified  $I^-$  mass fraction and  $U$ .

**Table 3.** Uncertainty budget for the IC-determined iodide mass fraction in the SRM <sup>a</sup>.

Source <sup>b</sup>	$c_i$	units <sup>c</sup>	$u_i$	units <sup>c</sup>	$c_i u_i$	units <sup>c</sup>	$\nu_{\text{eff}}$
$Q$	3.5527	$\frac{mg_{I^-}}{g_{IS}}$	0.000 119	$\frac{g_{IS}}{g_{SRM}}$	0.000 421	$\frac{mg_{I^-}}{g_{SRM}}$	5
$S$	-3.5523	$\frac{(mg_{I^-})^2}{(g_{SRM})(g_{IS})}$	0.000 140	$\frac{g_{IS}}{mg_{I^-}}$	-0.000 499	$\frac{mg_{I^-}}{g_{SRM}}$	7
$C$	0.999 91	$\frac{mg_{I^-}}{g_{SRM}}$	0.000 184	Dimension one	0.000 184	$\frac{mg_{I^-}}{g_{SRM}}$	$\infty$
Combined standard uncertainty, $u_c$					0.000 678 mg/g		14
Coverage Factor, $k$ , for a level of confidence of 95 %					2.145		
Expanded uncertainty, $U$					0.001 45 mg/g		

- a The determined mass fraction of iodide is 0.99991 mg/g.  
b For an explanation, see Eq. 1 and Eq. 8, and Sec. 3.2.1 and Sec. 3.2.2.  
c The subscripts given for units in this table do not follow standard notation, and only serve as means of recordkeeping for the reader to know source of the units in the intermediate steps of the uncertainty calculations.

**Table 4.** Standard uncertainty components for the IC-determined iodide mass fraction in the SRM.

Source <sup>a</sup>	Basis	Type <sup>b</sup>	$\nu_{\text{eff}}$
$Q$	Calculated as the standard deviation of the mean of the individual values of $Q_j$ .	A	5
$S$	Calculated as the standard deviation of the mean of the individual $S_j$ values.	A	7
$C$	Because $C$ is defined to be unity, the standard uncertainty of $C$ was estimated to be numerically equivalent to the largest relative standard uncertainty of the mass of $I^-$ present within any of the PSS aliquots used to prepare the calibration solutions. The degrees of freedom associated with $C$ were taken to be the smallest number of degrees of freedom associated with these standard uncertainty values. This approach is justified because the uncertainties associated with the PSS aliquots are dominated by the components of uncertainty that are unaccounted for by the experimental design. These components are the uncertainty in the assays of the PS materials, NP-I-1 and NP-I-2, on which the PSS aliquots were based and the method uncertainty associated with the gravimetric preparations of the PSS aliquots.	B	$\infty$

- a For an explanation, see Eq. 1 and Sec. 3.2.  
b A or B identifies whether a Type A or B approach is used to evaluate the standard uncertainty component.

### 5.3. Final Value Assignment of the Iodide Mass Fraction in SRM 3180

The value assignment and uncertainty of the iodide mass fraction in SRM 3180, Lot No. 230111 are described in this section and were determined using the method outlined in Sec. 4.2.

The mass fraction of iodide in the solution was determined by the gravimetric preparation of the solution (section 5.1) and analytically, via ion chromatography (section 5.2). The former yielded 1.000 78 mg/g, with associated combined standard uncertainty of 0.000 23 mg/g, based on 5.1 effective degrees of freedom. The latter yielded 0.999 91 mg/g, with associated combined standard uncertainty of 0.000 68 mg/g, based on 14.0 effective degrees of freedom. The potential, long-term instability of the solution during the period of validity of the certification is expected to shift the certified value by 0 mg/g, with a standard uncertainty of 0.000 75mg/g, based on 9 degrees of freedom.

From Eq. 9 and based on the current values of the intercept and slope,  $\hat{\alpha}$  and  $\hat{\beta}$ , the *a priori* estimate of dark uncertainty,  $\tau_M$ , for the measurement results obtained for the SRM is

$$\begin{aligned} \tau_M &= (1.000\ 776\ \text{mg/g}) \times \\ &\exp \left\{ (-0.068\ 458\ 9) + 1.053\ 09 \times \ln \left( \frac{|0.999\ 909 - 1.000\ 776|}{1.000\ 776} \right) \right\} \quad (10) \\ &= 0.000\ 557\ \text{mg/g} \end{aligned}$$

where  $\tau_M$  lies between the standard deviation, 0.000 613 mg/g, of the values measured via gravimetric preparation and ion chromatography, and the geometric average, 0.000 395 mg/g, of the standard uncertainties associated with these two measured values<sup>3</sup>. This ordering of these three values reflects the fact that such standard deviation typically overestimates  $\tau_M$ , and this geometric average quantifies the dispersion one would have expected the two measured values to exhibit if no dark uncertainty were present.

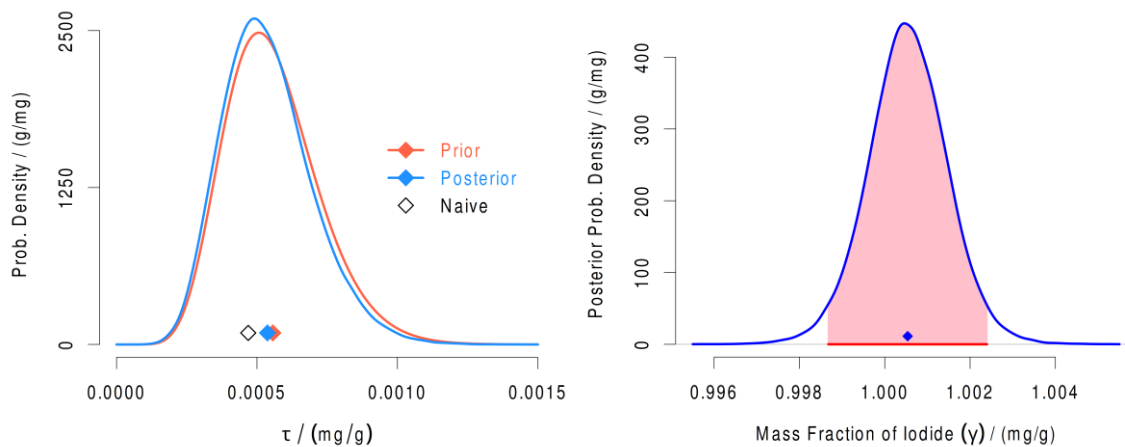
Since the REML estimate of  $\tau$  is positive,  $\tau = 0.000\ 346\ \text{mg/g}$ , following Lang et al. [24],  $\tau$  is assigned a gamma prior distribution with mean equal to this estimate and coefficient of variation 0.3. This coefficient expresses the assumption that the true  $\tau$  is not likely to differ from  $\tau_M$  by more than 60 %. In fact, according to this prior distribution, the (prior) probability of the true between-method standard uncertainty,  $\tau$ , lying between  $0.4\tau_M$  and  $1.6\tau_M$  is 96 %.

A sample of size 100 000 was drawn from the posterior distribution of the parameters of this model using Markov Chain Monte Carlo sampling as implemented in Stan's No-U-Turn sampler [33].

The mean and standard deviation of the values of  $\gamma = \omega + \kappa$  in this sample are the certified value and combined standard uncertainty of the mass fraction of the iodide anion in the solution. The expanded uncertainty for 95 % coverage is the shortest, symmetrical credible interval centered at the certified value that includes 95 % of the sample of values of  $\gamma$ , and the corresponding coverage factor is the ratio between this expanded uncertainty and the standard uncertainty.

<sup>3</sup> The determined values for the gravimetric preparation and IC determination are provided with extra digits in Equation 10 to minimize rounding errors.

Figure 7 depicts prior and posterior probability densities of  $\tau$ , and the posterior probability density for  $\gamma$ . The naive estimate of  $\tau$  is the square root of the difference between the sample variance of  $w_G$  and  $w_I$  and the square of the geometric average of  $u(w_G)$  and  $u(w_I)$ . The posterior density of  $\tau$  is only a slight shift toward the naive estimate because the data provide an evaluation of  $\tau$  based on a single difference between the gravimetric and instrumental values of the mass fraction of iodide.

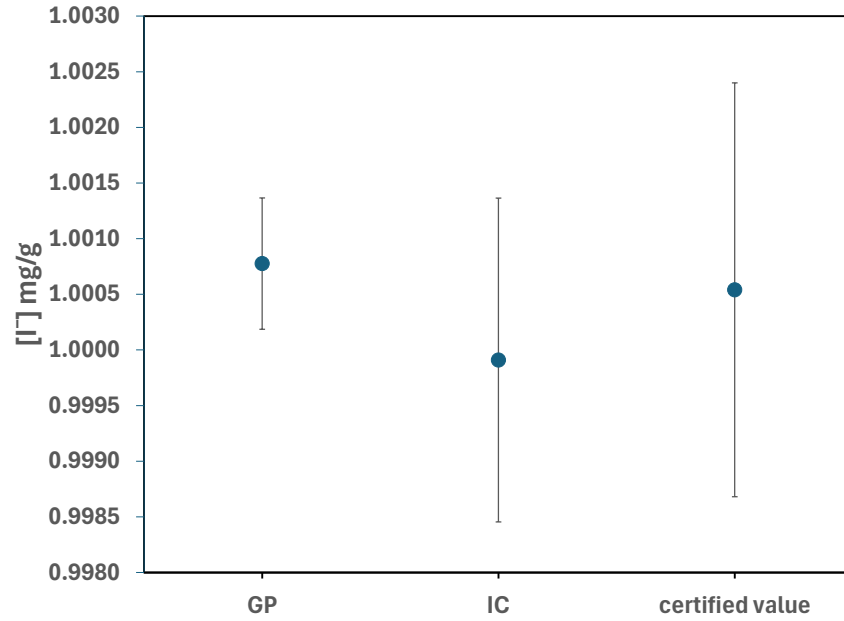


**Fig. 7. Probability densities for  $\tau$  and  $\gamma$ .**

LEFT PANEL: Prior and posterior probability densities of  $\tau$ , the means of the corresponding distributions (red and blue solid diamonds), and a naive estimate of  $\tau$  (black outline diamond).

RIGHT PANEL: Posterior probability density of  $\gamma$ , the corresponding mean (solid blue diamond), and 95 % credible interval for the true value of  $\gamma$ , which is the footprint of the shaded region that encompasses 95 % of the area under the (blue) curve.

The certified mass fraction value of iodide in the SRM is 1.0005 mg/g with expanded uncertainty 0.0019 mg/g for 95 % coverage. Figure 8 shows the iodide mass fractions as determined by gravimetric preparation and by ion chromatography (Sec. 5.1 and Sec. 5.2, respectively) and the final certified value. The implied corresponding coverage factor  $k = 2.02$  is the ratio between this expanded uncertainty and the standard uncertainty of 0.000 96 mg/g. The corresponding, effective number of degrees of freedom,  $\nu_{\text{eff}} = 40.7$ , is the solution of the nonlinear equation  $Q_{\nu}(0.975) = 2.02$ , where  $Q_{\nu}$  denotes the quantile function of Student's  $t$  distribution with  $\nu_{\text{eff}}$  effective degrees of freedom. The value assigned to the SRM was derived from the inputs specified above using the method described by Lang et al. [24] and in Sec. 4.2, which takes into account historical differences between gravimetric and instrumental methods of analysis observed for 3100 series SRMs (single-element solutions) and for 3180 series SRMs (anion solutions).



**Fig. 8. The iodide mass fraction,  $[I^-]$ , as determined by GP and IC, and the certified iodide mass fraction in the SRM.**

Uncertainty bars represent expanded uncertainties with level of confidence of 95 %.

## 6. Stability Monitoring

While the 3180 series SRM solutions are nominally stable for ten years, and with a stability component of the uncertainty based on a 12-year shelf life, the practical useful life of an SRM may vary depending on the anion and the particular SRM lot. With this variability in mind, the 3180 series SRM program routinely tests for the stability of the SRM production lots as the SRM solutions near their expiration dates. Typically, stability testing occurs within one year of a SRMs listed expiration date. If the SRM passes the stability testing, and based on current stock on hand, the expiration date may be extended.

Stability testing also provides valuable information on the expected lifetime of future SRM production lots and offers insights into which products may be prone to instability and would require more frequent testing.

The stability testing of the 3180 series SRMs uses IC to measure the anion mass fraction observed and follows the same protocols as Sec. 3.

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## Appendix A. List of Symbols, Abbreviations, and Acronyms

### A.1. Symbols

$C$	uncertainty in the purity of the primary calibration materials
$m_{A,i}$	assumed mass of analyte anion
$m_{IS,i}$	mass of internal standard stock solution
$Q$	instrument response
$R_i$	observed analyte to internal standard peak area ratio
$S$	instrument sensitivity
$\alpha$	intercept of logarithm of relative size of historical dark uncertainty
$\beta$	intercept of logarithm of relative size of historical dark uncertainty
$\gamma$	value of the mass fraction in solution at any future time between when the SRM was first certified, and when it reaches the end of its period of validity. ( $\gamma = \omega + \kappa$ )
$\varepsilon$	method-specific measurement errors
$\kappa$	contribution from long-term instability
$\lambda$	method effects
$\nu$	degrees of freedom
$\tau$	dark uncertainty
$\sigma$	standard deviation
$w_G$	mass fraction of anion solution determined gravimetrically
$w_I$	mass fraction of anion solution determined instrumentally
$\omega$	true value of a measurand

### A.2. Acronyms

ANOVA	Analysis of Variance
COA	Certificate of Analysis
GP	Gravimetric Preparation
HDPE	High-Density Polyethylene
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
IS	Internal Standard
ISO	International Organization for Standardization
LDPE	Low-Density Polyethylene
NIST	National Institute of Standards and Technology
NP	NIST Primary (standard)
PS	Primary Standard
PSS	Primary Standard Solution
ORM	NIST's Office of Reference Materials
PFA	Teflon perfluoroalkoxy
PTFE	Teflon polytetrafluoroethylene
REML	Restricted Maximum Likelihood
SRM	Standard Reference Material, a certified reference material provided by NIST