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A traceability protocol to the SI by gravimetric analysis

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Abstract An example is presented of a traceability protocol for the measurement of a single-element strontium reference material solution, executed by a "primary" method of measurement for certification. The method of measurement is briefly described together with the measurement equation and the associated calculations for the estimation of uncertainties. This is followed by a discussion and estimate of each component of

uncertainty associated with the measurement, together with a final estimate of uncertainty. The final estimate of uncertainty compares well with observed uncertainties for two previous laboratory measurements of the reference material.

Key words Certification · Gravimetric analysis · Measurement · Measurement uncertainty · Reference material · Traceability

Introduction

This example is of a traceability [1] protocol [2] for the chemical measurement of an element by a "primary" method of measurement [3]. It can be used for the certification of a single-element reference material by a national reference laboratory. This protocol relates to a very pure strontium nitrate solution, stabilized by 10% (by volume) nitric acid¹. This solution is to be certified for the amount of strontium substance $n(\text{Sr})$ per unit mass of aqueous solution $m(\text{sol})$. The general measurement method described is based in part on the experience of certifying a currently available certified reference material (CRM) [4], Standard Reference Material (SRM) 3153a [5].

¹ Highly purified 10% (by volume) nitric acid is a standard analytical reagent equivalent to a solution of approximately 1.6 molality of HNO_3 ; that value is not critical compared with its freedom from trace contaminants.

Method of assay

The underlying purpose of this paper is to demonstrate the steps required in estimating the uncertainty of a gravimetric measurement, the value of which is traceable to the SI. Therefore, the intent of this brief description of the method of measurement is to that end and not just to be able to reproduce the Sr measurement.

The traditional method of measuring Sr by measuring the mass of precipitated SrSO_4 , which is recommended in many textbooks, should not be used because SrSO_4 is volatile above 300 °C. An accurate measurement of Sr can be made using SrO as the chemical form for weighing. A measured mass of solution $m(\text{sol})$, diluted to ~50 ml, is added slowly and with stirring to a stoichiometric excess (~5:1) of saturated ammonium oxalate solution (~0.35 mol/L), both solutions being at room temperature and previously adjusted to pH 8.5 with NH_4OH . The precipitated strontium oxalate, SrC_2O_4 , is allowed to settle at room temperature for

~12 h. The resulting Ostwald-ripened [6] particles of SrC_2O_4 are quantitatively collected on fine-grain, ashless filter paper, the filtrate being reserved for subsequent Sr^{2+} determination. The precipitate is washed several times with saturated ammonium oxalate solution, diluted (1:1). The paper and precipitate are carefully dried and ignited to ~1100 °C, to constant mass (~3 h) in a tared, quartz (fused silica) crucible, to form stoichiometric strontium oxide of mass $m(\text{SrO})$, measured after cooling in air that is free of H_2O and CO_2 . A platinum crucible must not be used since SrO reacts with platinum at elevated temperatures. All mass measurements must be buoyancy corrected. A small negative correction $\delta_1 m(\text{SrO})$ is applied for traces of other substances coprecipitated and determined by X-ray fluorescence spectrometry. Another small, but significant, positive correction $\delta_2 m(\text{SrO})$ is also applied for Sr^{2+} ions remaining in the filtrate and measured by flame atomic emission spectrometry (AES)¹. On using AES or other types of spectrometry, no other ions should be detectable at a level greater than 10^{-6} mol/L in the filtrate or in any of the solutions used in the determination. In the chemical reaction of the determination, each Sr^{2+} entity is converted to one SrO, i.e., $n(\text{Sr}^{2+}) = n(\text{Sr}) = n(\text{SrO})$.

Calculation of the measurement result

By division of the measured $m(\text{SrO})$ by the known molar mass $M(\text{SrO})$, the corresponding amount of substance $n(\text{SrO})$ is obtained. Thus the value of the concentration to be certified is:

$$\frac{n(\text{Sr})}{m(\text{sol})} = \frac{m(\text{SrO})}{M(\text{SrO}) m(\text{sol})}$$

Note that $m(\text{SrO})$ is the mass of the SrO precipitate plus the mass of the Sr^{2+} ions in the filtrate, expressed as SrO [$\delta_2 m(\text{SrO})$], minus the mass of the coprecipitated impurities in the SrO precipitate [$\delta_1 m(\text{SrO})$].

Components of uncertainty of the measurement results

Uncertainty in $M(\text{SrO})$

The molar mass of SrO has an established relative standard uncertainty of 1.1×10^{-4} which is almost entirely due to the variability in the isotopic composition of terrestrial strontium. This uncertainty is small and could be reduced further by one order of magnitude by a direct molar-mass measurement of the specific stron-

tium in the solution, or by ascertaining that the source of the strontium had been free of major contamination by rubidium over a geologically significant period [7].

Uncertainty from SrO stoichiometry

Detectable changes in the mass of SrO variously heated in air are not observed and can be estimated confidently to be at a relative uncertainty level below 5×10^{-5} . Exact stoichiometry of SrO is generally assumed from long experience of consistent results. Nevertheless, the 1:1 ratio is confidently estimated to have a relative standard uncertainty of 0.7×10^{-4} . That statement of course includes any possible variability of the strontium valency manifested by strontium vacancies or interstitial ions.

Uncertainty of the gravimetric measurement

If the analyzed solution were perfectly pure, i.e., the compound SrO were pure, perfect, and free from adsorbed contaminants, and the chemical reaction proceeded perfectly, the relative standard uncertainty component derived solely from the measurement of the gravimetric ratio would be 1×10^{-4} . This assumes that a good analytical balance sensitive to $\cong 200 \mu\text{g}$ in a good environment, with a self-consistent set of external or built-in weights, is used for measuring the mass of the assayed portion of the solution. It is also assumed that a good analytical balance² sensitive to $\cong 3 \mu\text{g}$ in a good environment, with a self-consistent set of external or built-in weights, traceable to the kilogram, is used for measuring the mass of the SrO. The mass of the vessel holding the solution and that of the crucible containing the SrO should not exceed by more than twenty times $m(\text{sol})$ and $m(\text{SrO})$, respectively.

Uncertainties from possible departures from the ideal chemical compounds and reactions

Excellent laboratory conditions and expert handling are assumed for the estimation of these uncertainties.

Uncertainties associated with errors from contamination

Errors occur in transfer of the two solutions, to glassware, on the filter paper, on washing, on heating, on transfer to and on the balance; including adsorption effects of moisture or CO_2 , perhaps forming $\text{Sr}(\text{OH})_2$ or

¹ X-ray fluorescence spectrometry was performed by P. A. Pella and flame atomic emission spectrometry by T. A. Butler, both of the NIST Analytical Chemistry Division.

² A microbalance can be used to advantage

SrCO₃, as well as occlusions or solid solutions in the SrO. Contamination of the crucible during the heat cycle should also be included. Such small contamination errors are estimated to add up to not more than a contributing relative standard uncertainty of 2×10^{-4} .

Uncertainties associated with errors from loss of chemicals

Errors resulting in the loss of chemicals occur during transfer in solution, by water evaporation when sampling the solution, reduction in Sr²⁺ by adsorption on the silica, or of SrC₂O₄ when filtering, and/or loss of SrO for instance by evaporation before weighing. The largest contributor to these possible but unobserved errors would be loss of SrC₂O₄ precipitate during the transfer to the filter paper. With good laboratory technique the total contribution to the relative standard uncertainty should not exceed 2×10^{-4} .

Uncertainties associated with the correction terms, L₁m(SrO) and L₂m(SrO)

Both these corrections are themselves associated with uncertainties that are independent but probably partially off-setting. The larger of these corrections is evaluated to be about 1×10^{-3} with a relative standard uncertainty of $\pm 10\%$, so that these corrections should be included in the uncertainty budget as two relative standard uncertainties, one being $\sim 1 \times 10^{-4}$ and the other being $< 1 \times 10^{-4}$ (0.7×10^{-4} will be used as an estimate in subsequent calculations).

The budget of the relative uncertainty estimates (u_r)

Uncertainty in M(SrO): $u_r = 1.1 \times 10^{-4}$

Uncertainty from SrO stoichiometry:

$$u_r = 0.7 \times 10^{-4}$$

Uncertainty of gravimetric measurement:

$$u_r = 1 \times 10^{-4}$$

Uncertainty associated with errors from contamination:

$$u_r = 2 \times 10^{-4}$$

Uncertainty associated with errors from loss of chemicals:

$$u_r = 2 \times 10^{-4}$$

Uncertainties of correction terms:

$$u_r = 1 \times 10^{-4} + u_r = 0.7 \times 10^{-4}$$

The estimated combined relative standard uncertainty ($u_{c,r}$) is:

$$u_{c,r} = (12.2)^{1/2} \times 10^{-4} \cong 3.5 \times 10^{-4}$$

Discussion and Conclusion

It may be noted here that in the preparation of two individual lots of SRM 3153a, the experimental values of $u_{c,r}$ for the strontium assay on an aliquot of the bulk solution were 3.2×10^{-4} and 3.5×10^{-4} respectively [8]. These uncertainty data compare very well with the estimated $u_{c,r}$ of 3.5×10^{-4} .

It should be noted that for each of the lots of SRM 3153a mentioned above, the value of the expanded relative uncertainty, U_r , for the entire lot is considerably larger than the value for either the estimated $u_{c,r}$ of the Sr assay or the experimental $u_{c,r}$ of the Sr assay. This is true because U_r for the entire lot contains a "coverage factor" (k), and moreover, the value of $u_{c,r}$ used in calculating U_r is larger due to additional components of uncertainty resulting from bulk preparation, packaging, and transpiration of the solution through the container walls over time.

Careful consideration of the total analytical process was necessary prior to assignment of an estimated $u_{c,r}$ for the Sr measurement. This uncertainty is a critical part of the traceability of the measurement to the SI, because traceability has value only to the degree of the uncertainty, and one's confidence in the validity of that uncertainty.

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