

Traceability Tool for Elemental Solution Standards Using Ratio-Based Instrumental Comparison

*Version 1.2
March 7, 2005*

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Intended Use

This spreadsheet has been designed as an aid for establishing traceability of a batch of an elemental solution standard to the corresponding elemental spectrometric solution from the NIST SRM 3100 Series. It will work only with ratio-based instrumental comparison data, i.e. data from instrumental methods capable of utilizing internal standards. It has been tested using ICP-OES data, but should also be applicable to other multi-element methods. A spreadsheet with ICP-OES example data is included in this package. The measurements for that example took 95 minutes. When all required input data fields are filled, the spreadsheet will calculate the traceable mass fraction and uncertainty of the batch elemental solution standard.

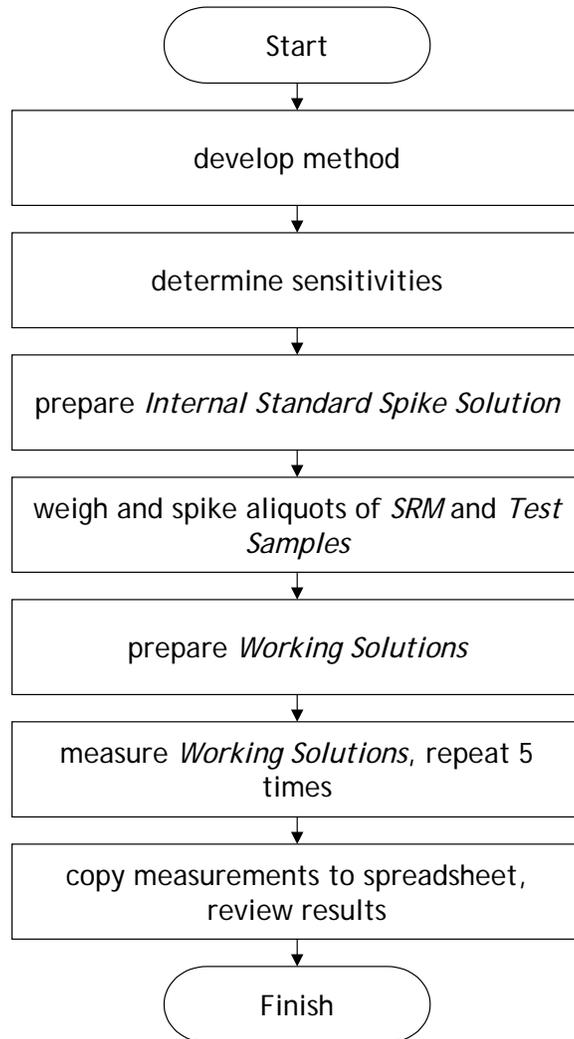
Prior to using this tool, the user must develop an appropriate measurement method for the analyte. This includes the selection of an appropriate internal standard element, verification that the analyte and internal standard are free of any interferences or solution cross-contamination, and verification that there are no blank contamination or instrument memory issues. The instrument must have a linear response to analyte and internal standard. For ICP-OES measurements, the publication by Salit, *et al.*¹ should be consulted.

Overview

The batch elemental solution standard for which traceability to an SRM is being sought is referred to as the *Test Sample*. Four weighed aliquots of the Test Sample and four weighed aliquots of the SRM will each be spiked with weighed aliquots of an *Internal Standard Spike Solution*. The mass fraction of the Internal Standard Spike Solution and the spike aliquot mass are chosen to yield an analyte/internal standard instrument response ratio near unity. Since this depends on the relative sensitivity of the analyte and internal standard, the procedure begins with the determination of the instrument sensitivity for the analyte and internal standard under the instrument operating conditions to be used for the measurement. This is done by recording the instrument response of an analyte *Sensitivity Solution* and an internal standard *Sensitivity Solution*. With this information, instructions are given for the preparation of the Internal Standard Spike Solution by dilution of an *Internal Standard Stock Solution*. Spiked Test Samples and SRMs are then prepared according to instructions. In most cases, it is expected that the spiked solutions will be too concentrated for direct instrumental analysis, and therefore *Working Solutions* must be prepared by dilution. Dilution instructions are given based on the mass of Working Solutions to be prepared and a user-specified instrument *Working Response Level*. A reasonable Working Response Level is one which is significantly above the blank and background level, and which is comfortably within the linear range of the detection system. Five measurements of the analyte and internal standard response

of each Working Solution of Test Sample and SRM are made in a specified run order. The traceable analyte mass fraction of the Test Sample is calculated based on the relative analyte/internal standard response of Test Sample to SRM, and the relative masses of Test Sample, SRM and Internal Standard Spike Solution. The uncertainty of the traceable mass fraction is calculated based on the observed variability of the measurements and uncertainty of the certified value of the SRM.

This process is diagrammed below.



Equipment and Supplies

- One ampoule, or 10 mL, of the appropriate SRM 3100 solution.
- Four units of the Test Sample. Each unit must contain at least 2.5 g at 10 mg/g, or 25 g at 1 mg/g (assuming the usual situation of a 10 mg/g SRM). Each unit should be chosen from a different section of the batch to achieve a good sampling of the batch.
- A solution containing the analyte at a known concentration that will yield an instrument response signal in a good working range of the instrument. This is the analyte Sensitivity Solution. The mass fraction of this solution need not be accurately known.
- A solution containing the internal standard at a known concentration that will yield an instrument response signal in a good working range of the instrument. This is the internal standard Sensitivity Solution. The accuracy of this solution is not important.
- A bottle of the Internal Standard Stock Solution. A 10 mg/g solution is best. The mass fraction of this solution need not be accurately known.
- A 250 mL bottle for the preparation of the Internal Standard Spike Solution.
- 8 bottles for spiked SRM and Test Samples. In most cases, 30 mL bottles will be suitable when the Test Sample has a nominal mass fraction of 10 mg/g. If the nominal mass fraction of the Test Sample is 1 mg/g, 60 mL bottles will be appropriate.
- 8 containers for the Working Solutions. Autosampler tubes are convenient.
- A balance with 1 mg precision (*i.e.* a “3-place top loader”).
- An adjustable digital pipette is useful to deliver solution mass near the specified target values.

Instructions

1. Open and complete the Descriptive Information worksheet. In this and all subsequent worksheets, cells requiring input information are shown with gold backgrounds.
2. Using the analyte and internal standard Sensitivity Solutions, measure the analyte and internal standard instrument response signal for these solutions. Enter the known mass fractions and the measured response signals in the Instrument Sensitivity Test worksheet.
3. Open and print the Solution Preparation worksheet. Following the target mass values given, prepare the Internal Standard Spike Solution, the spiked samples of the SRM and Test Sample, and the Working Solutions. Enter the exact mass

values for the preparation of the spiked Test Samples and SRMs into the worksheet. The exact mass values for the preparation of the Internal Standard Spike Solution and the Working Solutions are not used in any subsequent calculations, and are not entered into the spreadsheet.

4. Collect instrumental data following the experimental design in the Instrumental Measurements worksheet, recording between 1 and 10 replicate readings of each specified measurement. Enter the data into the spreadsheet.
5. The spreadsheet includes the possibility of using the Salit and Turk drift correction method.² The drift correction function should be visually inspected in the Drift Pattern spreadsheet to confirm that a reasonable model of observed drift has been calculated.
6. Final results can be found in either the Final Results (with Drift Correction) worksheet, or the Final Results (without Drift Correction) worksheet.

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1. M.L. Salit, G.C. Turk, A.P. Lindstrom, T.A. Butler, C.M. Beck II, and B. Norman, "Single-element Solution Comparisons with High-Performance ICP-OES," *Anal. Chem.* **73**, 4821-4829 (2001).
 2. M.L. Salit and G.C. Turk, "A drift correction procedure," *Anal. Chem.* **70**, 3184-3190 (1998).