A PRACTICAL TOOL FOR ESTABLISHING TRACEABILITY IN CHEMICAL MEASUREMENTS

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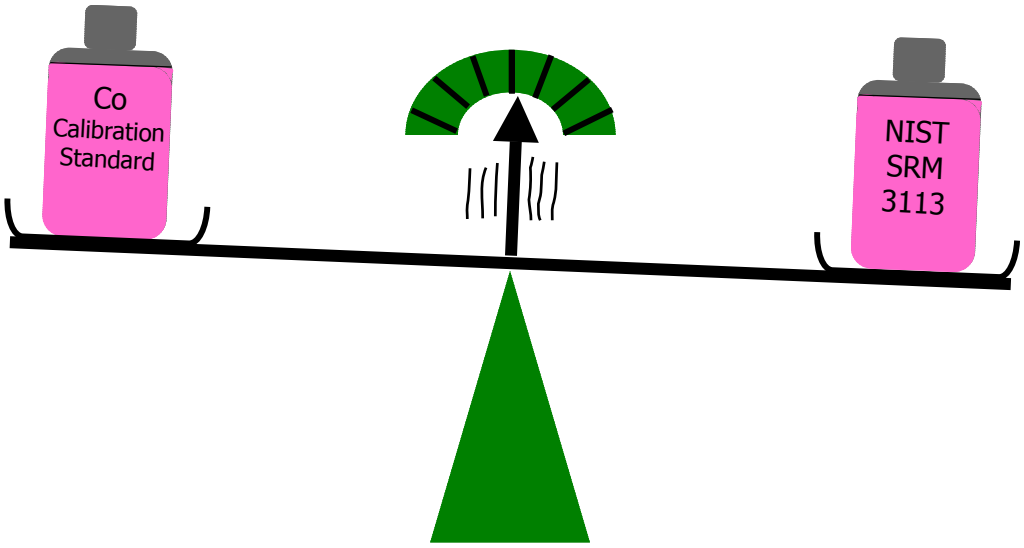
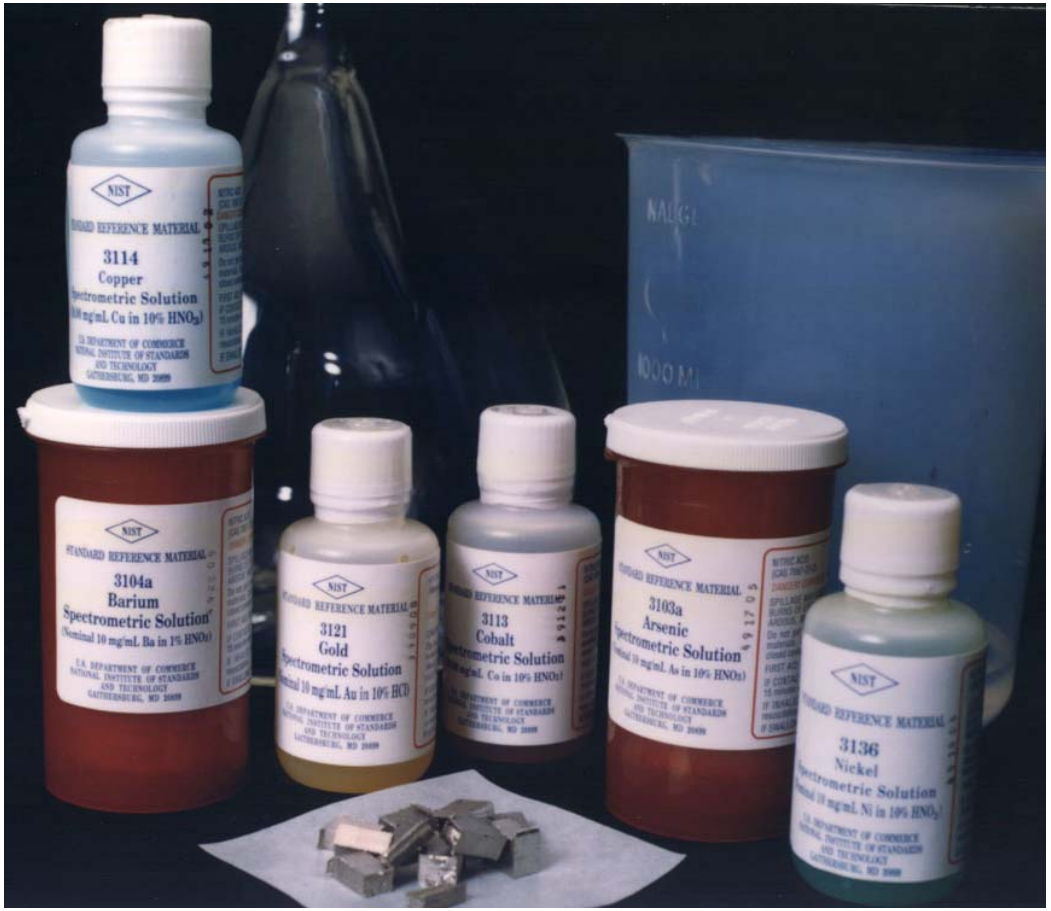
NIST

Specifically, a tool to establish traceability of the value of an elemental solution standard to the NIST SRM 3100 Series

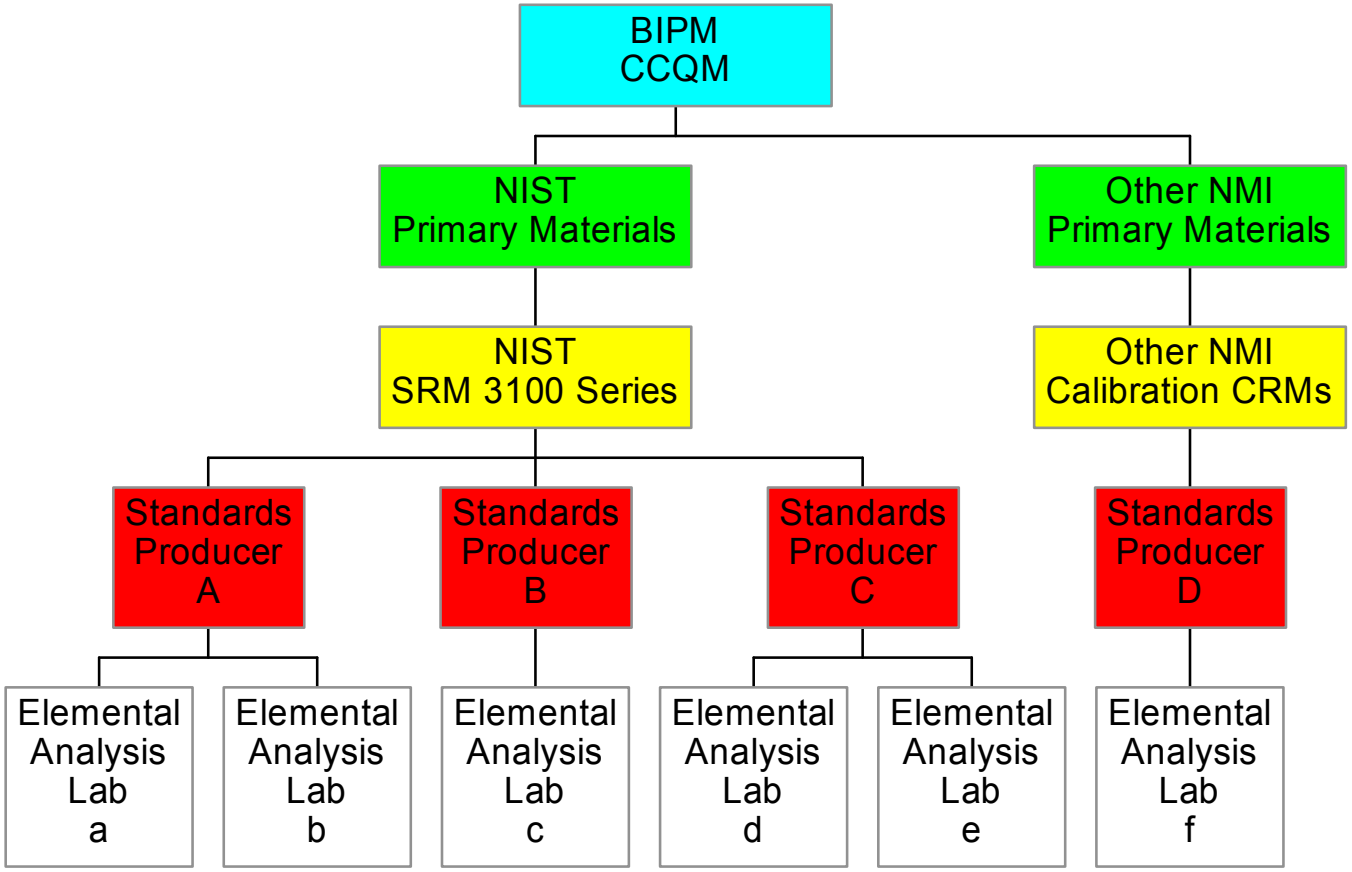


The NIST SRM 3100 Series -- Spectrometric Solutions

- NIST produces and certifies 69 Spectrometric Solution SRMs
- Typical mass fraction is 10 ± 0.03 mg/g
- Serve as national standards



An important link in the calibration infrastructure for elemental analysis



We have designed a "Traceability Tool" for Elemental Solution Standards

- a spreadsheet
  - an experimental design with replication of all critical measurements and preparation steps
    - » to assess measurement uncertainty
  - a ratio-based method
    - » interactively designs the correct "spike"
  - optional drift correction and diagnostics
  - calculates the traceable value
  - full uncertainty budget

What you need to use this tool

- An instrument that gives a signals linearly proportional to the mass fraction of the analyte and an internal standard mixed in a solution
  - Designed for ICP-OES, but not required

Plus

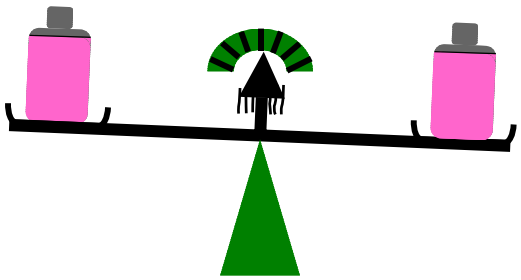
- 10 g of SRM
- 4 units of Test Solution
- Rough setup solutions for analyte and IS
- Stock solution of IS
- One 250 mL bottle
- Eight 30 mL bottles for spiked solutions
- Eight more bottles for diluted working solutions
- A 1 mg balance
- A digital pipette

The tool does NOT specify

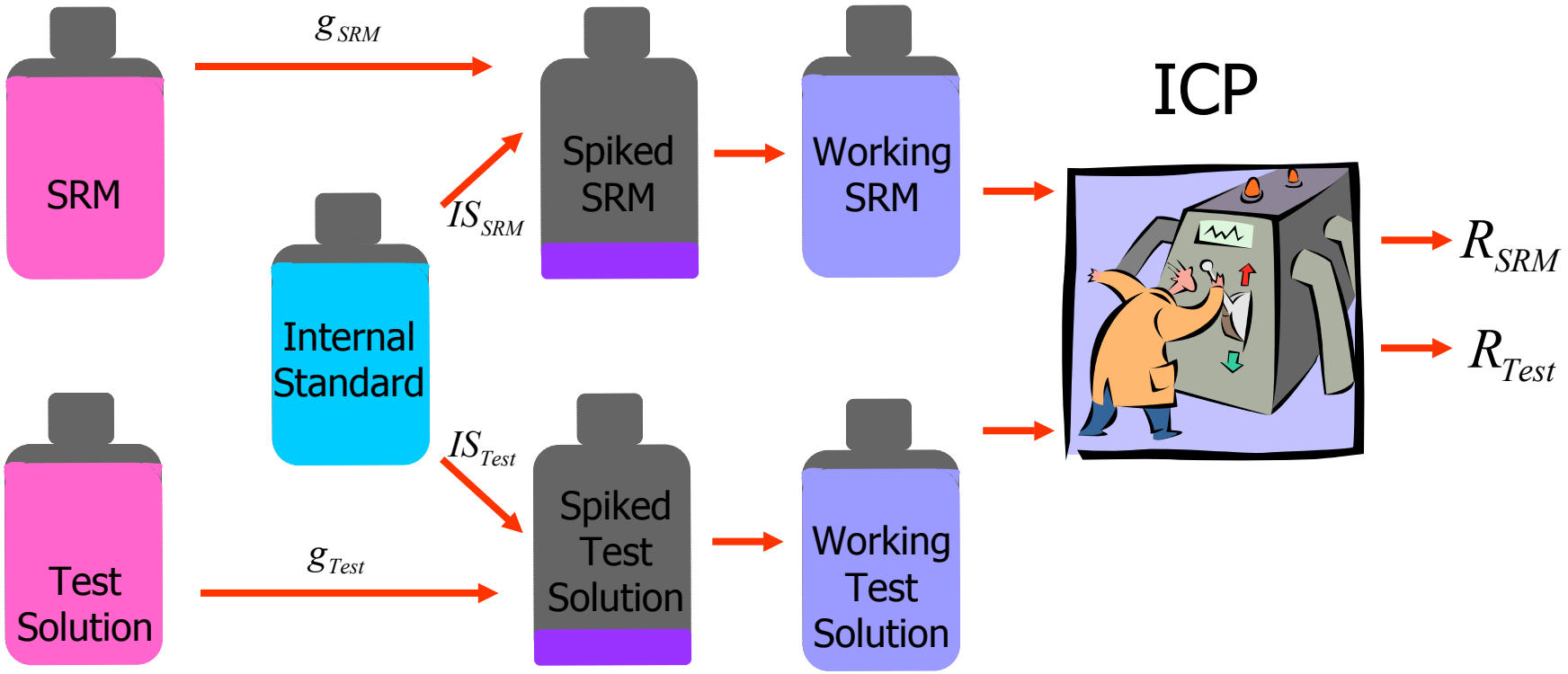
- Any instrumental operating parameters
  - Wavelengths, background correction points, integration times ……
- Choice of internal standard

ICP-OES is a great double-pan balance for comparing elemental solution standards.

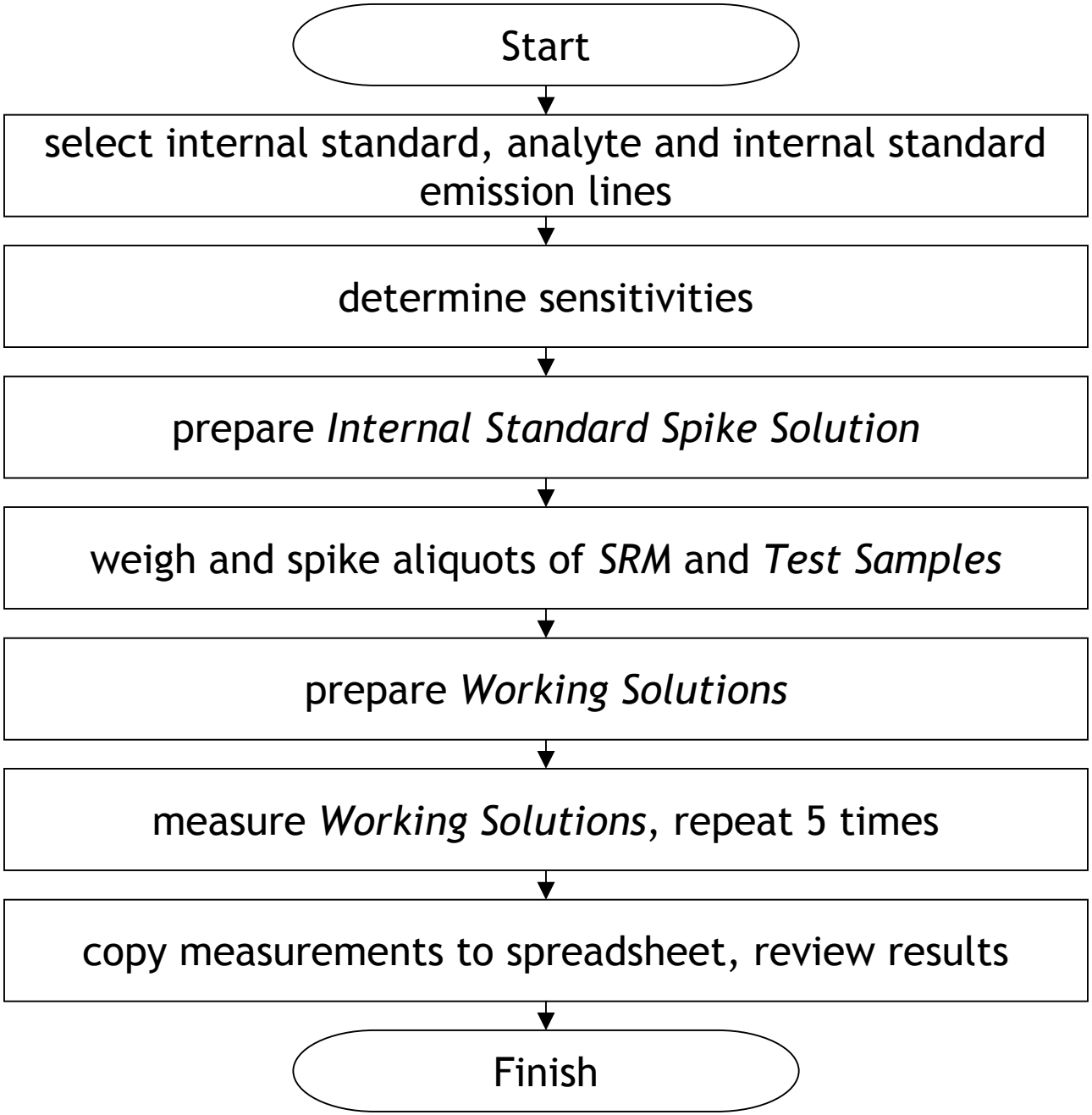
- spectroscopic elemental selectivity
- simultaneous detection of analyte and internal standard emission
  - highly correlated noise
- excellent precision
  - better than 0.03 % in most cases
  - thus adds negligible uncertainty to traceable values



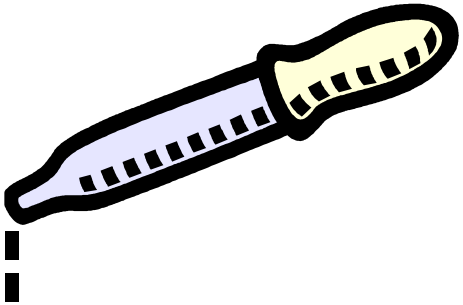
Ratio-Based Measurement



$$\left(\frac{mg}{g}\right)_{Test} = \left(\frac{R_{Test}}{R_{SRM}}\right)\left(\frac{IS_{Test}}{IS_{SRM}}\right)\left(\frac{g_{SRM}}{g_{Test}}\right)\left(\frac{mg}{g}\right)_{SRM}$$

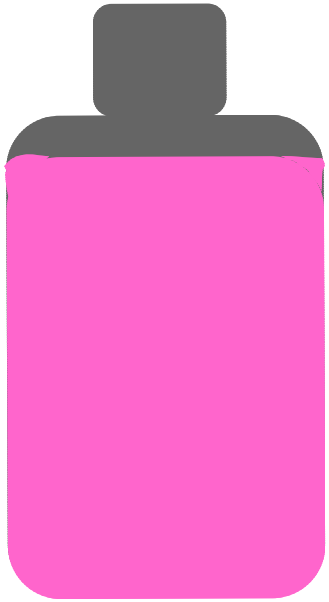

Start
select internal standard, analyte and internal standard emission lines
determine sensitivities
prepare *Internal Standard Spike Solution*
weigh and spike aliquots of *SRM* and *Test Samples*
prepare *Working Solutions*
measure *Working Solutions*, repeat 5 times
copy measurements to spreadsheet, review results
Finish

Example Cobalt Standard



+ 0.046 g water

10.305 g of SRM 3113
@ 9.996 mg/g



= 9.952 mg/g

Step 1. Experiment Related Information

Experiment related information	Input
Date of analysis	26-Oct-01
Element	Co
Identification label of the Test Sample	Example
Lot number of the Test Sample	1
Nominal mass fraction of Test Sample (mg/g)	9.952
SRM 3100 series number	3113
SRM lot number	000630
Certified Mass Fraction (mg/g) of SRM 3113, lot 000630	9.996
Uncertainty of Certified Mass Fraction (mg/g)	0.023
Coverage Factor, k, for the SRM Certified Uncertainty	2.31

SRM Certificates of Analysis can be found at
http://srmcatalog.nist.gov/

Step 1 (continued). Instrument Related Information

Instrument related information	Input
Instrumental comparison method	HP-ICP
Working Response Level	1000000
Mass of Working Solutions (g)	60
Internal standard element	Sc
Mass fraction of Internal Standard Stock Solution (mg/g)	10

Step 2. Sensitivity Test

HP-ICP Comparison of Example (lot 1) to NIST SRM 3113 (lot 000630), 10/26/2001.

☞ **measure instrument response for the *Sensitivity Solutions* of the analyte and internal standard**

	ug/g	HP-ICP response	Sensitivity (response/(µg/g))	Target working mass fraction	Sensitivity ratio
Co (Analyte) Sensitivity Solution	10	1.67E+06	*167086.9*	*5.98*	*0.038*
Sc (Int. Std.) Sensitivity Solution	5	2.20E+07	*4408475.2*	*0.23*	

Step 3. Solution Preparation

HP-ICP Comparison of Example (lot 1) to NIST SRM 3113 (lot 000630), 10/26/2001.

☞ **Prepare Sc Internal Standard Spike Solution.**

g of Sc Internal Standard Stock Solution to dilute to 200g
0.95

☞ **Into labeled bottles, prepare spiked Test Samples and SRMs following the target values listed below:**

	g of Test Sample				g of SRM 3113				g of IS Spike Solution			
	Target	Actual			Target	Actual			Target	Actual		
		Tare	Gross	*Net*		Tare	Gross	*Net*		Tare	Gross	*Net*
SRM 1					2.5	6.275	8.882	*2.607*	20	8.882	29.335	*20.453*
SRM 2					2.5	6.277	8.931	*2.654*	20	8.931	28.888	*19.957*
SRM 3					2.5	6.241	8.889	*2.648*	20	8.889	28.457	*19.568*
SRM 4					2.5	6.162	8.536	*2.374*	20	8.536	28.582	*20.046*
Test Sample 1	2.5	6.305	8.961	*2.656*					20	8.961	29.397	*20.436*
Test Sample 2	2.5	6.230	8.884	*2.654*					20	8.884	29.281	*20.397*
Test Sample 3	2.5	6.259	8.922	*2.663*					20	8.922	28.333	*19.411*
Test Sample 4	2.5	6.272	8.585	*2.313*					20	8.585	28.965	*20.380*

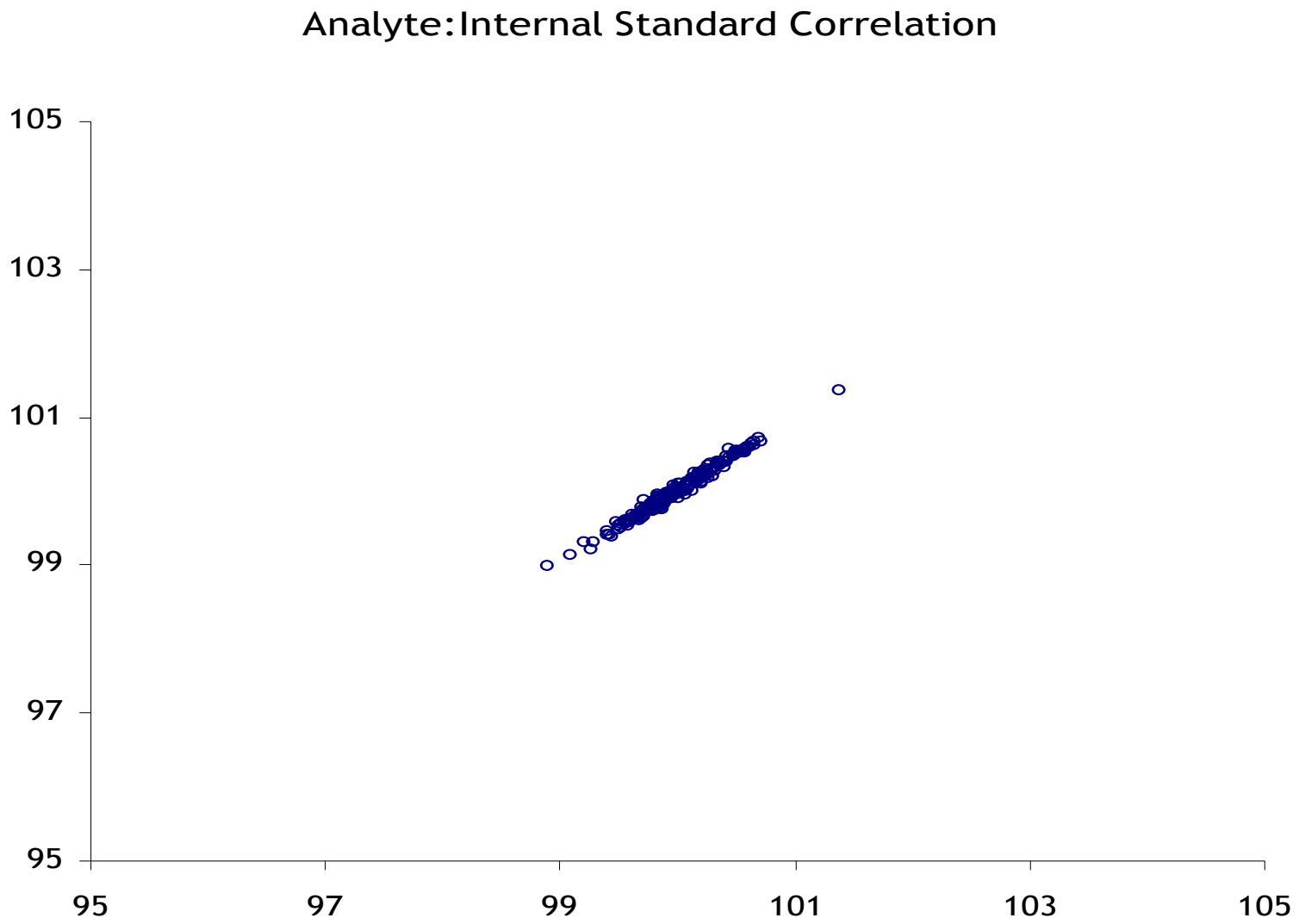
☞ **Prepare Working Solutions by dilution of spiked solutions.**

	g of spiked solution to dilute to 60 g
SRM Samples	*0.32*
Test Samples	*0.32*

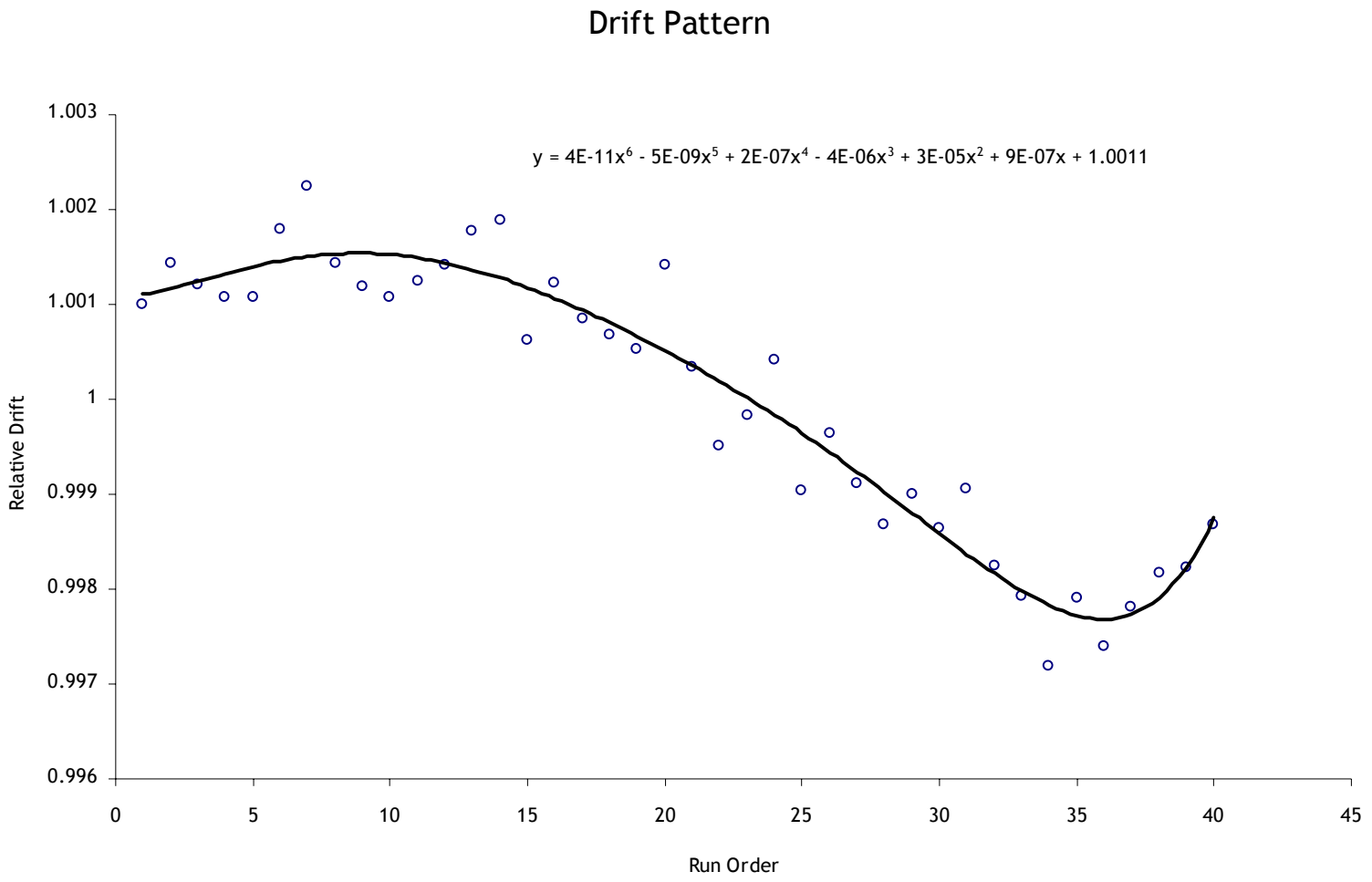
Step 4. Paste Data

Repeat #	ID	Element	Reading 1
1	SRM 1	Analyte	1137374.55
		IS	1113068.13
	Test Sample 1	Analyte	1141089.78
		IS	1099376.97
	SRM 2	Analyte	1196692.63
		IS	1123082.64
	Test Sample 2	Analyte	1108934.27
		IS	1068717.37
	SRM 3	Analyte	1208361.01
		IS	1114122.94
	Test Sample 3	Analyte	1243910.54
		IS	1137017.31
	SRM 4	Analyte	1038993.8
		IS	1092479.25
	Test Sample 4	Analyte	1077577.54
		IS	1188758.02
2	SRM 1	Analyte	1126370.41
		IS	1102142.82
	Test Sample 1	Analyte	1132849.54
		IS	1092214.67
	SRM 2	Analyte	1207295.28
		IS	1132187.5
	Test Sample 2	Analyte	1111136.64
		IS	1069968.02
	SRM 3	Analyte	1214994.39
		IS	1119541.71
	Test Sample 3	Analyte	1231031.77
		IS	1122825.22
	SRM 4	Analyte	1051854.31
		IS	1107376.21
	Test Sample 4	Analyte	1075063.37
		IS	1186723.38
3	SRM 1	Analyte	1139182.62
		IS	1115025.26
	Test Sample 1	Analyte	1128984.33
		IS	1088690.61
	SRM 2	Analyte	1197496.24
		IS	1124042.41
	Test Sample 2	Analyte	1107071.47
		IS	1066707.79
	SRM 3	Analyte	1214189.49
		IS	1119554.66
	Test Sample 3	Analyte	1233749.11
		IS	1128012.72
	SRM 4	Analyte	1040693.68
		IS	1096859.49
	Test Sample 4	Analyte	1067269.46
		IS	1179873.52
4	SRM 1	Analyte	1140342.82
		IS	1118347.55
	Test Sample 1	Analyte	1116463.3
		IS	1077175.94
	SRM 2	Analyte	1207101.01
		IS	1133854.78
	Test Sample 2	Analyte	1106567.61
		IS	1067109.36
	SRM 3	Analyte	1215341.11
		IS	1123379.19
	Test Sample 3	Analyte	1240087.04
		IS	1135925.69
	SRM 4	Analyte	1037383.85
		IS	1094632
	Test Sample 4	Analyte	1063956.92
		IS	1177214.46
5	SRM 1	Analyte	1123252.23
		IS	1103387.89
	Test Sample 1	Analyte	1128926.16
		IS	1092771.06
	SRM 2	Analyte	1196393.54
		IS	1124993.86
	Test Sample 2	Analyte	1106270.51
		IS	1069921.32
	SRM 3	Analyte	1215945.61
		IS	1123944.01
	Test Sample 3	Analyte	1235961.65
		IS	1132041.02
	SRM 4	Analyte	1042308.55
		IS	1099013.19
	Test Sample 4	Analyte	1073005.15
		IS	1186736.11

Correlation Diagnostic



Drift Diagnostic



Results (without drift correction)

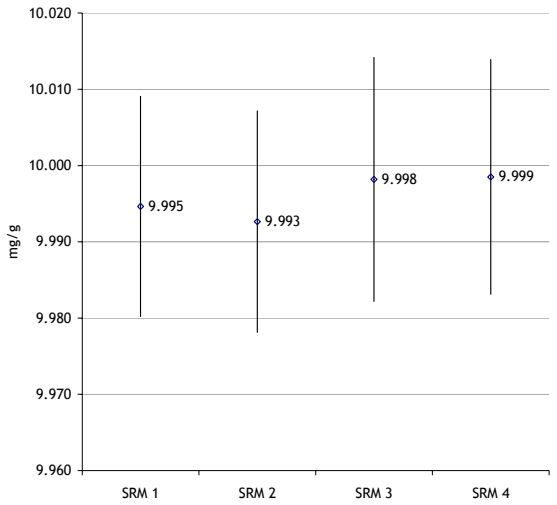
HP-ICP Comparison of Example (lot 1) to NIST SRM 3113 (lot 000630), 10/26/2001.

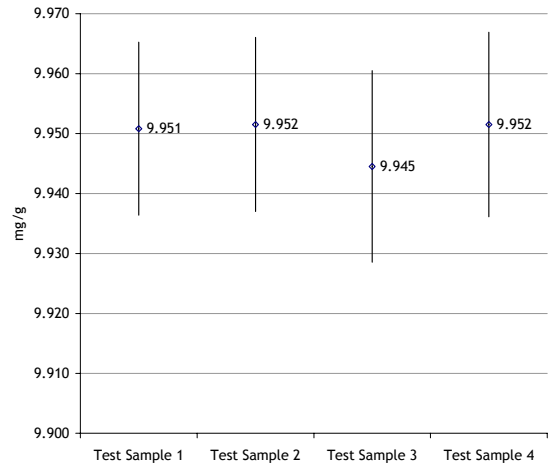
SRM 3113 Measurements	Average Signal Ratio	sd	rsd	Mass Ratio *(mg analyte/g IS)*	Slope of Calibration Curve *(signal ratio/mass*	Apparent Mass Fraction *mg/g*	sd *mg/g*
SRM 1	1.0209	0.0015	0.14%	1.2741	0.8013	9.995	0.014
SRM 2	1.0649	0.0015	0.15%	1.3293	0.8011	9.993	0.015
SRM 3	1.0843	0.0017	0.16%	1.3527	0.8016	9.998	0.016
SRM 4	0.9489	0.0015	0.15%	1.1838	0.8016	9.999	0.015
				Average slope	0.80138		
				sd of slope	0.00023		

Example Measurements	Average Signal Ratio	sd	rsd	Observed Mass Fraction *mg/g*	sd *mg/g*	Observed /Nominal
Test Sample 1	1.0364	0.0018	0.17%	9.951	0.017	99.99%
Test Sample 2	1.0377	0.0019	0.18%	9.952	0.018	100.00%
Test Sample 3	1.0933	0.0019	0.17%	9.945	0.017	99.92%
Test Sample 4	0.9051	0.0013	0.15%	9.952	0.015	100.00%
	Average mass fraction			9.950		
	sd of mass fraction			0.003		

Uncertainty Budget				
Source	(mg/g)	relative	df	coverage factor, *k*
SRM 3113 Measurements	0.001	0.01%	3	
Example Measurements	0.002	0.02%	3	
Certified Value of SRM 3113	0.010	0.10%	8	
Combined Uncertainty	0.010	0.10%	9	
Coverage Factor, k				2.26
Expanded Uncertainty	0.023	0.23%		

Determined Traceable Value >> 9.9496 mg/g ± 0.0230 mg/g





Results (with drift correction)

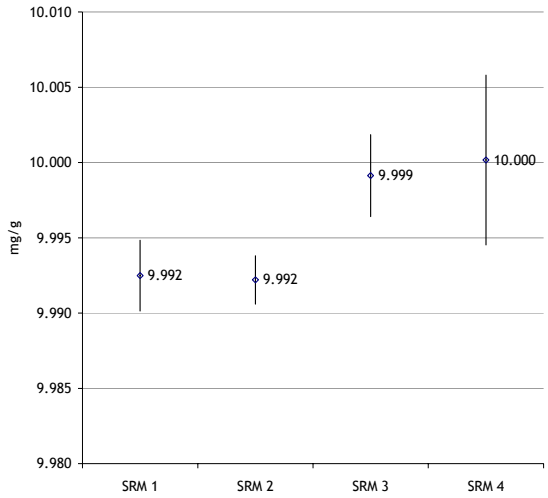
HP-ICP Comparison of Example (lot 1) to NIST SRM 3113 (lot 000630), 10/26/2001.

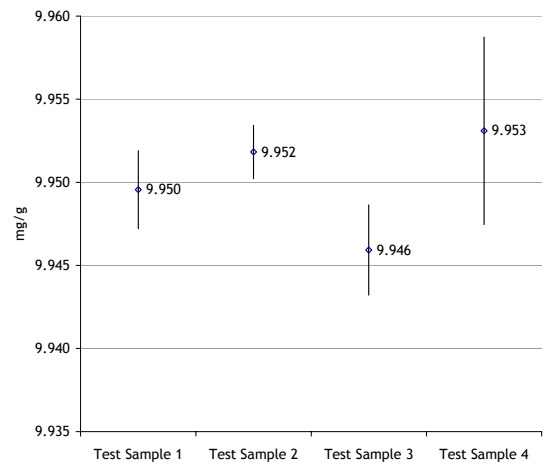
SRM 3113 Measurements	Average Signal Ratio	sd	rsd	Mass Ratio *(mg analyte/g IS)*	Slope of Calibration Curve *(signal ratio/mass*	Apparent Mass Fraction *mg/g*	sd *mg/g*
SRM 1	1.0207	0.0002	0.02%	1.2741	0.8011	9.992	0.002
SRM 2	1.0649	0.0002	0.02%	1.3293	0.8011	9.992	0.002
SRM 3	1.0843	0.0003	0.03%	1.3527	0.8016	9.999	0.003
SRM 4	0.9491	0.0005	0.06%	1.1838	0.8017	10.000	0.006
				Average slope	0.80136		
				sd of slope	0.00034		

Example Measurements	Average Signal Ratio	sd	rsd	Observed Mass Fraction *mg/g*	sd *mg/g*	Observed /Nominal
Test Sample 1	1.0362	0.0004	0.04%	9.950	0.004	99.98%
Test Sample 2	1.0377	0.0005	0.05%	9.952	0.005	100.00%
Test Sample 3	1.0934	0.0005	0.05%	9.946	0.005	99.94%
Test Sample 4	0.9052	0.0003	0.03%	9.953	0.003	100.01%
				Average mass fraction	9.950	
				sd of mass fraction	0.003	

Uncertainty Budget				
Source	(mg/g)	relative	df	coverage factor, *k*
SRM 3113 Measurements	0.002	0.02%	3	
Example Measurements	0.002	0.02%	3	
Certified Value of SRM 3113	0.010	0.10%	8	
Combined Uncertainty	0.010	0.10%	9.00	
Coverage Factor, k				2.26
Expanded Uncertainty	0.023	0.23%		

Determined Traceable Value >> 9.9501 mg/g ± 0.0232 mg/g





Uncertainty Budget (without drift correction)

Uncertainty Budget				
Source	(mg/g)	relative	df	coverage factor, *k*
SRM 3113 Measurements	0.001	0.01%	3	
Example Measurements	0.002	0.02%	3	
Certified Value of SRM 3113	0.010	0.10%	8	
Combined Uncertainty	0.010	0.10%	9	
Coverage Factor, k				2.26
Expanded Uncertainty	0.023	0.23%		

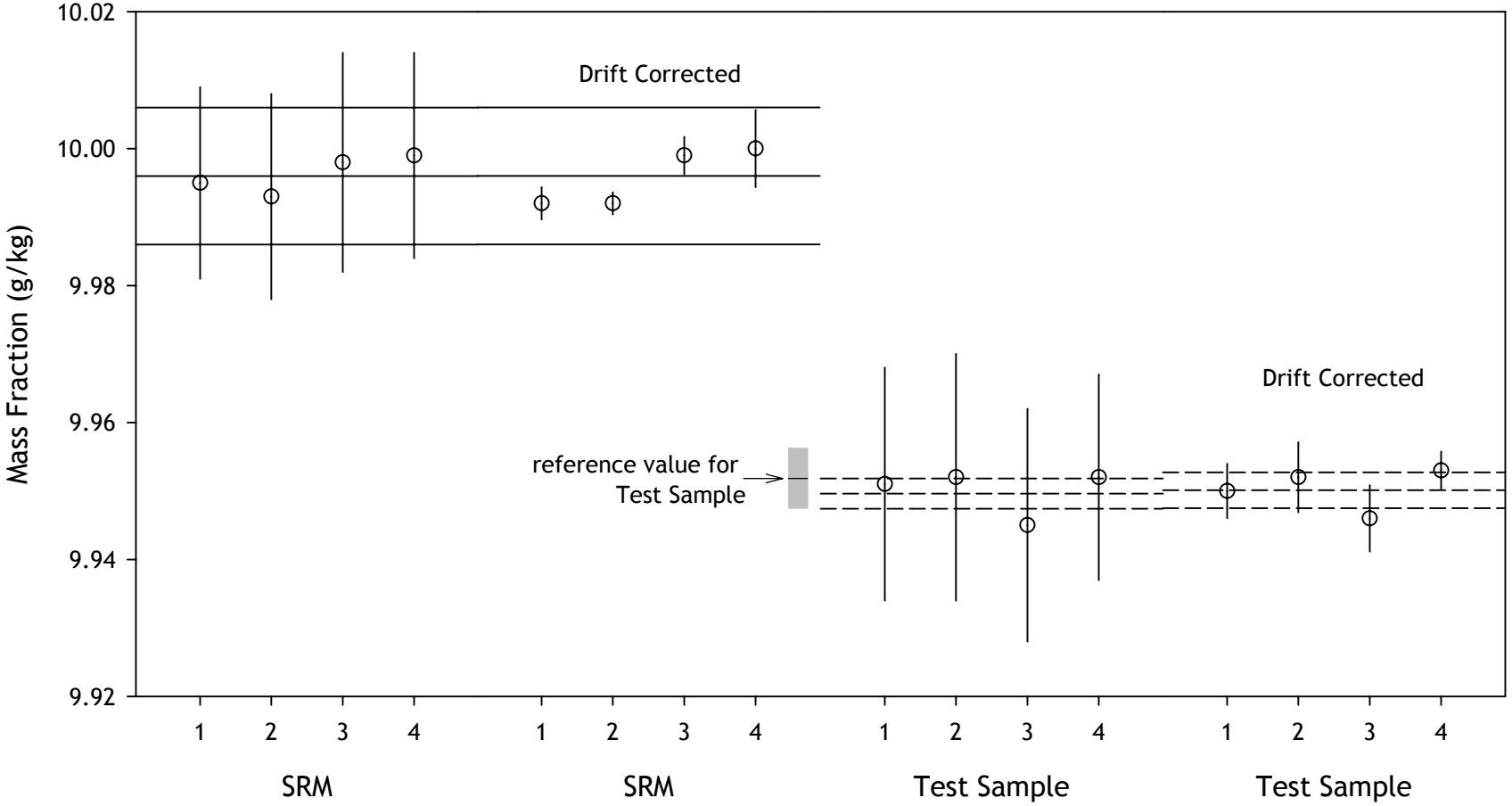
Determined Traceable Value >> 9.9496 mg/g ± 0.0230 mg/g

Uncertainty Budget (with drift correction)

Uncertainty Budget				
Source	(mg/g)	relative	df	coverage factor, *k*
SRM 3113 Measurements	0.002	0.02%	3	
Example Measurements	0.002	0.02%	3	
Certified Value of SRM 3113	0.010	0.10%	8	
Combined Uncertainty	0.010	0.10%	9.00	
Coverage Factor, k				2.26
Expanded Uncertainty	0.023	0.23%		

Determined Traceable Value >> 9.9501 mg/g ± 0.0232 mg/g

Summary of Results



The uncertainty of the traceable value is identical to the uncertainty of the SRM.

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 3113

Cobalt Standard Solution

Lot No. 000630

This Standard Reference Material (SRM) is intended for use as a primary calibration standard for the quantitative determination of cobalt. One unit of SRM 3113 consists of five 10 mL sealed borosilicate glass ampoules of an acidified aqueous solution prepared gravimetrically to contain a known mass fraction of cobalt. The solution contains nitric acid at a volume fraction of approximately 10 %.

Certified Value of Cobalt: 9.996 mg/g ± 0.023 mg/g

- SRM 3113: 9.996 ± 0.023 mg/g
- Test Solution: 9.950 ± 0.023 mg/g