

SRM 1877 Beryllium Oxide Powder: Certification of Be Mass Fraction

Michael R. Winchester, Gregory C. Turk, and Therese A. Butler
National Institute of Standards and Technology
Gaithersburg, MD 20899

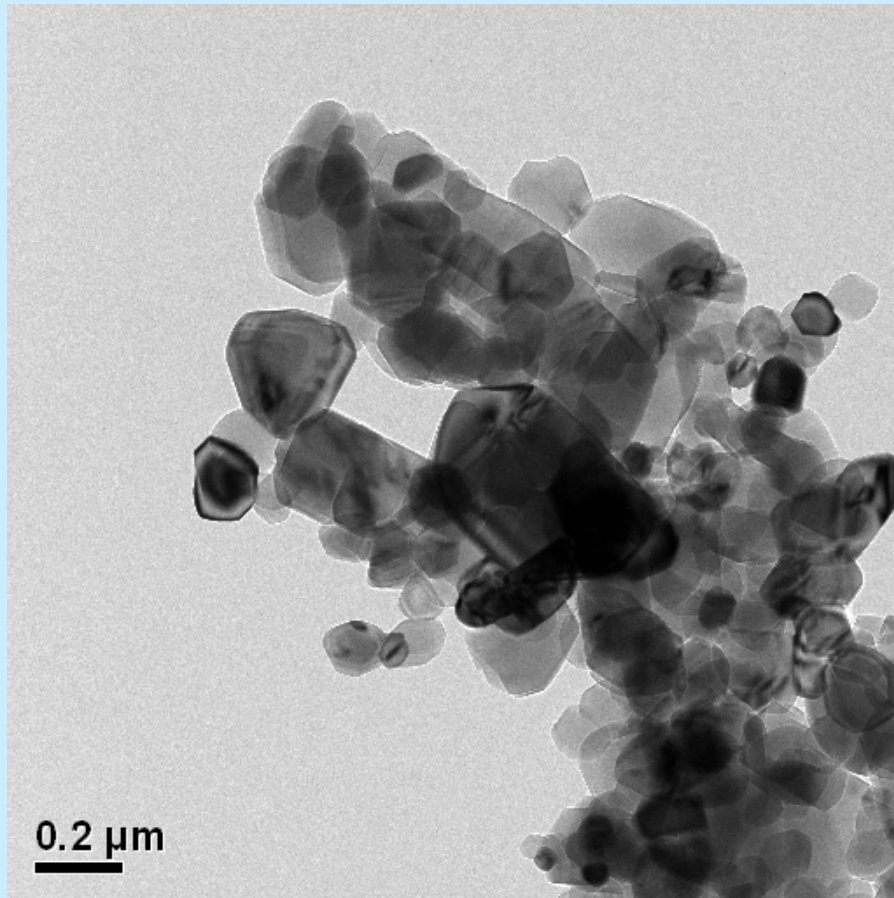
Thomas J. Oatts
Y-12 National Security Complex
Oak Ridge, TN

Charles Coleman
Savannah River Site
Aiken, SC

Dan Nadratowski and Ritu Sud
Bureau Veritas North America, Inc.
Novi, MI

Aleksandr B. Stefaniak and Mark D. Hoover
National Institute for Occupational Safety and Health
Morgantown, WV

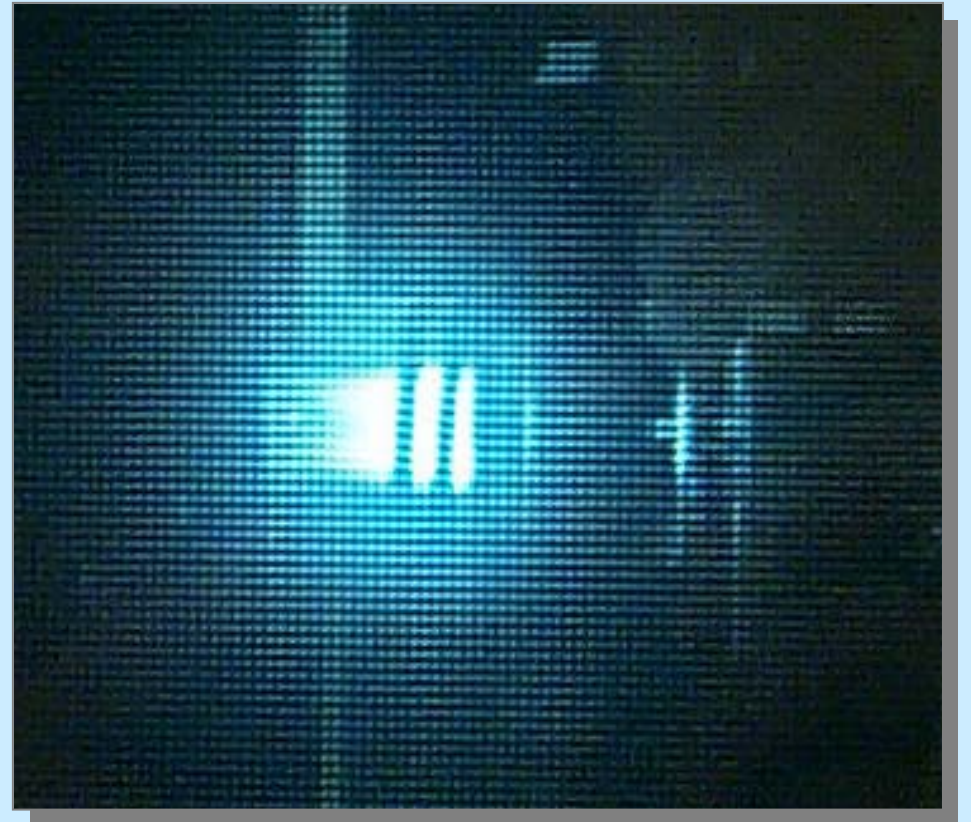
SRM 1877 Beryllium Oxide Powder



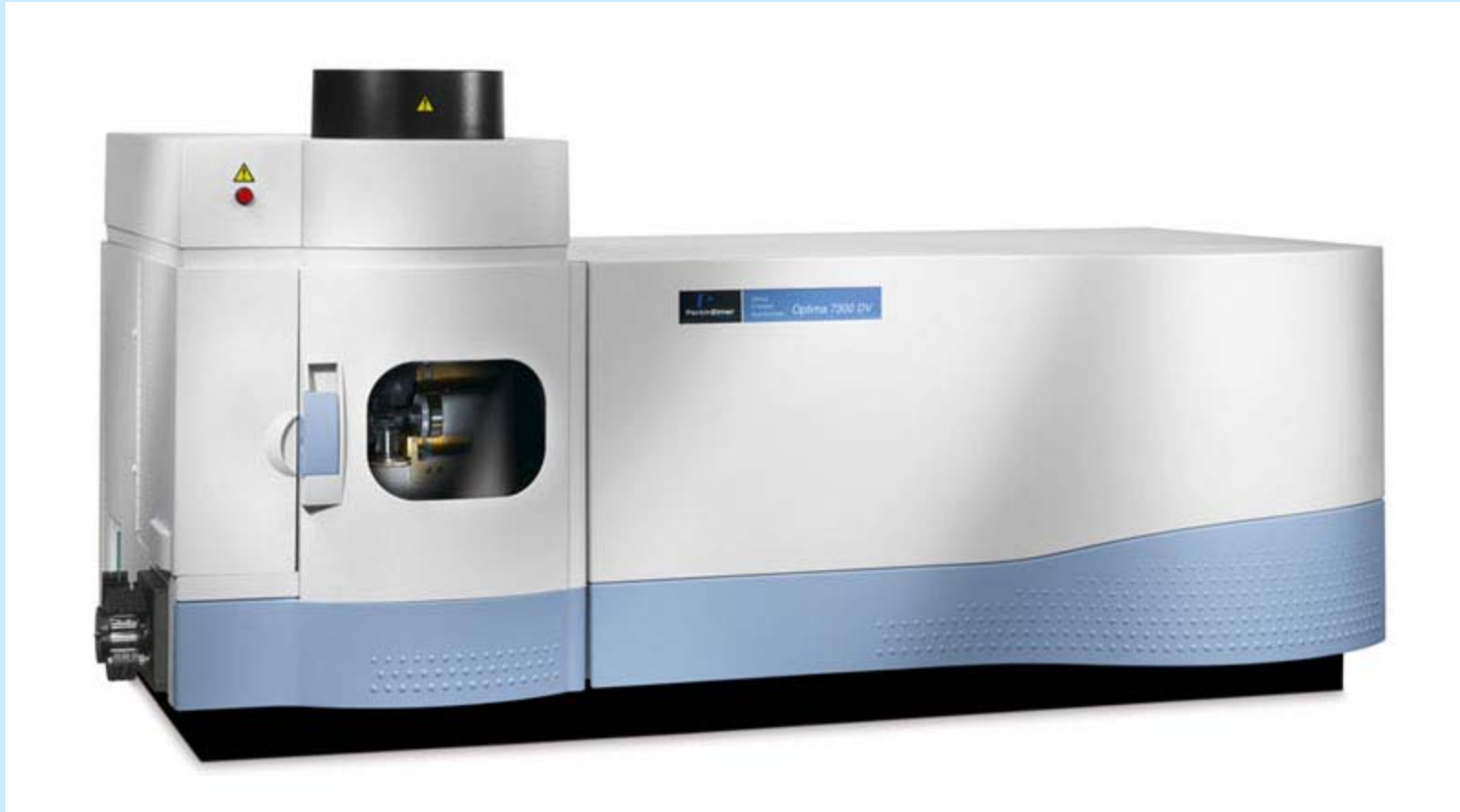
- Be mass fraction is certified at (0.3576 ± 0.0024) g/g
- Information values are given for:
 - Specific surface area
 - Specific gravity
 - Count median diameter (and geometric standard deviation)
 - Mass median diameter (and geometric standard deviation)

Inductively Coupled Plasma (ICP)

- Atmospheric pressure Ar plasma
 - 7000 K
- Atomic and ionic emission for optical spectroscopy
- Ionization source for mass spectrometry

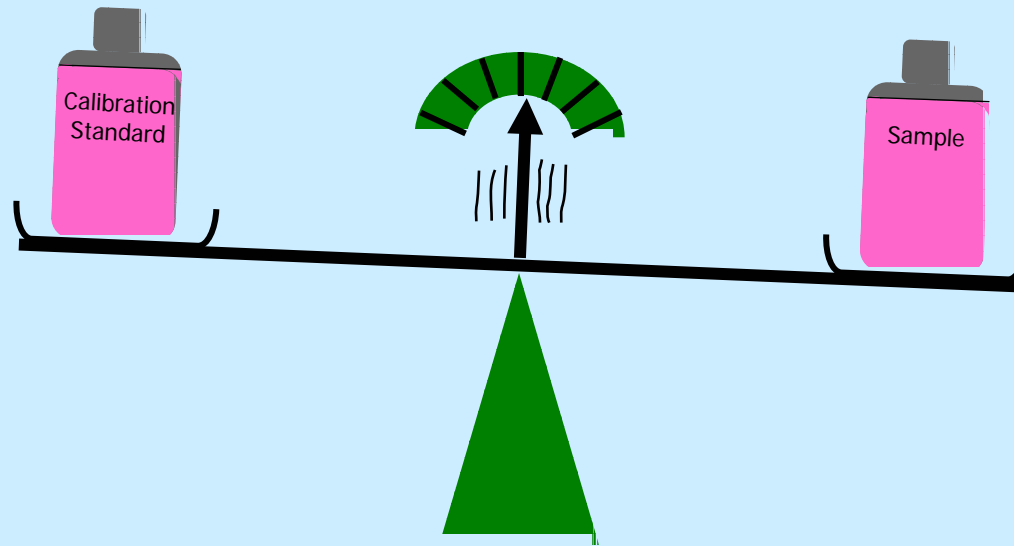


ICP Optical Emission Spectroscopy (ICP-OES)



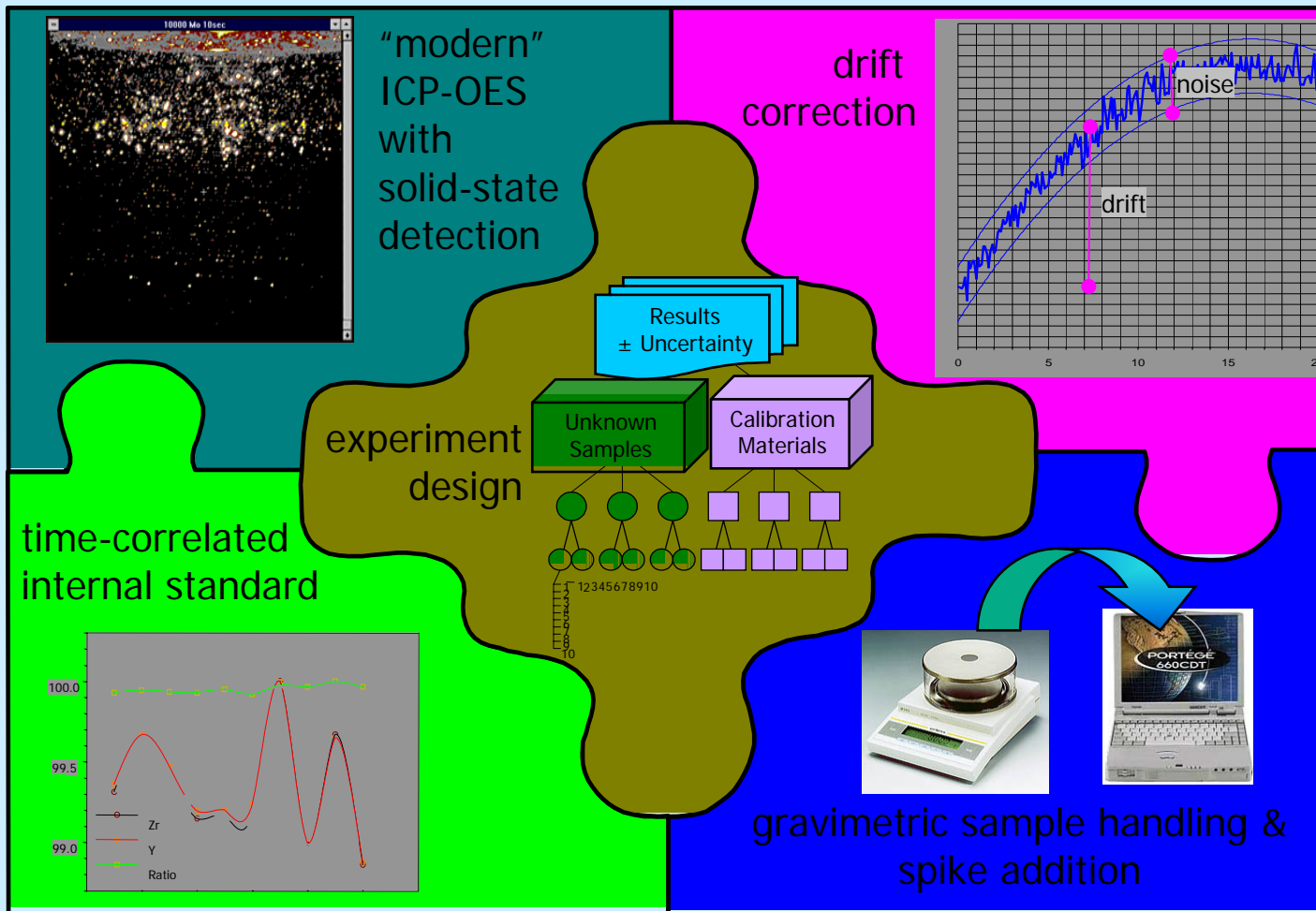
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High Performance (HP-) ICP-OES



A spectroscopic double-pan balance!

HP-ICP-OES: Several Measurement Strategies Under a Single Umbrella



HP-ICP-OES With Exact Matching

- Careful matching of the following parameters between sample solutions and calibration solutions:
 - Be:Mn (Mn is the internal standard) mass fraction ratios
 - Be mass fractions
 - Matrix compositions
- Improved accuracy and uncertainty over HP-ICP-OES without exact matching
- **Other research groups:**
 - Merson S, Evans P (2003) J Anal At Spectrom 18:372-375
 - Simpson LA, Hearn R, Merson S, Catterick T (2005) Talanta 65:900-906
 - Rabb SA, Olesik JW (2008) Spectrochim Acta B 63:244-256

Safety Obstacle and Solution

- NIST does not have infrastructure or experience to work with Be-containing powders safely
- **Solution:** Collaborating laboratories prepared sample digestions for subsequent analysis at NIST
 - *Bureau Veritas North America, Inc.*
 - *Savannah River Site*
 - *Y-12 National Security Complex (two sets)*

Establishing SI Traceability

- SI traceability is necessary for a certified value
- To establish SI traceability, each collaborating laboratory was provided:
 - Sample preparation kit
 - Interactive spreadsheet

Sample Preparation Kit

- Each kit comprised:
 - High-purity, NIST-assayed, Be metal pieces
 - Candidate SRM 1877 BeO powder
 - Internal standard (Mn) stock solution
 - 2 % nitric acid
 - Pre-cleaned bottles and shipping materials
 - Au test masses – assure SI traceability of balances

Interactive Spreadsheet

Label	g of BeO or Be		g of NIST-supplied Mn stock solution	
	Target	Actual	Target	Actual
Be #1	0.0724			
Be #2	0.0724			
Be #3	0.0724			
Be #4	0.0724			
BeO #140a	0.1998			
BeO #140b	0.1998			
BeO #482a	0.1998			
BeO #482b	0.1998			
BeO #765a	0.1998			
BeO #765b	0.1998			
BeO #1058a	0.1998			
BeO #1058b	0.1998			
Blank #1	0	0.0000		
Blank #2	0	0.0000		

Label	g of solution after transfer and addition of nitric acid	
	Target	Actual
Be #1 Digest Lab A	50	
Be #2 Digest Lab A	50	
Be #3 Digest Lab A	50	
Be #4 Digest Lab A	50	
BeO #140a Digest	50	
BeO #140b Digest	50	
BeO #482a Digest	50	
BeO #482b Digest	50	
BeO #765a Digest	50	
BeO #765b Digest	50	
BeO #1058a Digest	50	
BeO #1058b Digest	50	
Blank #1 Digest Lab A	50	
Blank #2 Digest Lab A	50	

Interactive Spreadsheet

Label	g of BeO or Be		g of NIST-supplied Mn stock solution		Label	g of solution after transfer and addition of nitric acid	
	Target	Actual	Target	Actual		Target	Actual
Be #1	0.0724	0.0735	6.2950	6.2982	Be #1 Digest Lab A	50	50.0100
Be #2	0.0724	0.0721	6.1751	6.1819	Be #2 Digest Lab A	50	49.9900
Be #3	0.0724	0.0685	5.8668	5.8671	Be #3 Digest Lab A	50	49.9900
Be #4	0.0724	0.0556	4.7619	4.7610	Be #4 Digest Lab A	50	50.0000
BeO #140a	0.1998	0.1999	6.2024	6.2204	BeO #140a Digest	50	49.9800
BeO #140b	0.1998	0.1998	6.1993	6.2035	BeO #140b Digest	50	50.0000
BeO #482a	0.1998	0.1999	6.2024	6.2182	BeO #482a Digest	50	50.0200
BeO #482b	0.1998	0.2000	6.2055	6.2070	BeO #482b Digest	50	50.0300
BeO #765a	0.1998	0.1999	6.2024	6.2102	BeO #765a Digest	50	50.0300
BeO #765b	0.1998	0.2000	6.2055	6.2250	BeO #765b Digest	50	50.0100
BeO #1058a	0.1998	0.1998	6.1993	6.2009	BeO #1058a Digest	50	49.9900
BeO #1058b	0.1998	0.1999	6.2024	6.2060	BeO #1058b Digest	50	50.0000
Blank #1	0	0.0000	6.0599	6.2001	Blank #1 Digest Lab A	50	50.0100
Blank #2	0	0.0000	6.0599	6.1989	Blank #2 Digest Lab A	50	50.0000

Digestion →

Interactive Spreadsheet

Label	g of BeO or Be		g of NIST-supplied Mn stock solution		Label	g of solution after transfer and addition of nitric acid		Label	g before dilution		g after dilution	
	Target	Actual	Target	Actual		Target	Actual		Target	Actual	Target	Actual
Be #1	0.0724	0.0735	6.3	6.2982	Be #1 Digest	50	50.0100	Be #1 Dil B	0.8			
Be #2	0.0724	0.0721	6.2	6.1819	Be #2 Digest	50	49.9900	Be #2 Dil B	0.8			
Be #3	0.0724	0.0685	5.9	5.8671	Be #3 Digest	50	49.9900	Be #3 Dil B	0.8			
Be #4	0.0724	0.0556	4.8	4.7610	Be #4 Digest	50	50.0000	Be #4 Dil B	0.8			
BeO #140a	0.1998	0.1999	6.2	6.2204	BeO #140a Digest	50	49.9800	BeO #140a Dil B	0.8			
BeO #140b	0.1998	0.1998	6.2	6.2035	BeO #140b Digest	50	50.0000	BeO #140b Dil B	0.8			
BeO #482a	0.1998	0.1999	6.2	6.2182	BeO #482a Digest	50	50.0200	BeO #482a Dil B	0.8			
BeO #482b	0.1998	0.2000	6.2	6.2070	BeO #482b Digest	50	50.0300	BeO #482b Dil B	0.8			
BeO #765a	0.1998	0.1999	6.2	6.2102	BeO #765a Digest	50	50.0300	BeO #765a Dil B	0.8			
BeO #765b	0.1998	0.2000	6.2	6.2250	BeO #765b Digest	50	50.0100	BeO #765b Dil B	0.8			
BeO #1058a	0.1998	0.1998	6.2	6.2009	BeO #1058a Digest	50	49.9900	BeO #1058a Dil B	0.8			
BeO #1058b	0.1998	0.1999	6.2	6.2060	BeO #1058b Digest	50	50.0000	BeO #1058b Dil B	0.8			
Blank #1	0	0.0000	6.1	6.2001	Blank #1 Digest	50	50.0100	Blank #1 Dil B	0.8			
Blank #2	0	0.0000	6.1	6.1989	Blank #2 Digest	50	50.0000	Blank #2 Dil B	0.8			

Digestion To NIST

Interactive Spreadsheet

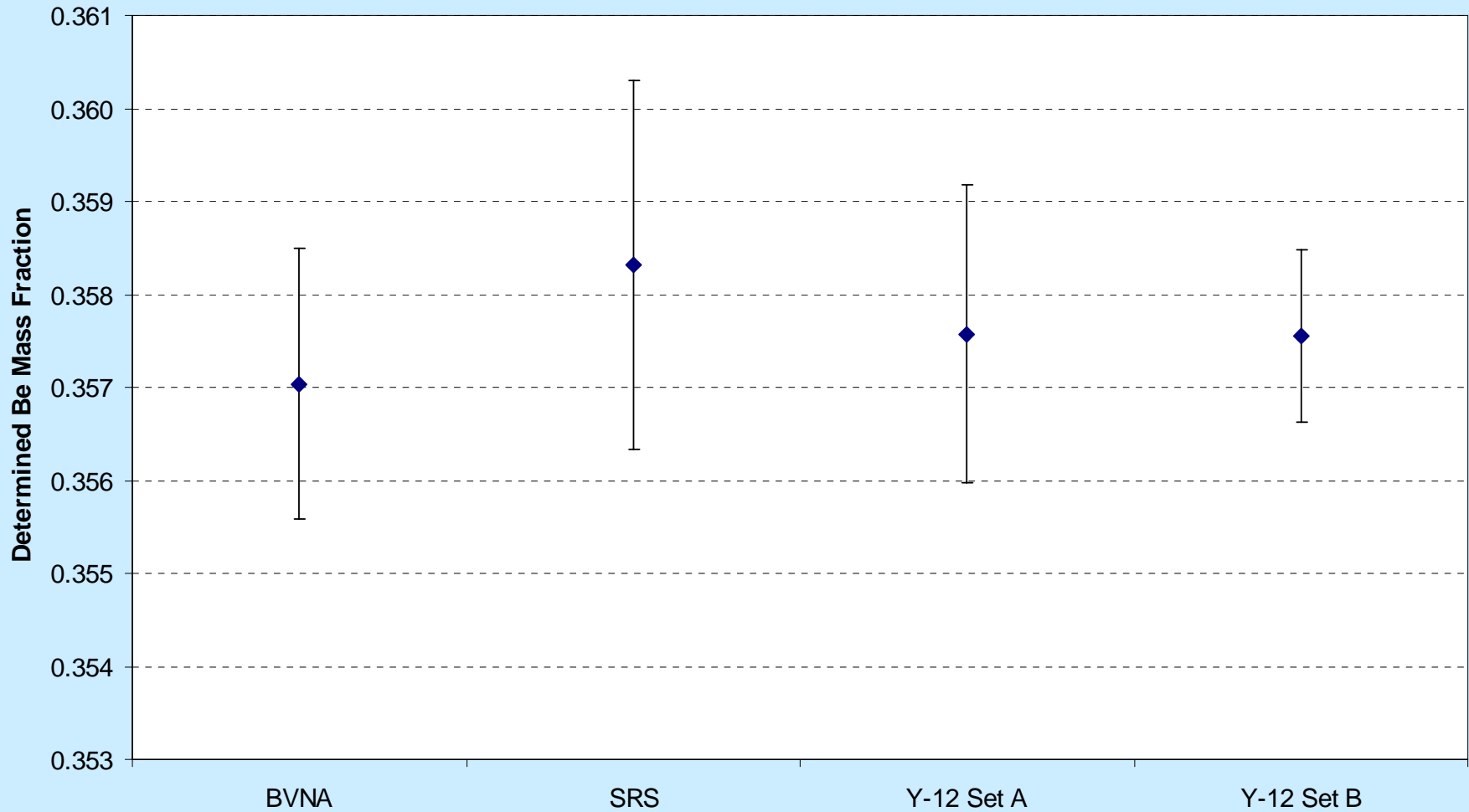
Label	g of BeO or Be		g of NIST-supplied Mn stock solution		Label	g of solution after transfer and addition of nitric acid		Label	g before dilution		g after dilution	
	Target	Actual	Target	Actual		Target	Actual		Target	Actual	Target	Actual
Be #1	0.0724	0.0735	6.3	6.2982	Be #1 Digest	50	50.0100	Be #1 Dil B	0.8	0.8016	53.2616	53.2603
Be #2	0.0724	0.0721	6.2	6.1819	Be #2 Digest	50	49.9900	Be #2 Dil B	0.8	0.8011	52.2354	52.2352
Be #3	0.0724	0.0685	5.9	5.8671	Be #3 Digest	50	49.9900	Be #3 Dil B	0.8	0.8024	49.7078	49.7091
Be #4	0.0724	0.0556	4.8	4.7610	Be #4 Digest	50	50.0000	Be #4 Dil B	0.8	0.7991	40.1728	40.1746
BeO #140a	0.1998	0.1999	6.2	6.2204	BeO #140a Digest	50	49.9800	BeO #140a Dil B	0.8	0.8022	52.5493	52.5464
BeO #140b	0.1998	0.1998	6.2	6.2035	BeO #140b Digest	50	50.0000	BeO #140b Dil B	0.8	0.8016	52.4627	52.4673
BeO #482a	0.1998	0.1999	6.2	6.2182	BeO #482a Digest	50	50.0200	BeO #482a Dil B	0.8	0.8020	52.4942	52.4924
BeO #482b	0.1998	0.2000	6.2	6.2070	BeO #482b Digest	50	50.0300	BeO #482b Dil B	0.8	0.8016	52.4837	52.4845
BeO #765a	0.1998	0.1999	6.2	6.2102	BeO #765a Digest	50	50.0300	BeO #765a Dil B	0.8	0.7997	52.3331	52.3299
BeO #765b	0.1998	0.2000	6.2	6.2250	BeO #765b Digest	50	50.0100	BeO #765b Dil B	0.8	0.8011	52.4720	52.4729
BeO #1058a	0.1998	0.1998	6.2	6.2009	BeO #1058a Digest	50	49.9900	BeO #1058a Dil B	0.8	0.8012	52.4470	52.4458
BeO #1058b	0.1998	0.1999	6.2	6.2060	BeO #1058b Digest	50	50.0000	BeO #1058b Dil B	0.8	0.8037	52.6265	52.6471
Blank #1	0	0.0000	6.1	6.2001	Blank #1 Digest	50	50.0100	Blank #1 Dil B	0.8	0.8005	51.2705	51.2708
Blank #2	0	0.0000	6.1	6.1989	Blank #2 Digest	50	50.0000	Blank #2 Dil B	0.8	0.8007	51.2705	51.2708

Digestion To NIST

Digestion Protocols

- Bureau Veritas North America
 - $(\text{NH}_4)_2\text{SO}_4 / \text{H}_2\text{SO}_4$ for both Be and BeO
- Savannah River Site
 - HCl for Be
 - $(\text{NH}_4)_2\text{SO}_4 / \text{H}_2\text{SO}_4$ for BeO
- Y-12 (Set #1)
 - $\text{HNO}_3 / \text{H}_2\text{SO}_4$ for both Be and BeO
- Y-12 (Set #2)
 - NH_4HF_2 for both Be and BeO

High-Performance ICP-OES Results Summary



Analytical Equation

Individual Be mass fraction values

Moisture component of uncertainty
(set to zero with uncertainty)

Certified Be mass fraction

Bias among ICP-OES values
(set to zero with uncertainty)

Uncertainty in Be assay
(set to zero with uncertainty)

$$[Be]_{Certified} = \frac{\sum_{i=1}^4 [Be]_i}{4} + B + M + A$$

The diagram illustrates the analytical equation for the certified Be mass fraction. The equation is $[Be]_{Certified} = \frac{\sum_{i=1}^4 [Be]_i}{4} + B + M + A$. Arrows point from descriptive text to the corresponding terms in the equation: 'Individual Be mass fraction values' points to the summation term; 'Moisture component of uncertainty (set to zero with uncertainty)' points to the 'M' term; 'Certified Be mass fraction' points to the left side of the equation; 'Bias among ICP-OES values (set to zero with uncertainty)' points to the 'B' term; and 'Uncertainty in Be assay (set to zero with uncertainty)' points to the 'A' term.

Calculation of Certified Be Mass Fraction Value and Expanded Uncertainty

BVNA

$[Be]_i$	0.35704
u	0.00064
% u	0.18
Degrees of Freedom	8.6

SRS

$[Be]_i$	0.35832
u	0.00086
% u	0.24
Degrees of Freedom	8.5

Y-12 #1

$[Be]_i$	0.35757
u	0.00073
% u	0.20
Degrees of Freedom	10.8

Y-12 #2

$[Be]_i$	0.35755
u	0.00045
% u	0.13
Degrees of Freedom	22.0

Average, $[Be]$	0.35762
u	0.00026
% u	0.074
Degrees of Freedom	3

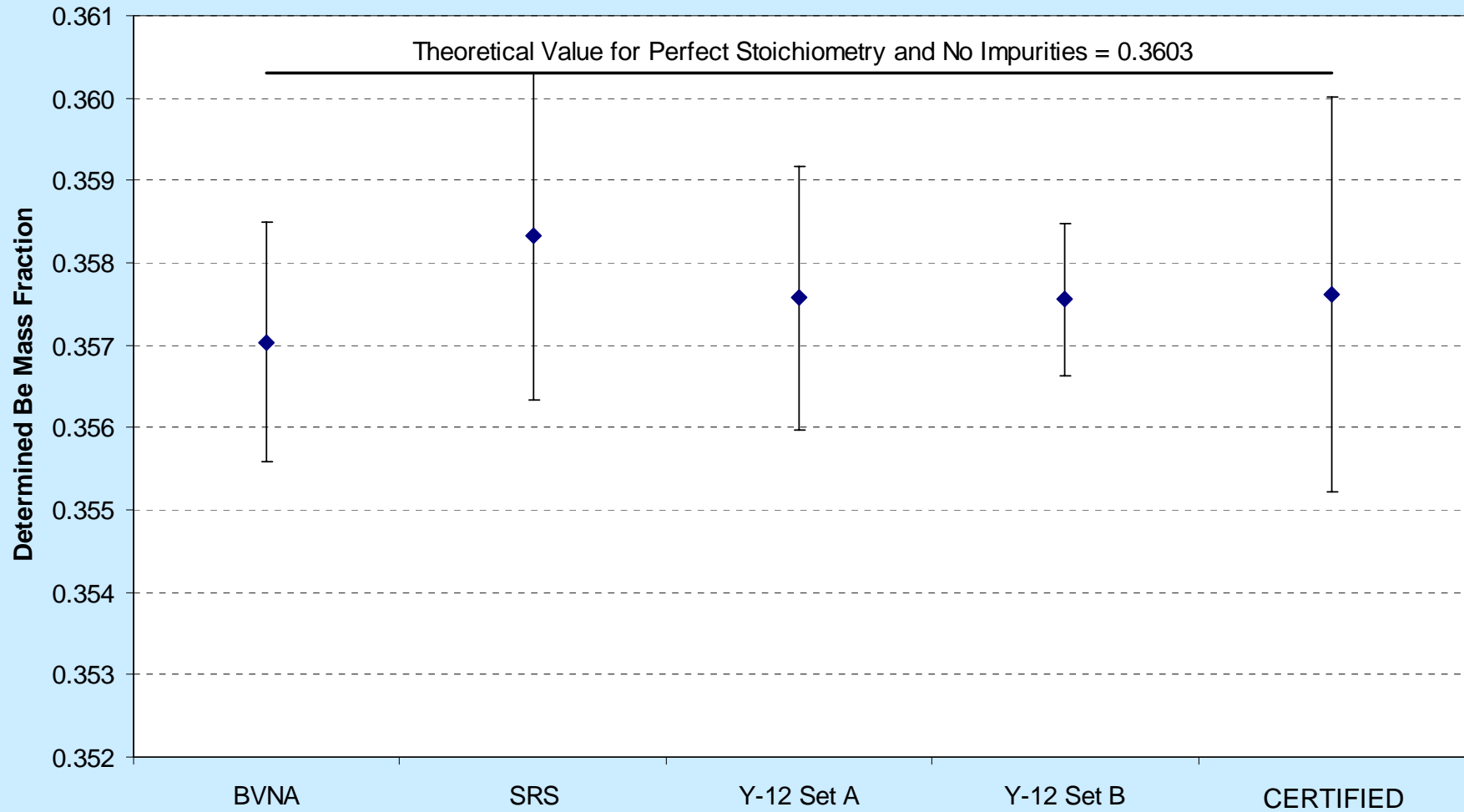
B	0
u_B	0.00037
% u_B	0.10
Degrees of Freedom	3

M	0
u_M	0.0011
% u_M	0.31
Degrees of Freedom	∞

A	0
u_A	0.00022
% u_A	0.060
Degrees of Freedom	6.1

Certified Value, $[Be]_{Certified}$	0.3576
Combined Standard Uncertainty, u_c	0.0012
Degrees of Freedom	256
k (95 % confidence)	1.97
Expanded Uncertainty, U (95 % confidence)	0.0024

Final Results Plotted





National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 1877

Beryllium Oxide Powder

This Standard Reference Material (SRM) is intended for use in laboratory analysis and health research for the development and validation of analytical methods and instruments used to determine beryllium, as well as for proficiency testing of laboratories involved in beryllium determinations [1, 2]. One unit of SRM 1877 consists of 20 g of beryllium oxide powder.

Certified Value of Beryllium Mass Fraction: $0.3576 \text{ g/g} \pm 0.0024 \text{ g/g}$

The certified value is based on inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of four sets of independently prepared samples. Each set was digested using a different digestion protocol. The ICP-OES instrument was calibrated with primary standards prepared gravimetrically from assayed, high-purity, beryllium metal.

The uncertainty in the certified value is calculated as

$$U = ku_c$$

where $k = 1.99$ is the coverage factor for a 95 % confidence interval, and u_c is the combined standard uncertainty calculated according to the ISO and NIST Guides [3]. The value of u_c is intended to represent, at the level of one standard deviation, the combined effects of the uncertainty components associated with the ICP-OES results, possible bias among those results [4], and the uncertainty due to possible changes in moisture content during storage due to changing environmental conditions (see "Instructions for Use").

Expiration of Certification: The certification of **SRM 1877** is valid, within the measurement uncertainty specified, until **15 March 2023**, provided the SRM is handled in accordance with instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is damaged, contaminated, or modified.

Appreciation

- **Sponsor:** United States National Nuclear Security Administration
- **People:**
 - L.D. Welch (Y-12)
 - D.J. Weitzman (DOE)
 - S.D. Johnson (NNSA)
 - D. Sbarra, M. Duling, and G.A. Day (NIOSH)
 - T. Civic and K. Kampfer (Brush Wellman, Inc.)
 - R.M. Dickerson (LANL)
 - M.P. Cronise and S.D. Leigh (NIST)
 - **AND MANY MORE**

Results of Matrix Matching for the Savannah River Solution Set

Solution Type	H₂SO₄ (v/v)	(NH₄)₂SO₄ (m/m)	HNO₃ (v/v)	HCl (v/v)
Calibration	2.0 %	---	0.0019 %	0.016 %
SRM 1877	2.0 %	0.0015 %	0.0024 %	---
Control	2.0 %	---	0.0039 %	---

NOTE: All solutions were diluted as much as possible while retaining sufficiently strong Be and Mn emission intensities

Evaluation of Moisture Behavior

- Samples of BeO powder repeatedly dried to constant mass and allowed to regain moisture at ambient, recorded, laboratory conditions
- Observed relative mass gain/loss $< 0.35\%$
- Component of uncertainty modeled as triangular probability distribution centered at zero with limits of $\pm 0.75\%$ of the determined Be mass fraction

Exactly Matched Solutions

- The average RSDs across the four sets of solutions were:
 - 1 % for the Be:Mn mass fraction ratios
 - 0.006 % for the Be mass fractions
- Matrices matched through the dilutions