Interlaboratory Evaluation of a Standardized ICP-MS Method for the Determination of Trace Beryllium in Air Filter Samples

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Objective:

- Generate supporting interlaboratory round-robin data for ASTM D7439, *Standard Test Method for Determination of Elements in Airborne Particulate Matter by Inductively Coupled Plasma Mass Spectrometry*

Designation: D 7439 – 08

Standard Test Method for Determination of Elements in Airborne Particulate Matter by Inductively Coupled Plasma–Mass Spectrometry[1]

This standard is issued under the fixed designation D 7439; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This standard test method specifies a procedure for sample preparation and analysis of airborne particulate matter for the content of metals and metalloids in workplace air samples using inductively coupled plasma–mass spectrometry (ICP-MS).

1.2 This standard test method assumes that samples will have been collected in accordance with Test Method D 7035.

1.3 This standard test method should be used by analysts experienced in the use of ICP-MS, the interpretation of spectral and matrix interferences and procedures for their correction.

1.4 This standard test method specifies a number of alternative methods for preparing test solutions from samples of airborne particulate matter. One of the specified sample preparation methods is applicable to the measurement of soluble metal or metalloid compounds. Other specified methods are applicable to the measurement of total metals and metalloids.

1.5 It is the user's responsibility to ensure the validity of the standard method for filters of untested matrices.

1.6 Table 1 provides a non-exclusive list of metals and metalloids for which one or more of the sample dissolution methods specified in this document is applicable.

1.7 This standard test method is not applicable to compounds of metals and metalloids that are present in the gaseous or vapor state.

1.8 No detailed operating instructions are provided because of differences among various makes and models of suitable ICP-MS instruments. Instead, the analyst shall follow the instructions provided by the manufacturer of the particular instrument. This test method does not address comparative accuracy of different devices or the precision between instruments of the same make and model.

1.9 The values stated in SI units are to be regarded as standard.

1.10 This standard test method contains notes that are explanatory and are not part of the mandatory requirements of the method.

1.11 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D 1193 Specification for Reagent Water

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres

D 4185 Practice for Measurement of Metals in Workplace Atmospheres by Flame Atomic Absorption Spectrophotometry

D 6785 Test Method for Determination of Lead in Workplace Air Using Flame or Graphite Furnace Atomic Absorption Spectrometry

D 7035 Test Method for Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D 7202 Test Method for Determination of Beryllium in the Workplace Using Field-Based Extraction and Fluorescence Detection

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E 1613 Test Method for Determination of Lead by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Flame Atomic Absorption Spectrometry (FAAS), or Graphite Furnace Atomic Absorption Spectrometry (GFAAS) Techniques

2.2 *ISO and European Standards:*

ISO 1042 Laboratory Glassware—One-Mark Volumetric Flasks[3]

ISO 3585 Borosilicate Glass 3.3—Properties[3]

ISO 8655 Piston-Operated Volumetric Apparatus (6 parts)[3]

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.
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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

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Interlaboratory Study (ILS)

- 21 elements on MCE filters
- 3 different loading levels, plus media blanks
- 3 filters @ each level + blanks = 12 per laboratory
- 20 participating laboratories from North America (12), Europe (7) & Asia (1)

➡ Beryllium results presented here

Beryllium ILS (ICP-MS)

- Spikes @ 0.025, 0.50 & 10 µg Be/filter (as beryllium sulfate)
- Labs requested to follow ASTM D7439 method: Acid digestion (hotplate / microwave / hotblock) & ICP-MS analysis
- Precision statistics: ASTM E691
- Uncertainty estimations: ASTM D7440

Precision Statistics* (ASTM E691)

Spike level (µg)	Mean (µg)	Std. dev. (µg)	RSD (%)	% Rec.
0.025	0.0233 (n=13)	0.0038	16.5	93.2
0.50	0.509 (n=19)	0.0550	10.8	102
10	8.06 (n=20)	1.22	15.1	80.6

*[Media blank corrected (n=6); Avg. blank = 0.009 µg]

Repeatability & Reproducibility (ASTM E691)

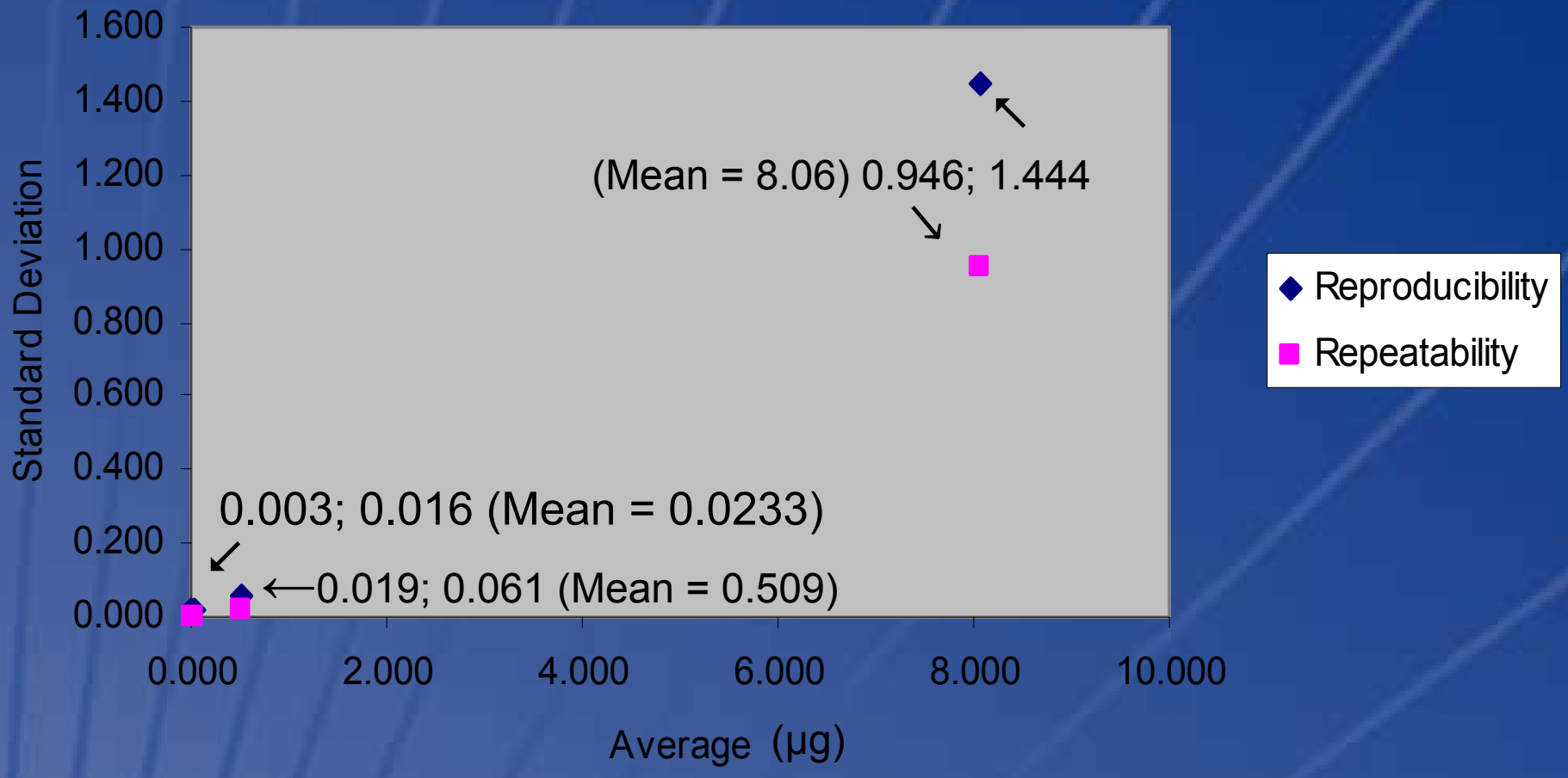
Repeatability: Ability of a single analyst to repeatedly obtain a result using same equipment and test specimen.

- ☞ Estimated by within-lab variance

Reproducibility: Ability of different analysts and/or different equipment to get same result.

- ☞ Estimated by between-lab variance

Standard Deviations of Reproducibility (o) and Repeatability (•) Versus Average (ASTM E691)



Uncertainty Budget* (ASTM D7440)

Concept:

Estimate contribution to uncertainty of each component of the overall measurement.

Examples:

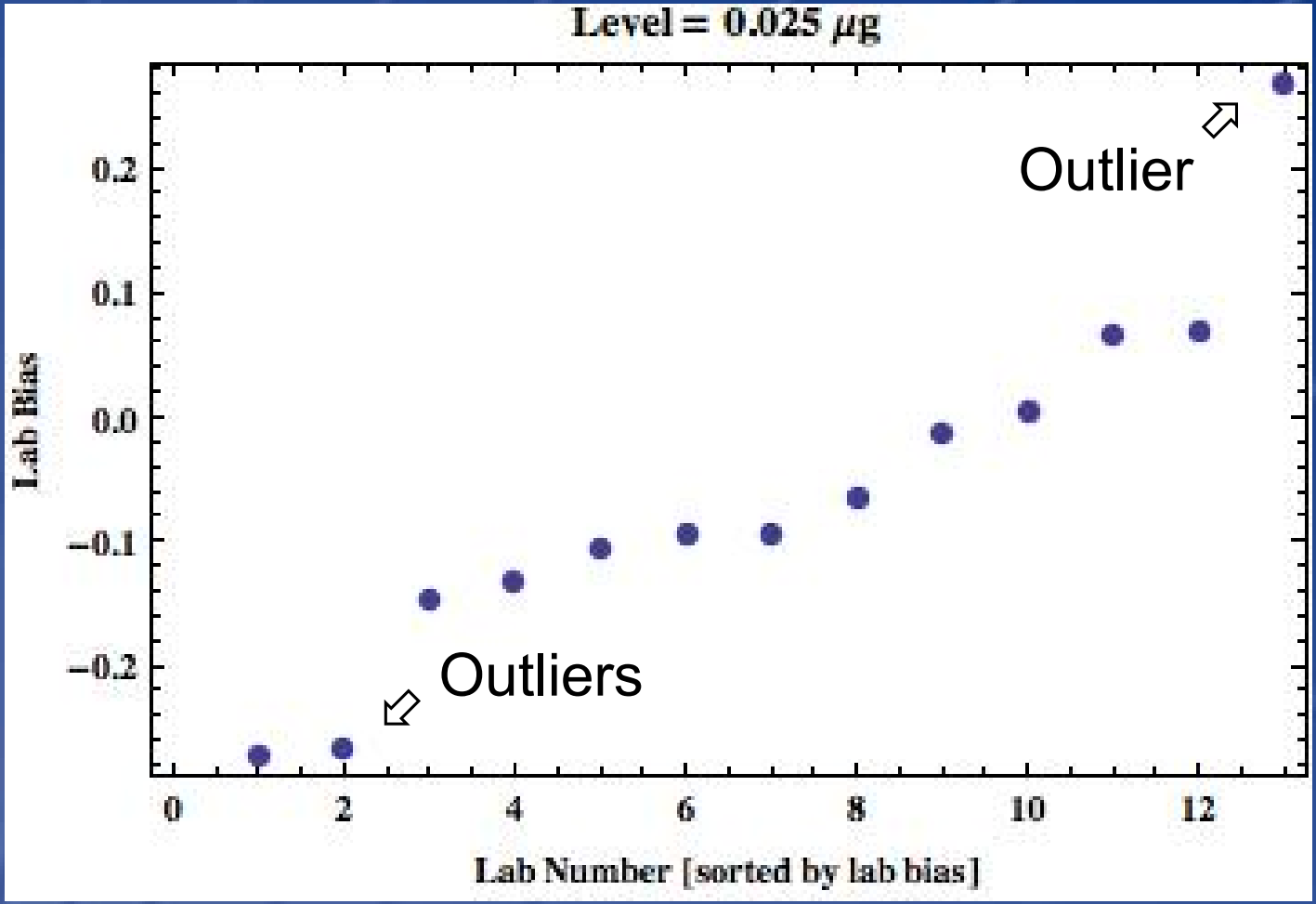
Intra-lab & Inter-lab variance

Measurement equipment tolerances

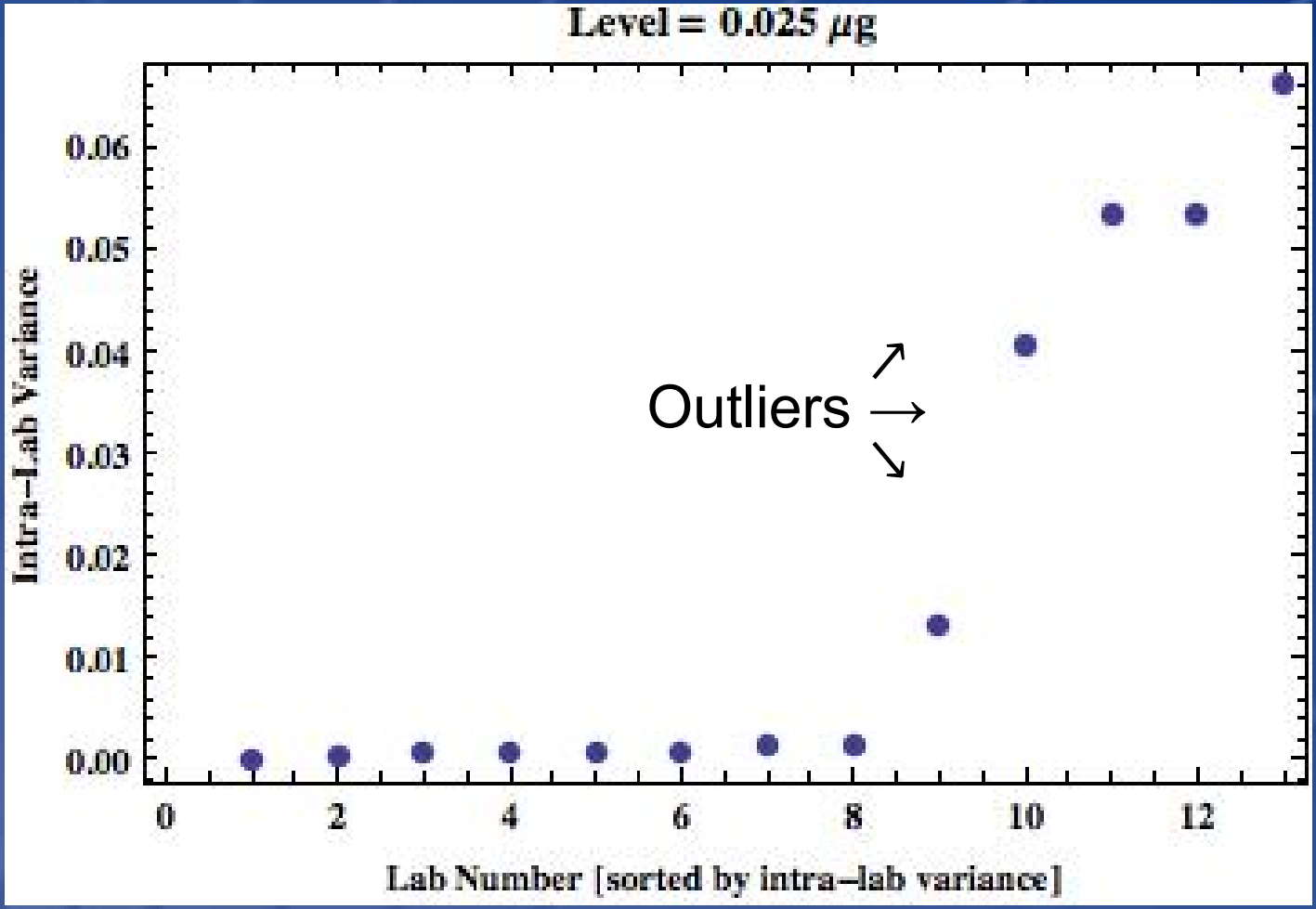
Measurement bias

*[from ISO GUM]

Blank-corrected lab bias estimates (low Be level)



Within-lab variance (low Be level)



Uncertainty budget at 0.025 µg Be

Uncertainty source	Uncertainty component	Degrees of freedom	Error type
Inter-lab	0.083	6	A
Intra-lab	0.029	14	A
Bias estimate	0.032	–	A
Pipette bias*	0.008 (negl.)	–	B

*(EN ISO 8655-2)

Estimated bias & correction factor at 0.025 µg Be

- Estimated Bias $\Delta = (1/L) \cdot \sum_{\ell=1}^{L} \Delta_\ell = -7.1\%$
- Correction Factor = $1/(1 + \Delta) = 1.08$
- Bias 95% Confidence Limits: (-0.14, 0.00)

Uncertainty at 0.025 µg Be

- Combined Uncertainty* = 9.4%

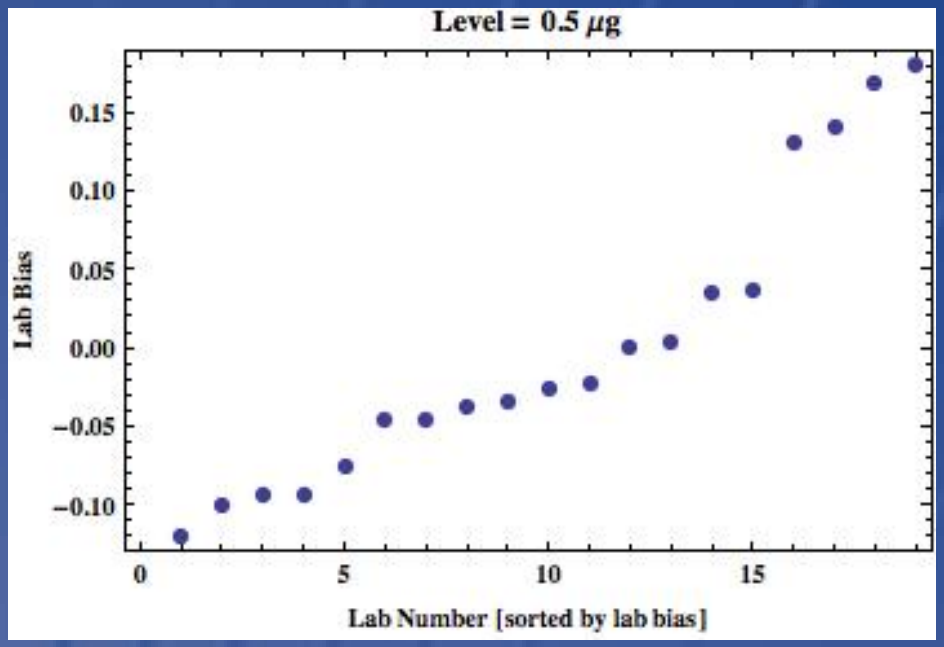
  *[$U_c = \sum_i (U_i^2)^{1/2}$]

⇨ **Expanded Uncertainty‡ = 18.8 %**

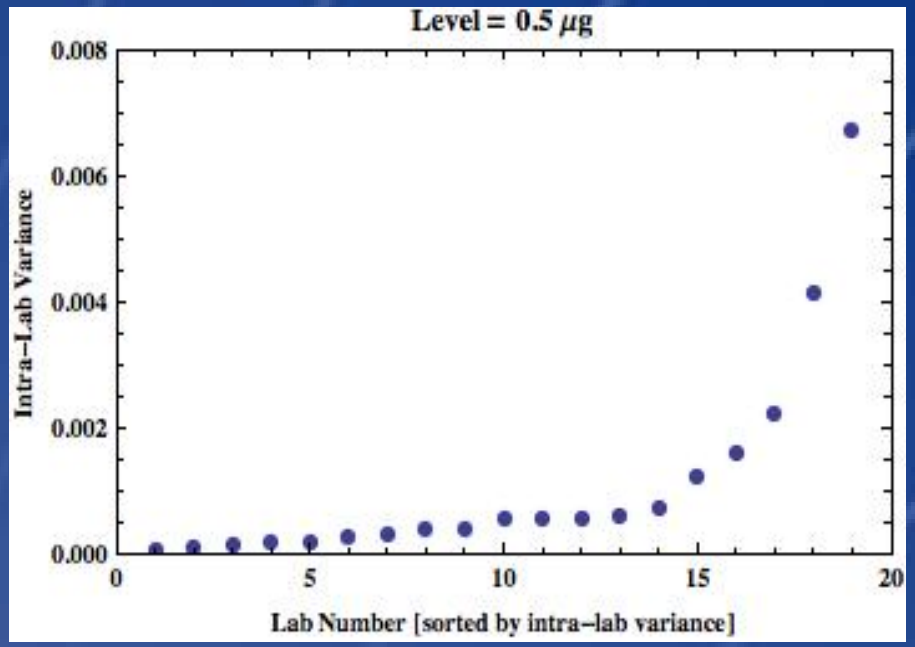
at coverage factor $k = 2$

‡[$U = k \cdot U_c$]

Medium Be spike level (0.50 µg)

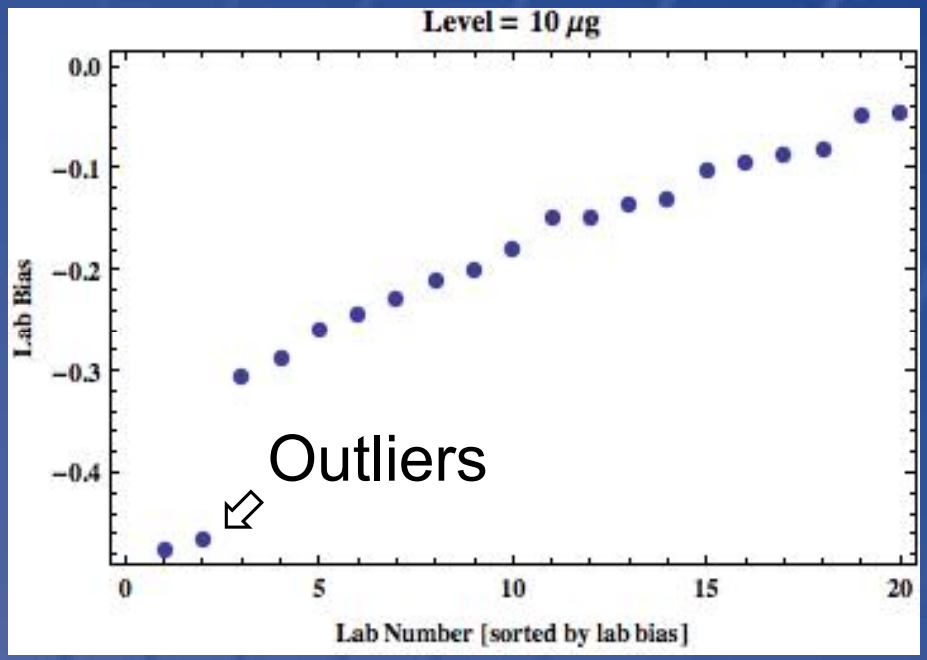


Lab Bias

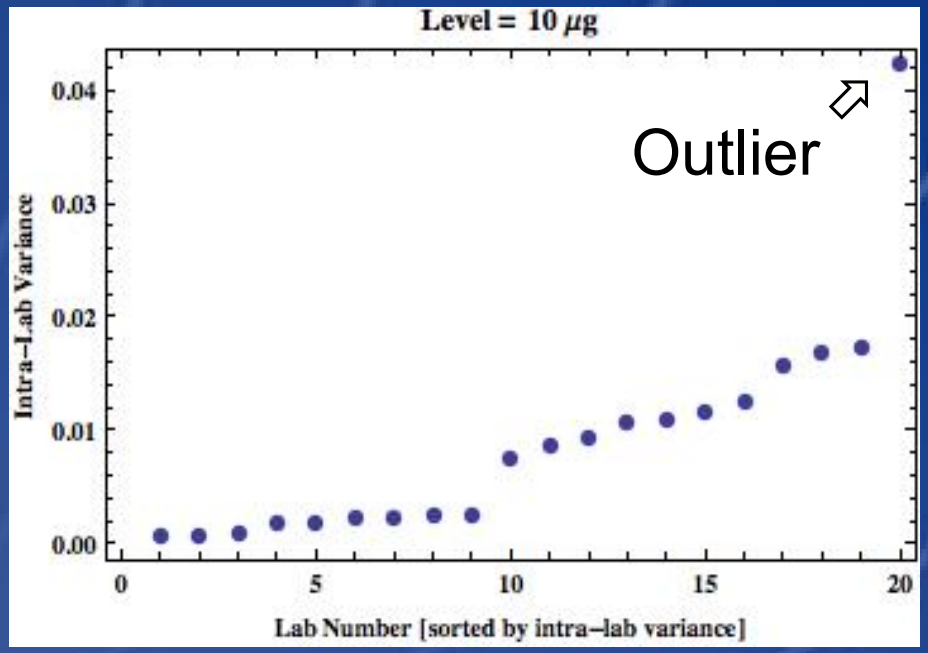


Within-Lab Variance

High Be spike level (10 µg)



Lab Bias



Within-Lab Variance

Expanded Uncertainty at 0.50 & 10 µg

@ 0.50 µg:

Δ = 0.0%; 95% CLs: (-0.04, 0.04)
Correction factor = 1.00
Combined Uncertainty = 9.9%
Expanded Uncertainty = 19.8% (k = 2)

@ 10 µg:

Δ = -15.5%; 95% CLs: (-0.19, -0.12)
Correction factor = 1.18
Combined Uncertainty = 12.2%
Expanded Uncertainty = 24.4% (k = 2)

Considerations

- ICP-MS estimated method detection limit (MDL): ≈0.001 µg Be per sample
  - ☞ However, many labs reported [<] values @ much higher Be levels for low spikes
- A few labs reported significant Be blank values
- Several labs noted loss of material from filters at high Be loading upon receipt

Accuracy / Uncertainty Estimates and Applicable Guidelines

- *NIOSH Accuracy Criterion*:

  25% (95% CL)

- *EN 482 Uncertainty Requirements*:

  30%: "definitive" analysis

  50%: "screening" measurements

Summary & future work

- Analytical figures of merit satisfy applicable uncertainty requirements
- ILS data support ASTM D7439
- Parallel ISO draft being developed (CD 30011)
- Further work on other elements
- Generation of realistic aerosols (e.g., welding fumes)

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High-Purity Standards

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BHSC