ELEMENTAL ANALYSIS OF GLASS EXAMINATIONS (PART 1)
Module 4

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Outline

- Solution Analysis
- Ruggedness Studies
- Standard Method for Solution Analysis
- Round Robin Study Results

Analytical Techniques for Elemental Analysis (solution based)

FAAS - Flame Atomic Absorption Spectrometry
GFAAS - Graphite Furnace Atomic Absorption Spectrometry
ICP-OES - Inductively Coupled Plasma Optical Emission Spectrometry = Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
ICP-MS - Inductively Coupled Plasma Mass Spectrometry

Inductively Coupled Plasma Mass Spectrometry

- **Plasma is electrical discharge, not chemical flame**
  - ➔ Ar gas used
  - ➔ plasma at atmospheric pressure -> very high temperature
    - ➔ (a low pressure plasma is a fluorescent lamp)
  - ➔ plasma is generated through inductive coupling of free electrons with rapidly oscillating magnetic field (27 MHz)
  - ➔ Energy is transferred collisionally to argon molecules
  - ➔ plasma is contained in gas flow in a quartz tube (torch)
  - ➔ sample aerosol is carried through the center of the plasma
  - ➔ proximity to 10,000 C plasma causes dissociation, atomization and ionization
  - ➔ ions are extracted into the spectrometer

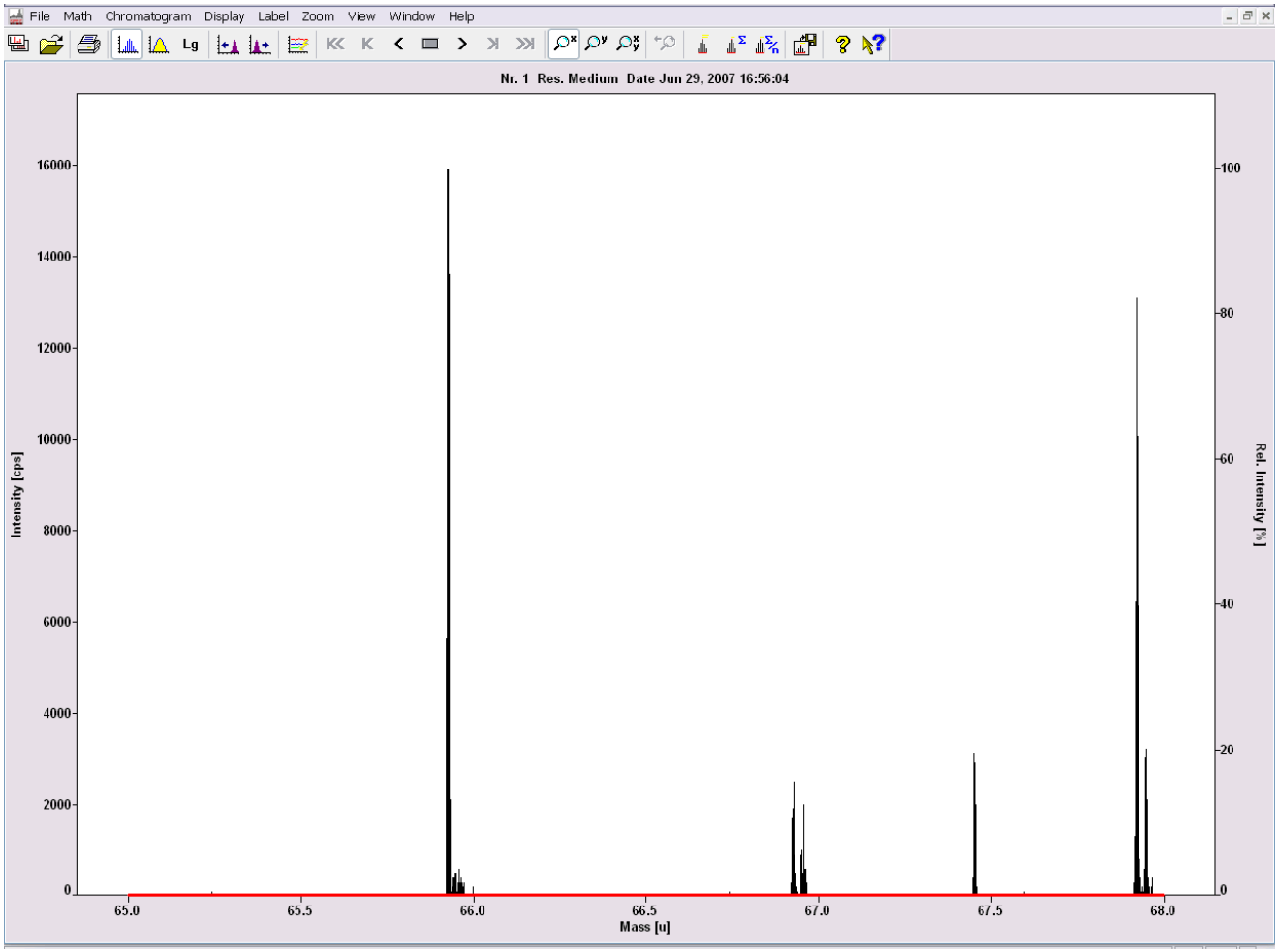
Why Argon?

- Ar is inert
- Ar is relatively inexpensive!
- Ar is easily obtained at very high purity

Most importantly -

- Ar has a 1st ionization potential of **15.75** electron volts (eV)
  - higher than the 1st ionization potential of most other elements (except He, F, Ne) and
  - lower than the 2nd ionization potential of most other elements (except Ca, Sr, Ba, etc)

- **Since the plasma ionization environment is defined by the Ar, most analyte elements are efficiently singly charged**


File Math Chromatogram Display Label Zoom View Window Help
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Intensity [cps]
Rel. Intensity [%]
Mass [u]
16000
14000
12000
10000
8000
6000
4000
2000
0
100
80
60
40
20
0
65.0
65.5
66.0
66.5
67.0
67.5
68.0

Isotopes and isobars

- Isotopes
  - **Atomic number (number of protons) is the same, but number of neutrons is different (e.g. Pb204 & Pb 208)**
  - **Chemical characteristics are same, but physical properties are different.**
- Isobars
  - **Atomic number is different, but atomic weight is almost identical so species appear at same mass (e.g. Pb204 & Hg204)**
  - **Chemical characteristics are different, but physical properties are similar**

Interferences in ICP-MS

- Mass Spectroscopic Interferences
  - Inability to resolve same nominal masses
- Non-spectroscopic Interferences
  - Result from sample matrix

Mass Spectroscopic Interferences

- Isobaric (i.e Ba^{138} and La^{138})
- Polyatomic
  - Argides
  - Oxides (i.e Fe^{56} and $Ar^{40}O^{16}$)
  - Other (i.e. Chlorides, Hydrides, etc.)
- Doubly-charged (i.e $^{138}Ba^{++}$ and ^{69}Ga)

Mass Spectroscopic Interferences

- **Choose an isotope free of interferences**
  - 137Ba instead of 138 Ba
- **Optimize instrument to minimize interference**
  - Oxides, doubly-charged ions
  - Use equations
- **Technology to reduce interferences**
  - Cool plasma
  - Collision Cells
  - Dynamic Reaction Cell
  - High Resolution Sector Field

Cool plasma

- **Main differences:**
- RF power, sampling depth and carrier gas.

- A cool plasma uses low temperature plasma to minimize the Ar and matrix-based polyatomic interferences.

- Shield plasma minimizes secondary discharge

- Shield Plate removes potential difference between plasma and interface, so no polyatomic ions form behind the sample cone.

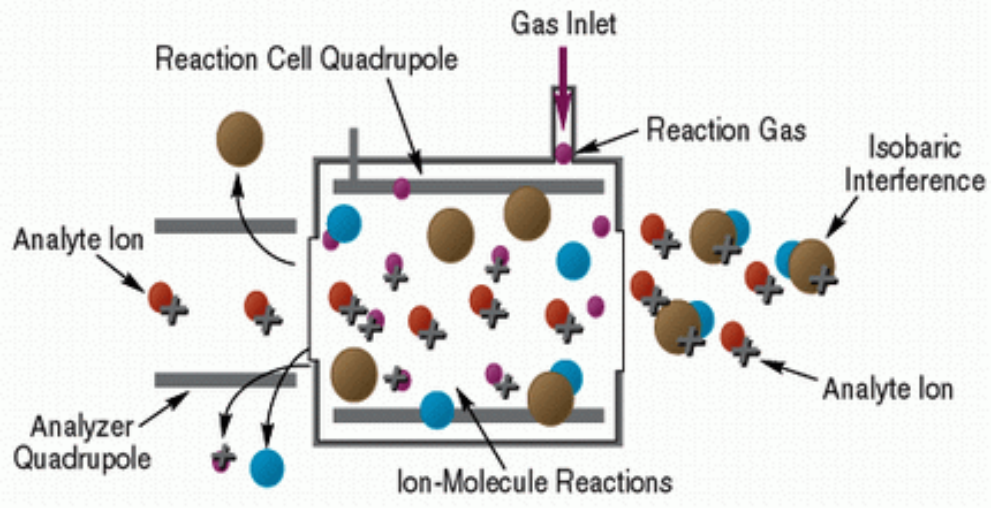
- Cool central channel of plasma gives low Ar and Ar-based ion populations

Dynamic Reaction Cell

Diagram courtesy of Perkin Elmer

$^{40}Ar^{+} + NH_3 = NH_3^{+} + {}^{40}Ar$

$^{40}Ca^{+} + NH_3 = NH_3^{+} + {}^{40}Ca$



- Based on ion molecule reactions and relies on the constant rate of those reactions, which will determine which ones will be thermodynamically favored.
- Since these reactions can be predicted, they are highly specific and can be used to eliminate polyatomic interferences by reaction of a gas with either the interference specie or the analyte of interest.
- Uses a quadrupole as a mass filter to discriminate products of secondary reactions or collisions by mass

High Resolution SF-ICP-MS

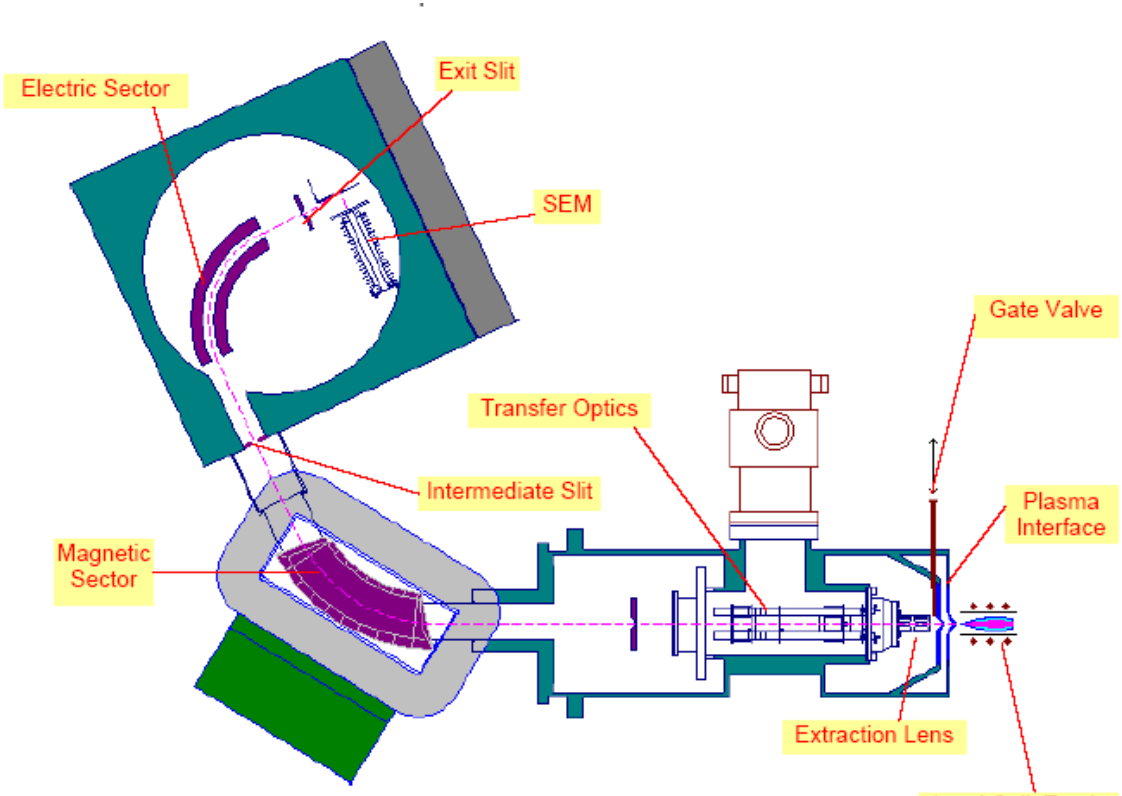
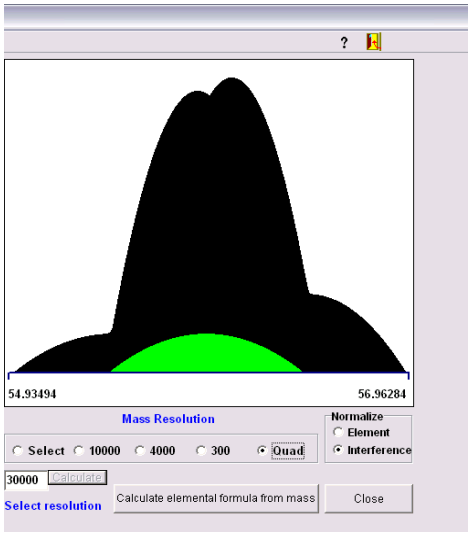
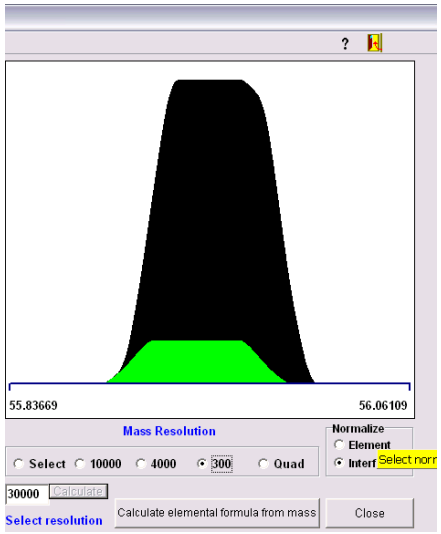


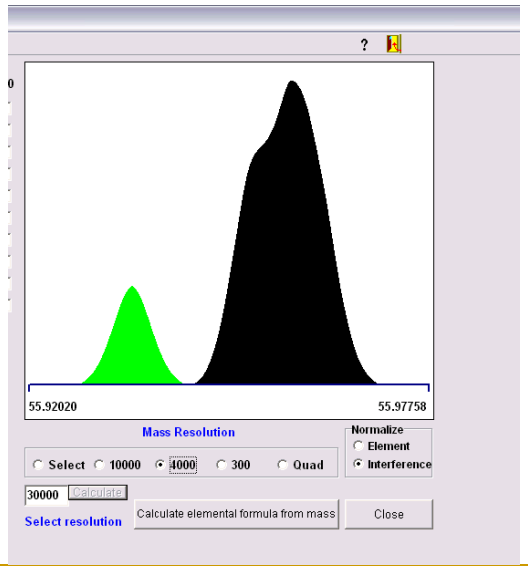
Figure 1 Components of the ***ELEMENT2***

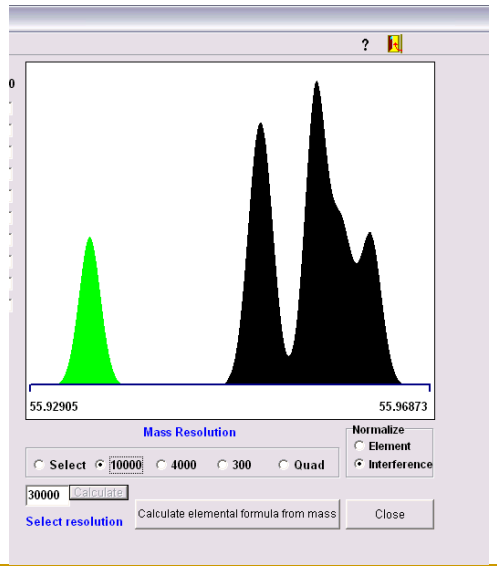
Diagram courtesy of Thermo Scientific

Mass	Formula	Relative Intensity (0 1 10 100)
55.45209	111Cd++	
55.93494	Fe	
55.95138	112Cd++	
55.95241	112Sn++	
55.95729	40Ar16O	
55.95750	40Ca16O	
55.95999	20Ne36Ar	
55.96284	39K17O	
56.45203	113In++	
56.45220	113Cd++	









ICP-MS: Summary

- ICP-MS is a technique for quantitative elemental analysis of materials
- ICP-MS detect "ions" and separate them based on mass to charge ratio
- Excellent sensitivity and wide range (%-ppt)
- Excellent selectivity, few interferences (and different approaches to deal with them)

Previous Work

- **Analysis of Variance (ANOVA)**
  - Within a method
  - Within a population
- **Refine ICP-MS methodology for glass**
  - Identify potentially discriminating elements
  - Application of method to a select data set (vehicle side windows)
- **Statistical analysis of this data**

ASTM Standards

Designation: E 1967 – 98 (REapproved 2003)

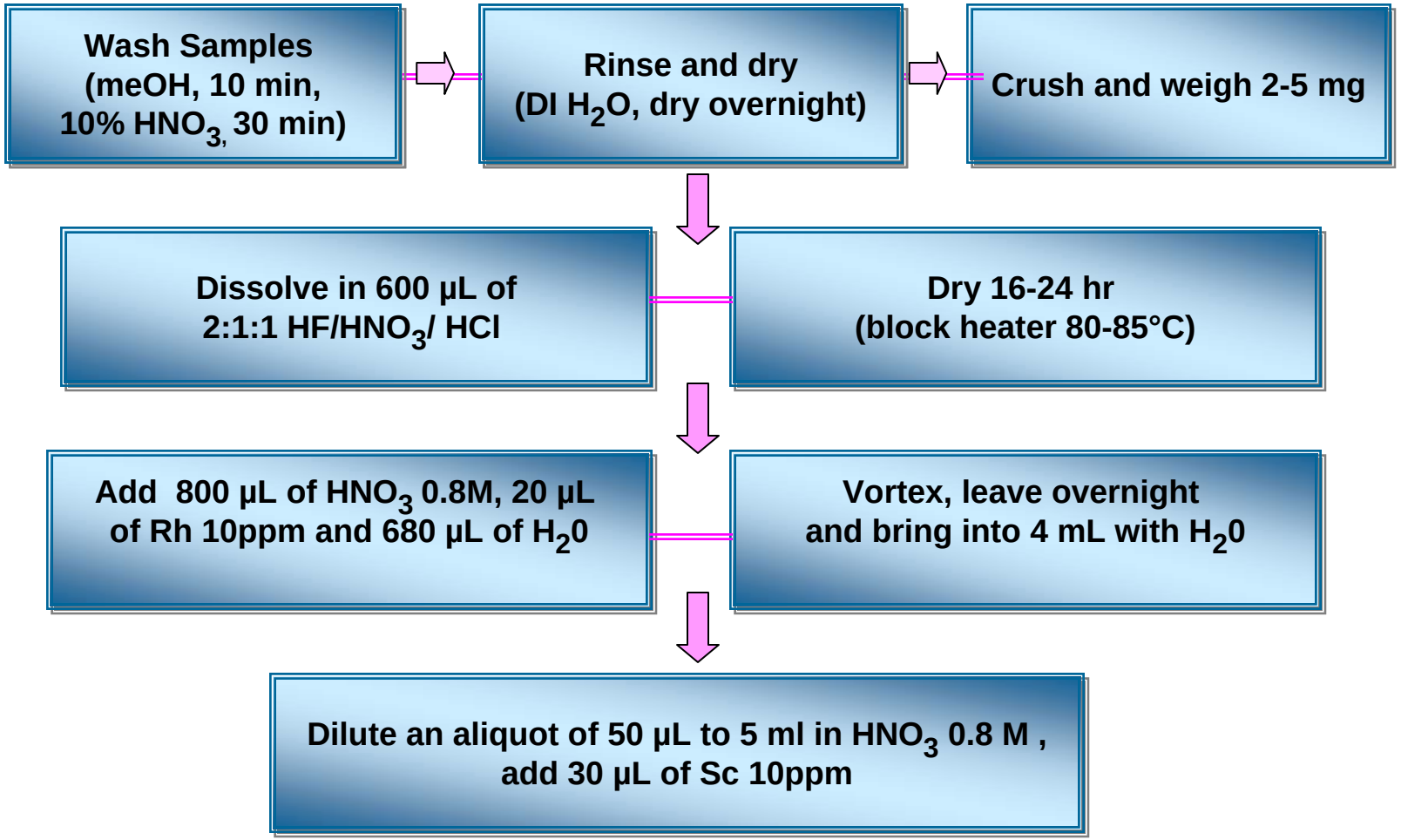
Standard Test Method for the Automated Determination of Refractive Index of Glass Samples Using the Oil Immersion Method and a Phase Contrast Microscope[1]

This standard is issued under the fixed designation E 1967; 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.

Designation: E 2330 – 04

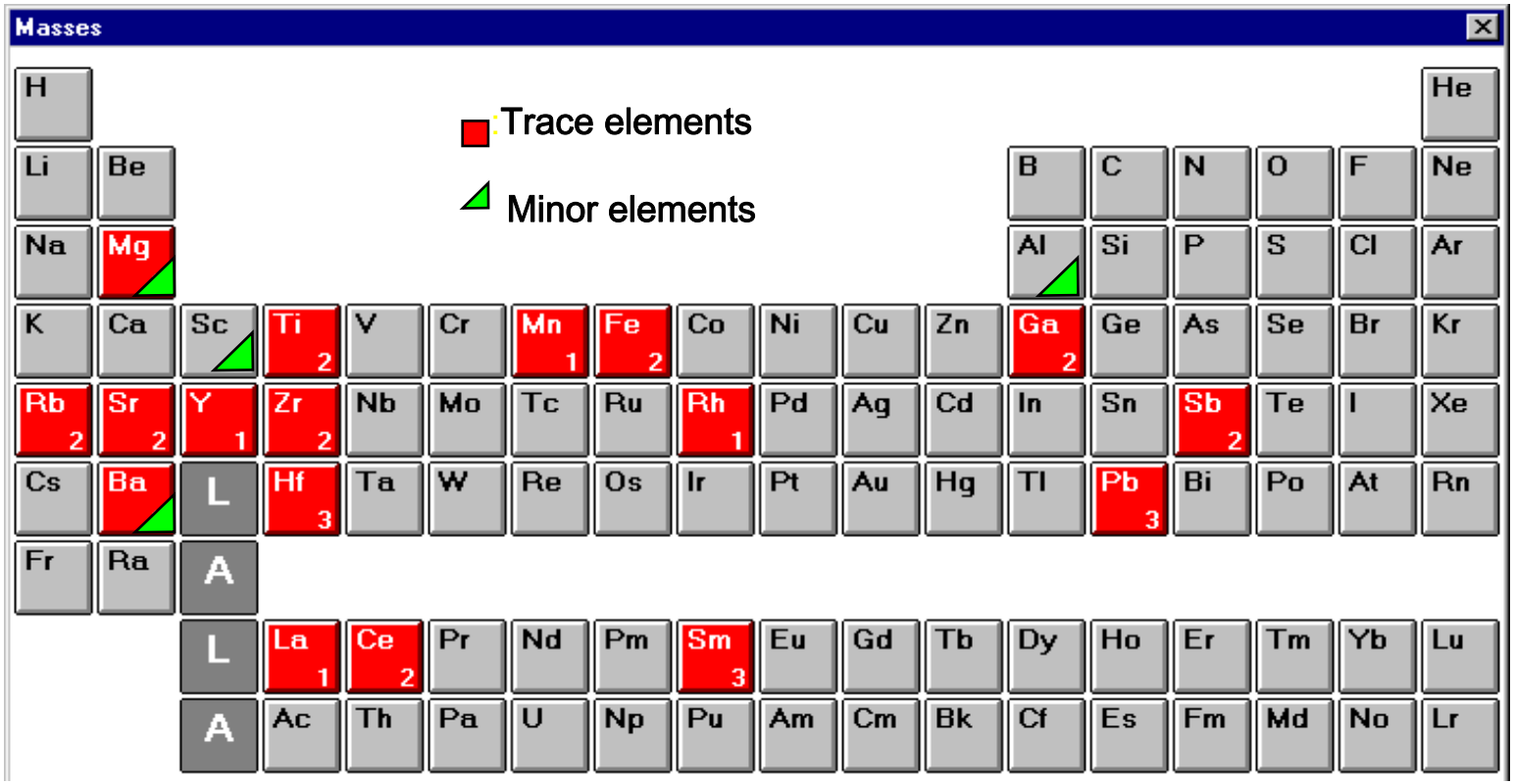
Standard Test Method for Determination of Trace Elements in Glass Samples Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[1]

This standard is issued under the fixed designation E 2330; 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.



ASTM Method E-2330

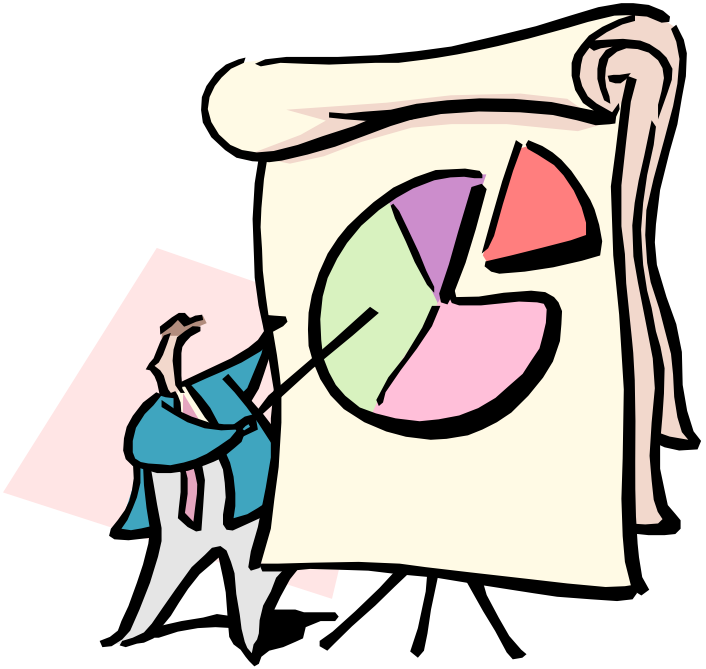
External Calibration Method

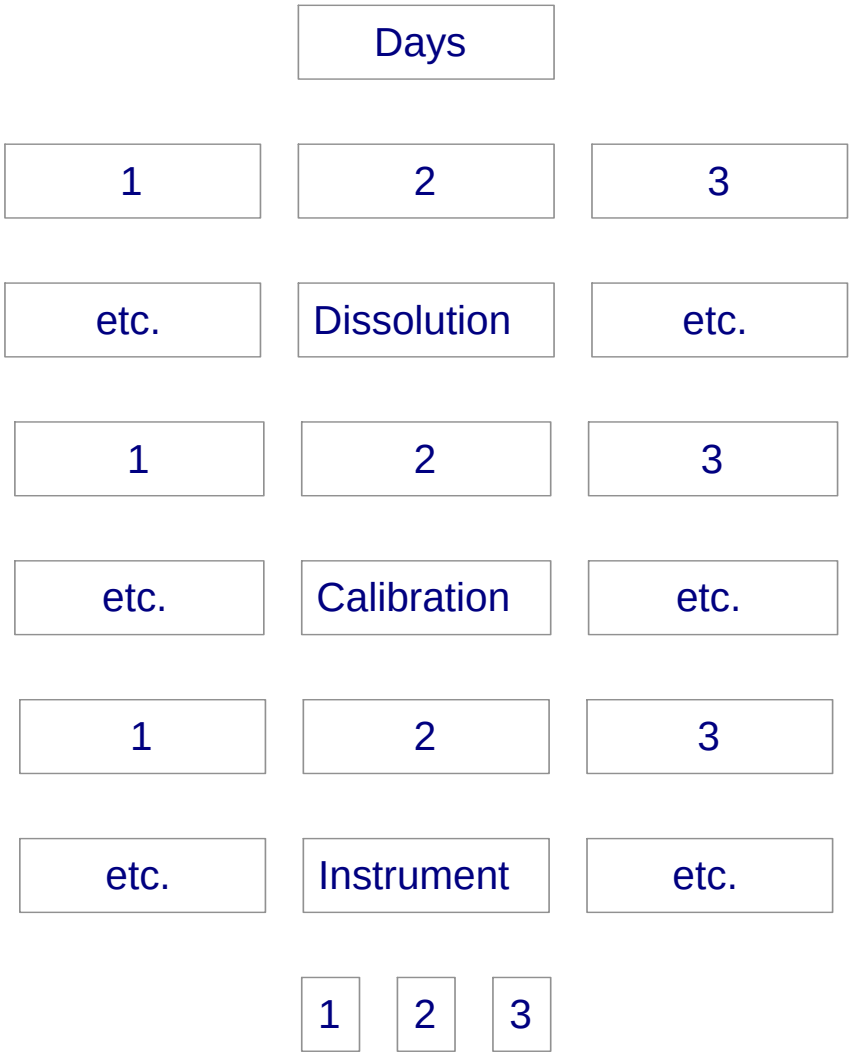


Proposed Elemental Menu

The need for Analysis of Variance

- Quantitation of "informing power"
  - Elemental variations within a population
  - Elemental variations within a sheet
    - Intralaboratory variations
      - Day-to-day
      - Dissolution
      - Calibration
      - Instrumental
    - Interlaboratory variations
      - FIU-ORNL-FBI

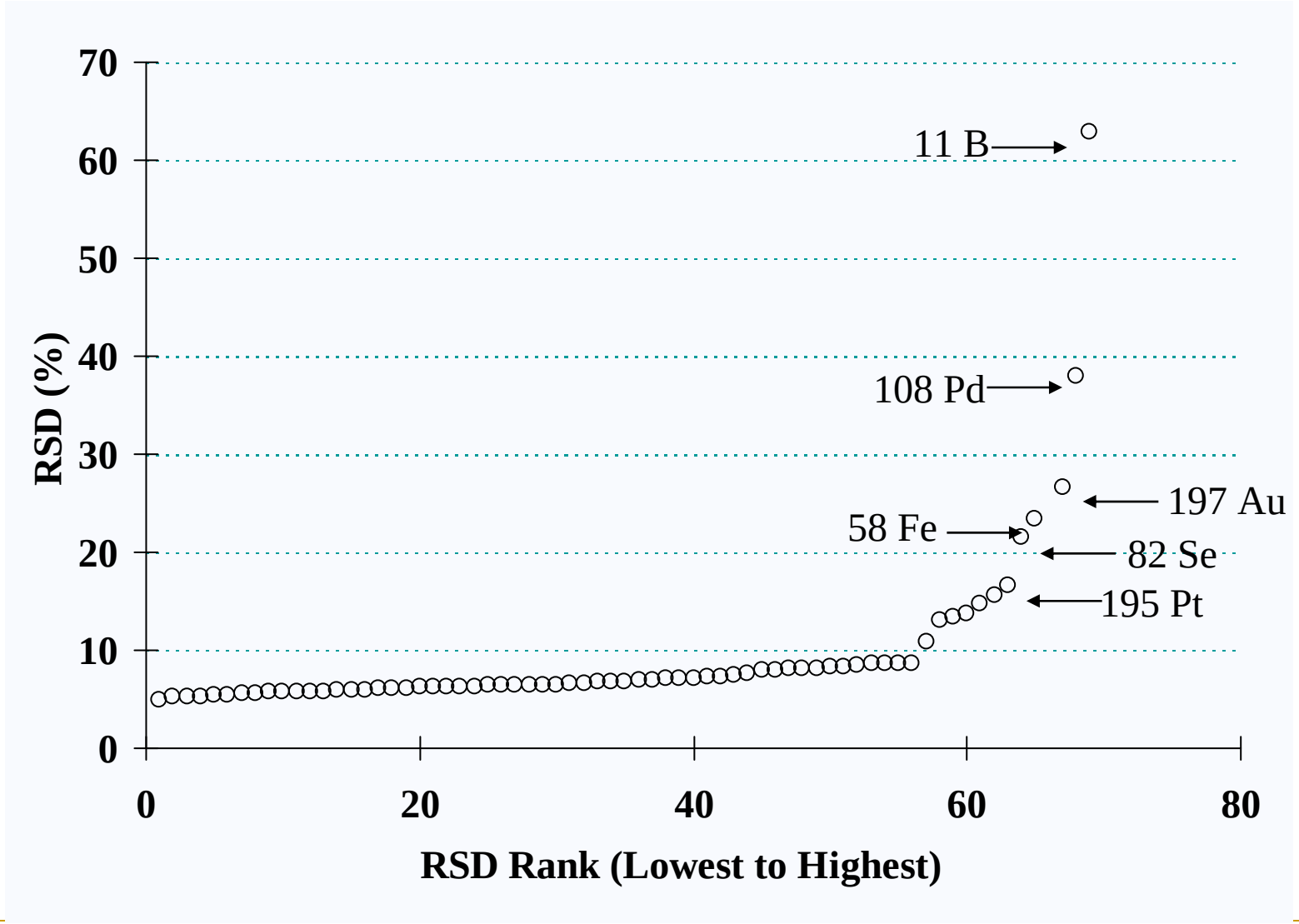




ANOVA Experiment

$$[M]_{ijkl} = \text{Mean} + T_i + D_{j(i)} + C_{k(ij)} + I_{l(ijk)}$$

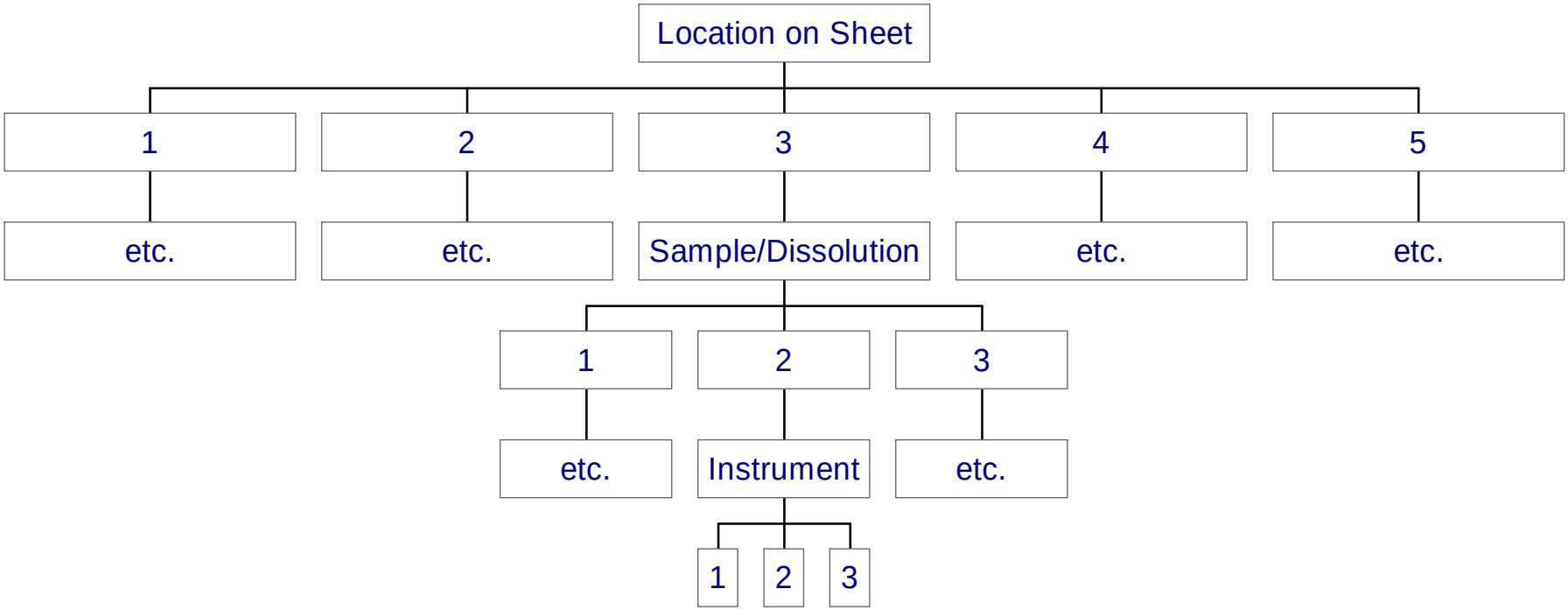
ICP-MS Relative Standard Deviation Versus Ranking In NIST SRM 612



Element Classification by Accuracy and Precision

Precision	Accuracy	
	| Bias | < 5ppm and | %BIAS | ≤10%.	| Bias | ≥5ppm or | %BIAS | > 10%
RSD < 10% and SD < 3ppm	**Quadrant 1** 52Cr, 55Mn, 59Co, 63Cu, 70Ge, 75As, 85Rb, 89Y , 115In, 118Sn, 120Sn, 121Sb, 133Cs, 138Ba, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 151Eu, 157Gd, 159Tb, 162Dy, 165Ho, 166Er, 169Tm, 174Yb, 175Lu, 177Hf, 178Hf, 181Ta, 182W, 184W, 185Re, 203Tl, 205Tl, 208Pb, 209Bi, 232Th, 238U	**Quadrant 2** 7Li 69Ga 90Zr 91Zr 93Nb 95Mo 111Cd 114Cd
RSD > 10% or SD ≥3ppm	**Quadrant 3** 24&26Mg 49Ti, 60Ni 64Zn, 65Cu 66Zn, 73Ge 82Se, 88Sr 107Ag, 108Pd 109Ag, 195Pt	**Quadrant 4** 9Be 11B 45Sc 51V 58Fe 106Pd 197Au

ANOVA Within A Sheet



Variance Components For Elements Within a Sheet

Element	Average (µg/g, n=39)	Standard Deviation (µg/g)	Percent Variance Across Sheet (Vs)	Percent Dissolution Variance (Vd)	Percent Instrument Variance (Vi)	Total Variance (Vt)
178Hf	1.1	0.08	0.0	34.5	65.5	.01
69Ga	4.0	0.23	0.0	78.4	21.6	0.06
208Pb	2.5	0.66	42.3 (0.45)	55.5	2.2	0.49
90Zr	48.2	1.89	0.0	88.9	11.1	4.24
55Mn	73.8	2.64	28.0 (1.5)	55.2	16.8	7.56
88Sr	94.3	3.09	0.0	91.0	9.0	10.68
138Ba	77.4	3.43	26.8 (2.0)	64.5	8.7	12.81
49Ti	193.0	9.11	0.0	88.4	11.6	88.2
57Fe	807.4	36.99	17.0 (15.8)	66.7	16.3	1470.88

() indicates standard deviation in µg/g

Analysis of Variance Within The Population

- 76 Automobile Side Windows
  - 46 elements
  - Three dissolutions per sample
  - Three replicate measurements per dissolution

Vehicle windows (76 sample set)

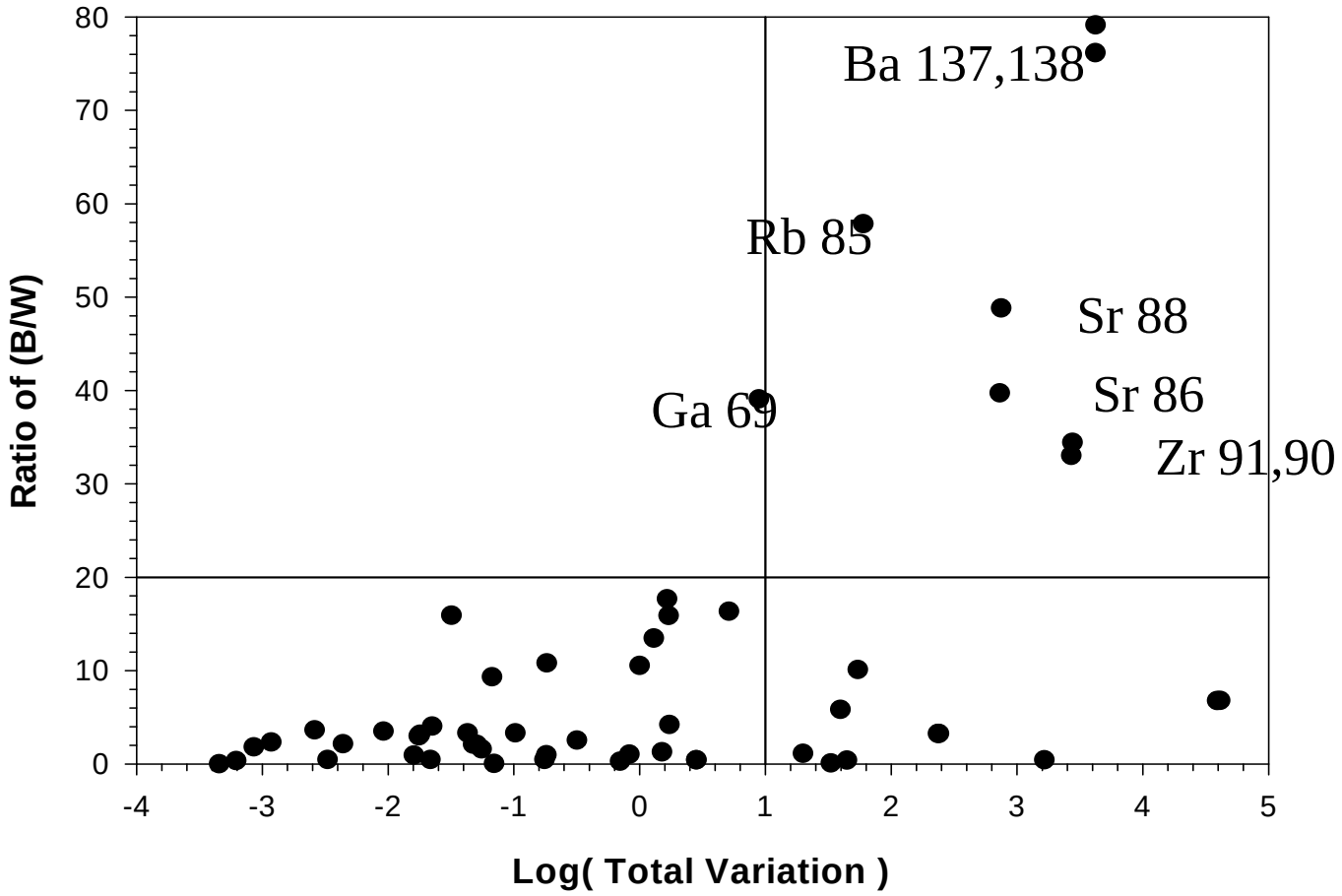
- 3 dissolutions, triplicate, N=684 for 54 isotopes
- Variance components ($V_{population}$, $V_{dissolution}$, $V_{instrument}$)

$$Ratio\ of\ (B/W) = \frac{V_P}{V_D + V_I}\ .$$

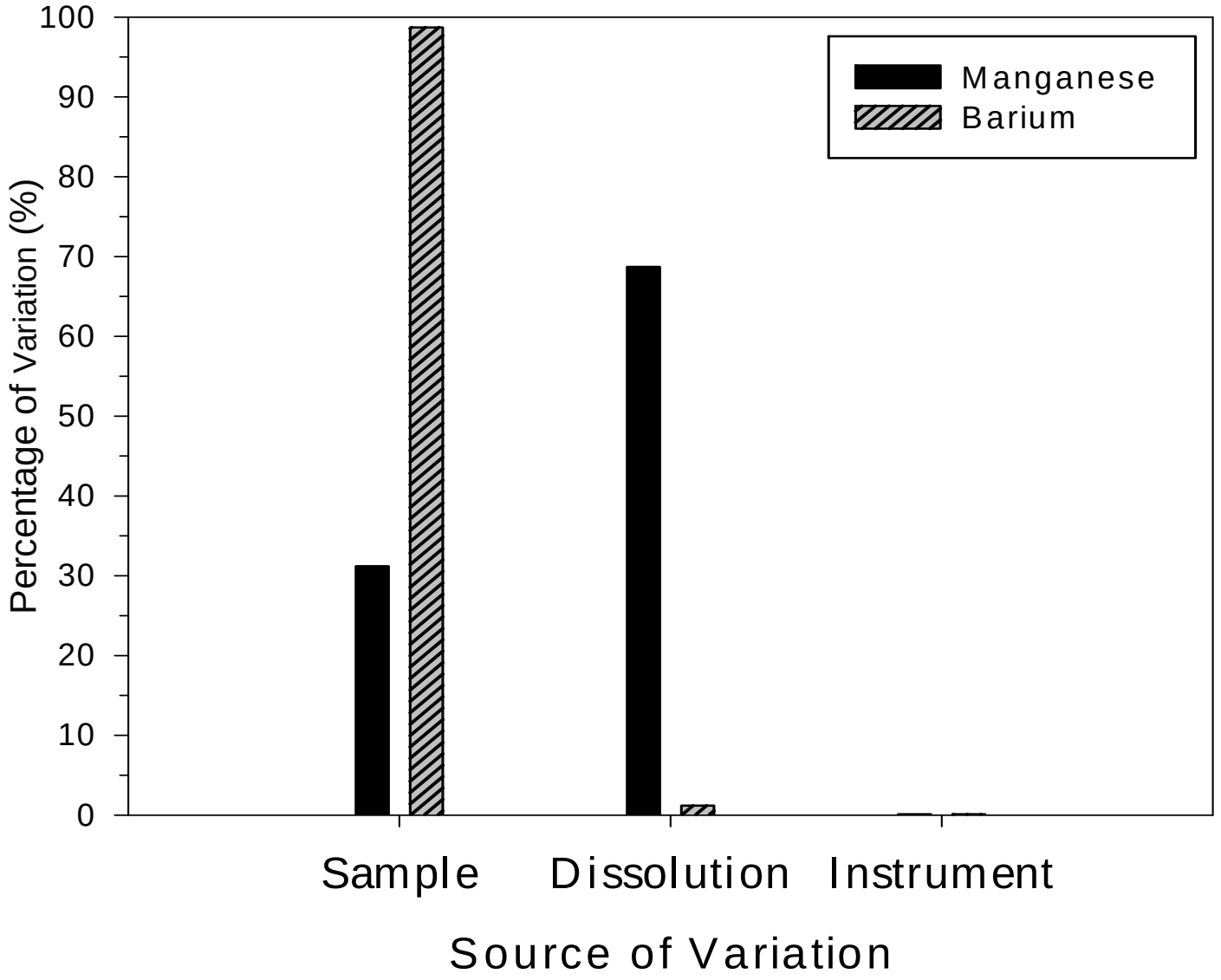
provides measure of discriminating power for element and technique

- Most elements show limited usefulness
- Ba, Rb, Sr, and Zr were found as most discriminating (large V_P and large B/W ratio)

Informing power analysis for isotopes



Manganese & Barium -- Variance Components



ANOVA Results: Auto Side Windows

Element	Population Average (µg/g), n=684	Standard Deviation (µg/g)	Population Variance (Vp)	Dissolution Variance (Vd)	Instrument Variance (Vi)	Ratio Vp (Vd+Vi)
55Mn	37.2	72.5	1648.8	3633.3	1.6	0.5
149Sm	0.4	0.3	0.1	0.0	0.0	1.6
121Sb	15.0	17.4	239.0	73.2	0.4	3.2
208Pb	29.7	210.3	38966.5	5695.4	46.2	6.8
90Zr	96.3	52.9	2753.1	76.1	3.9	34.4
69Ga	1.9	3.0	8.9	0.2	0.0	39.1
88Sr	50.2	27.5	748.4	13.9	1.4	48.8
85Rb	4.1	7.8	59.7	1.0	0.0	57.9
138 Ba	39.8	64.9	4206	51.9	1.2	79.1

Discriminating Power (Ratio Vp/(Vd+Vi)):

Ba>Rb>Sr>Ga>Zr>Hf>Ce>Cs>Y>Th>Nd>Co>Nb>Pb> Ratio = 5.0

Koons vehicle glass study

Comparison parameter and criteria	Number of indistinguishable pairs	Frequency
(1) nD ±0.0002	648	1:5.0
(2) nD ±0.0001	418	1:7.8
(3) (1) and nC ±0.0004 and nF ±0.0004	487	1:6.7
(4) (2) and nC ±0.0002 and nF ±0.0002	178	1:18.2
(5) EDXRF	305	1:10.6
(6) (5) and (3)	81	1:40
(7) (5) and (4)	33	1:98
(8) ICP-AES	3	1:1080
(9) (8) and (3)	3	1:1080
(10) (8) and (4)	2	1:1620

3240 possible comparisons

Koons et al, *J. Anal. At. Spectrom.*, **6**, (1991), 451.

Conclusions:

- ANOVA of the method
  - 48 elements identified as potentially discriminating
- ANOVA within a sheet
  - Initial characterization of expected variation across a sheet
- ANOVA of the population
  - Database start
  - Discriminating elements indicated
  - ID-ICP-MS holds promise

Ruggedness Test of the Method

"The ruggedness test of a test method should precede an interlaboratory study. The interlaboratory (round robin) study should be the final proof test for determining the precision of the test method"

"Ruggedness testing should be done within a single laboratory so the effects of the variable are easier to see"

ASTM E 1169-89 (Reapproved 1996)
Standard Guide for Conducting Ruggedness Tests

- low level
+ high level

experiment	factors						
	A	B	C	D	E	F	G
1	-	-	-	-	-	-	-
2	-	-	+	-	+	+	+
3	-	+	-	+	-	+	+
4	-	+	+	+	+	-	-
5	+	-	-	+	+	-	+
6	+	-	+	+	-	+	-
7	+	+	-	-	+	+	-
8	+	+	+	-	-	-	+

Plackett-Burman design for N=8

Ruggedness of the Method

^{90}Zr in SRM NIST 612

A: time of initial wash with acid
B: concentration of the acid in the initial wash
C: range of sample mass
D: time of digestion in ultrasonic bath
E: time of redisolution in the ultrasonic bath
F: concentration of the acid for redisolution
G: time from preparation to analysis

sample	A (min)	B (%)	C (mg)	D (min)	E (min)	F (%)	G (days)	Results ($\mu g g^{-1}$)	Results ($\mu g g^{-1}$)
1	30	10	2-4	90	90	13	0	41.62	40.35
2	30	10	8-10	90	180	25	2	44.31	45.19
3	30	50	2-4	180	90	25	2	43.04	43.44
4	30	50	8-10	180	180	13	0	41.62	40.76
5	90	10	2-4	180	180	13	2	42.17	42.88
6	90	10	8-10	180	90	25	0	41.50	41.97
7	90	50	2-4	90	180	25	0	40.12	40.28
8	90	50	8-10	90	90	13	2	44.63	44.92

Ruggedness of the Method

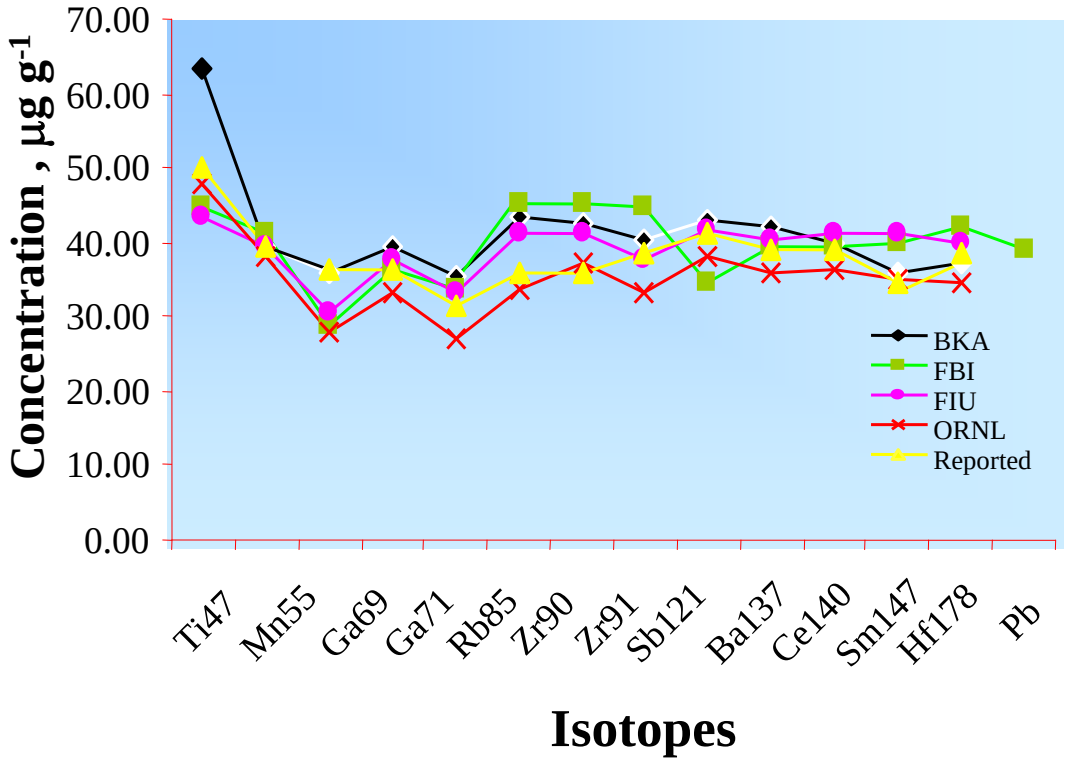
For SRM NIST 1831 and 612 the sample preparation protocol is rugged if the following parameter values are controlled

- C: range of sample mass
- G: time from preparation of the sample to analysis of the sample

Interlaboratory Study (Round Robin)

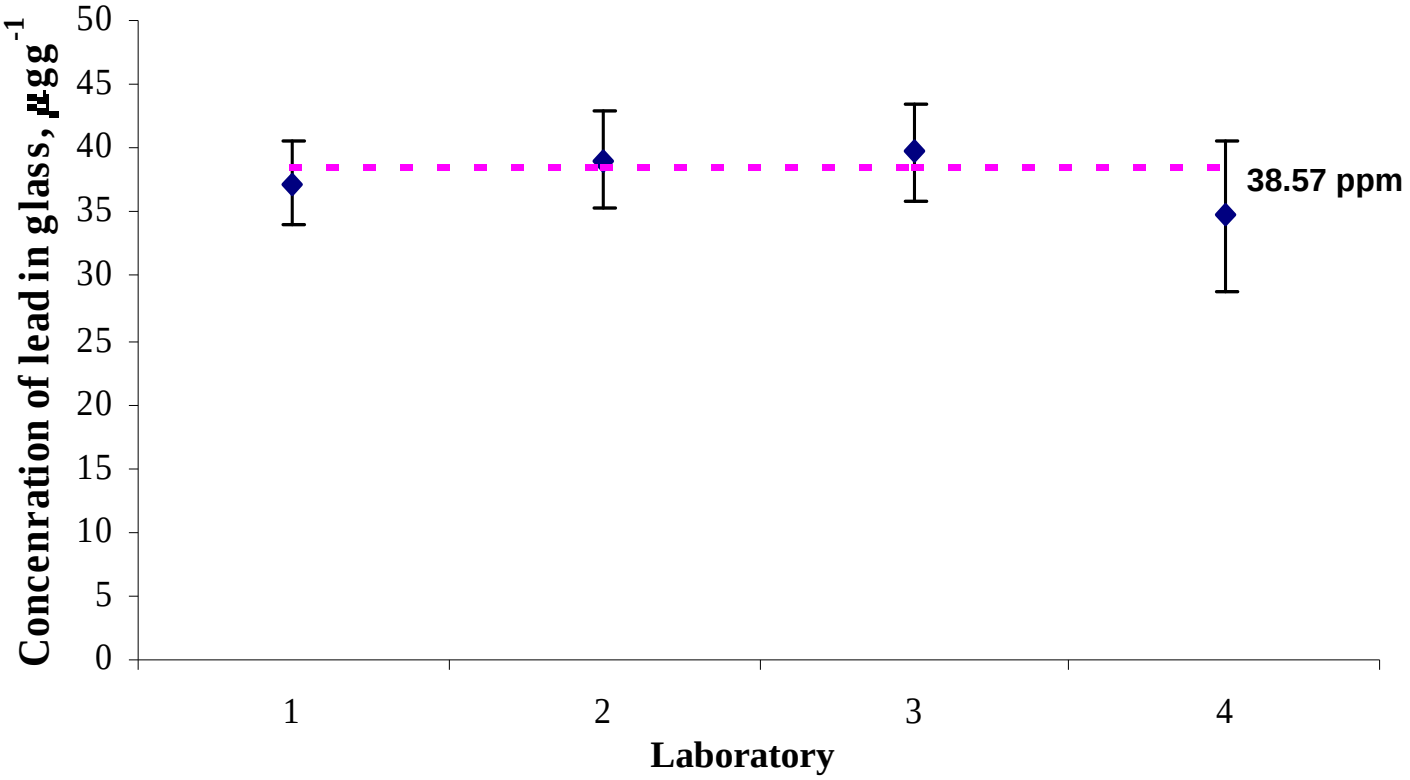
- **SRM NIST**
  - 612 (trace metal ~ 50 $\mu g g^{-1}$)
  - 614 (trace metal ~ 1-10 $\mu g g^{-1}$)
  - 621 (soda-lime container)
  - 1831 (soda-lime sheet)
- **FIU, FBI, ORNL, BKA**

Results of the Round Robin for SRM NIST 612



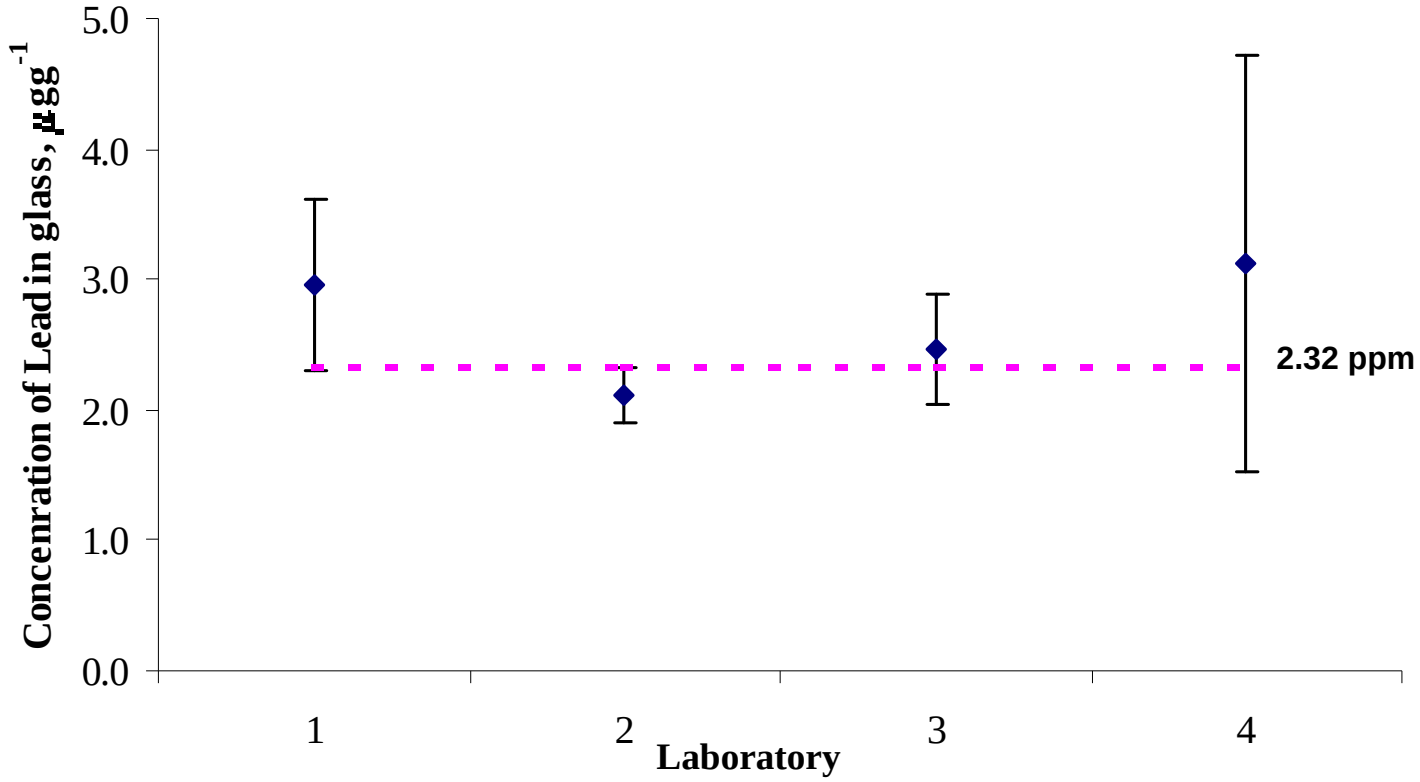
Round Robin Results:

Pb in SRM NIST 612



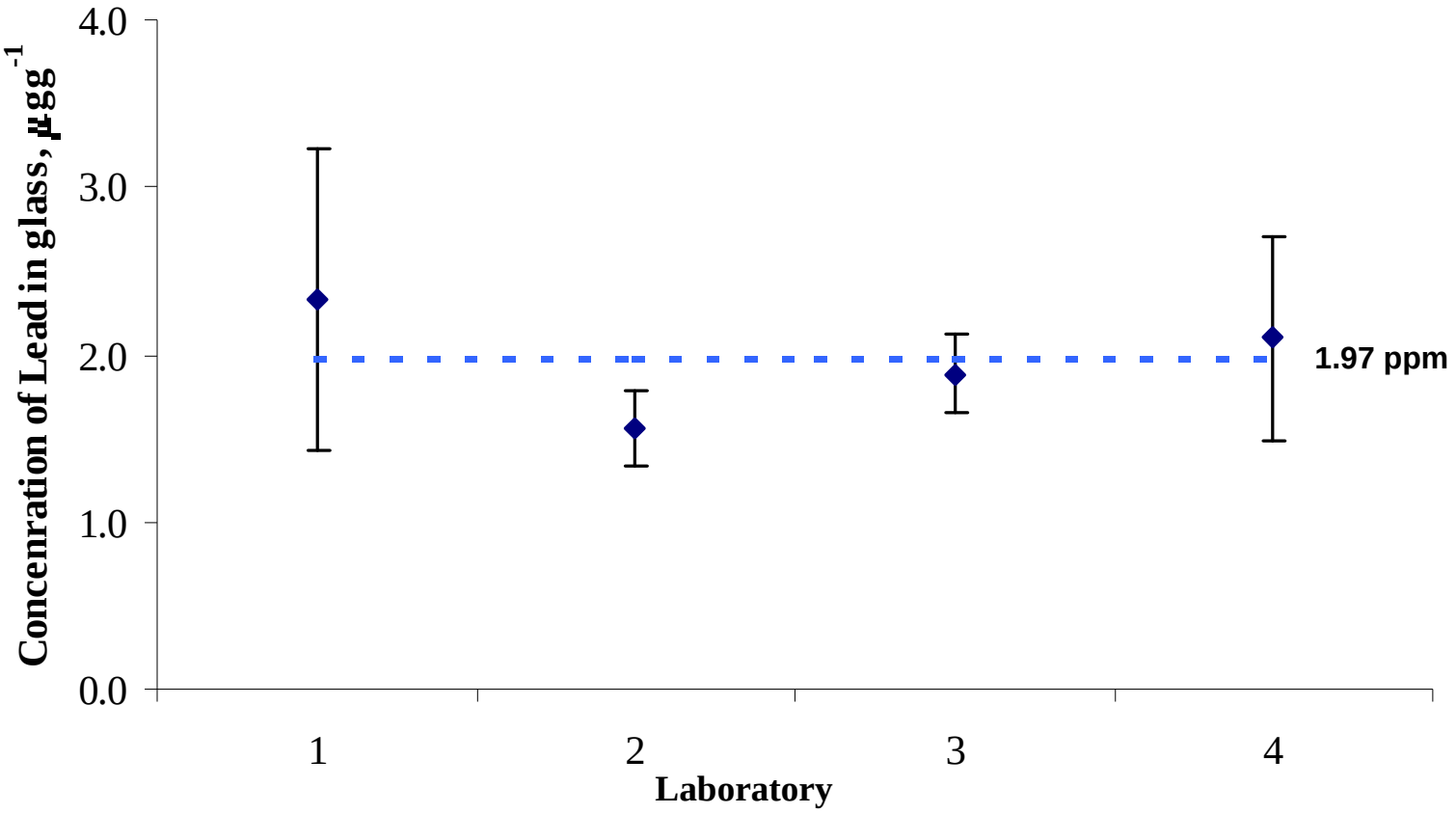
Round Robin Results:

Pb in NIST SRM 614

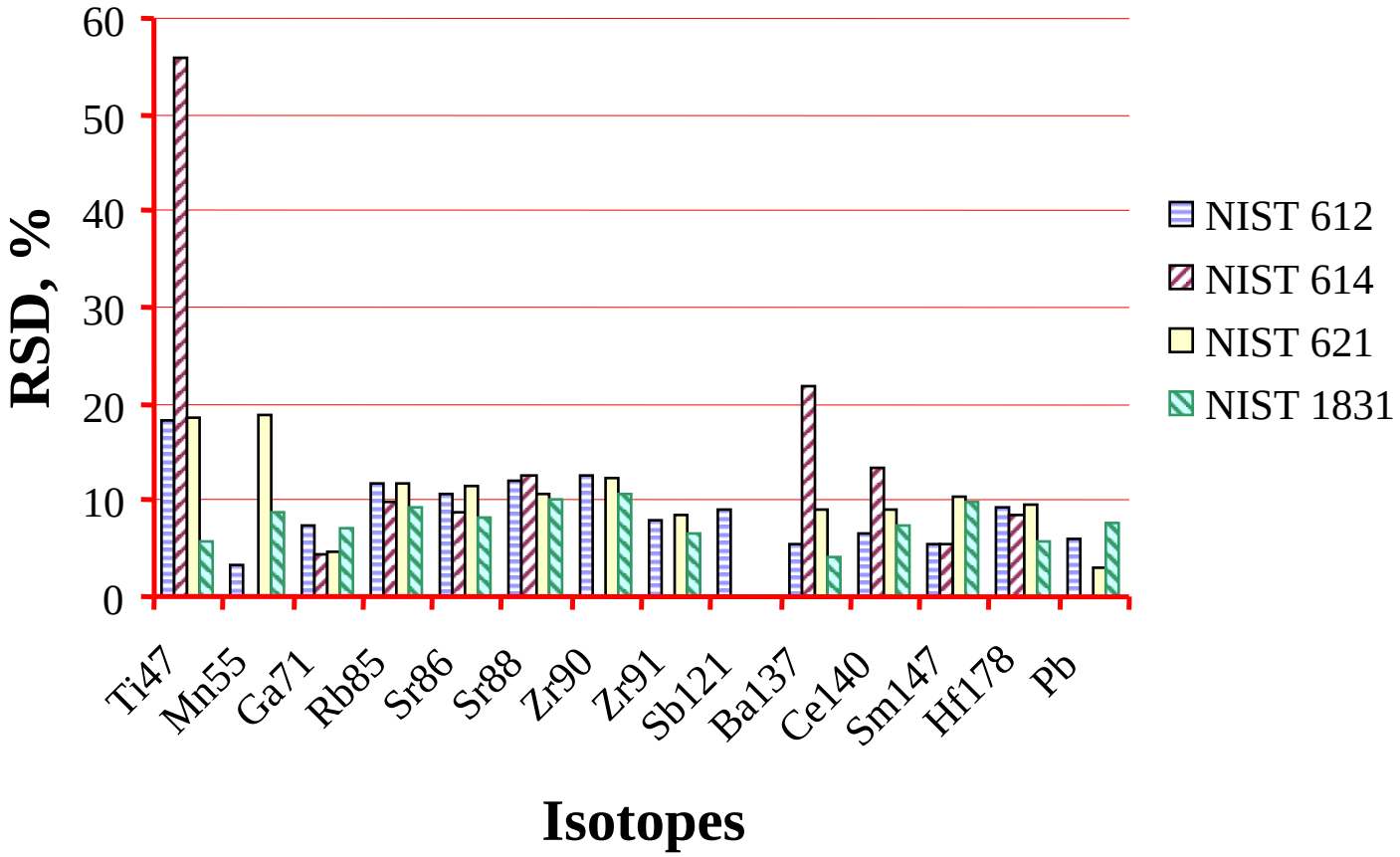


Round Robin Results:

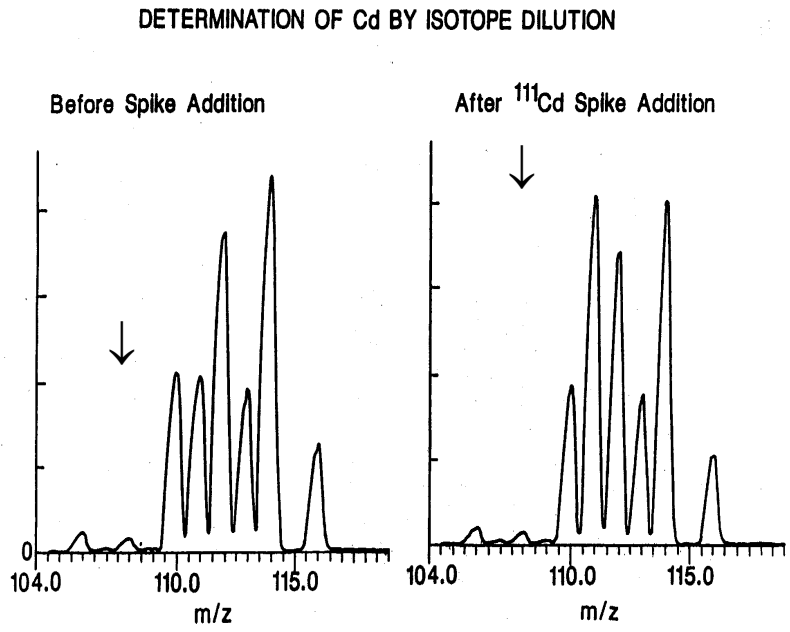
Pb in NIST SRM 1831



Round Robin: Reproducibility of the Method



Isotope Dilution ICP-MS



$$Cx = Cs \frac{Ws}{Wx} \frac{As\text{-}RBs}{RBx\text{-}Ax}$$

C: concentration of analyte
W: weight of sample
A: abundance for reference isotope
B: abundance for spike isotope
R: isotopic ratio
x,s: unspiked or spike subindex

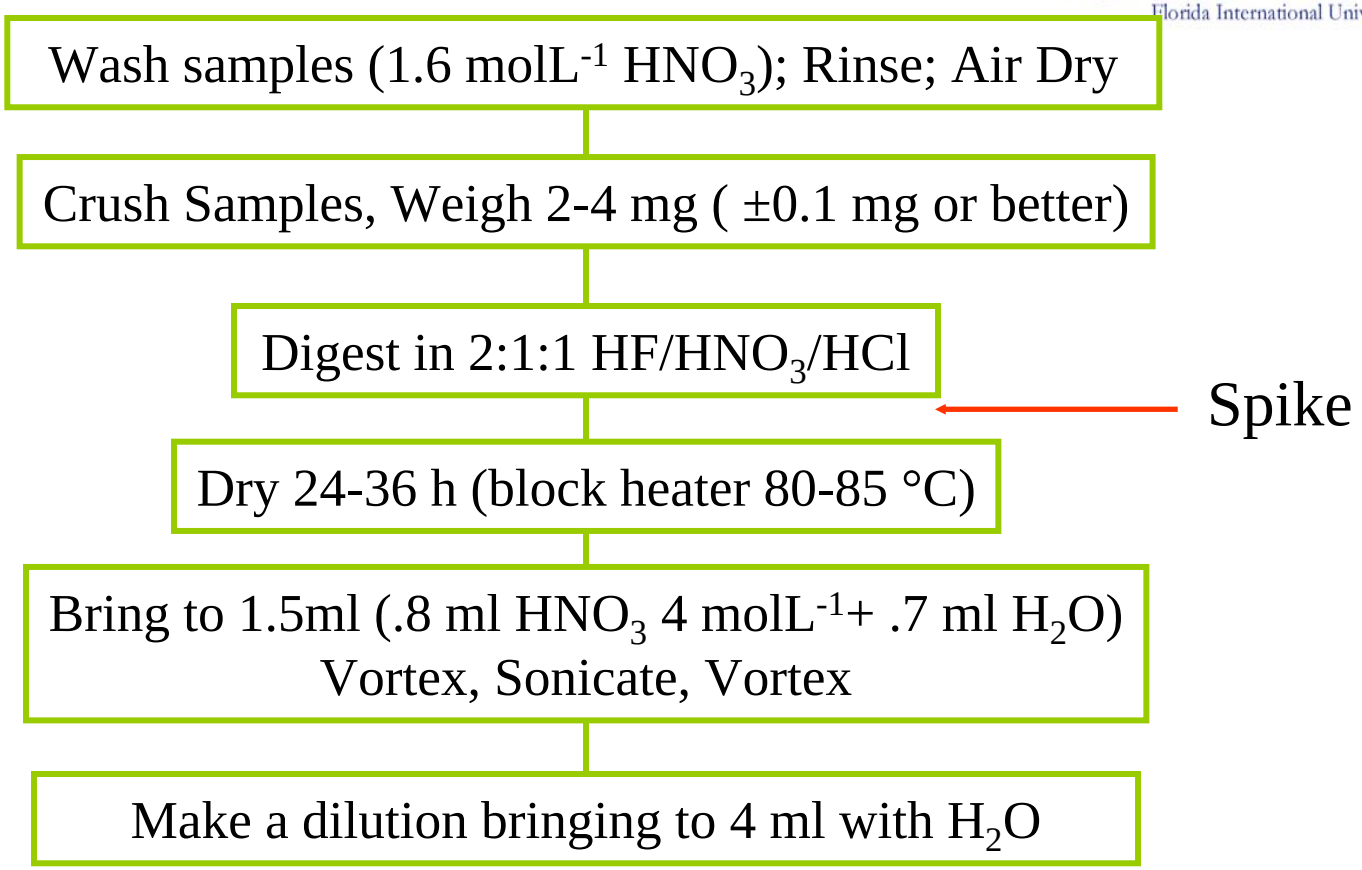
Isotope Dilution ICP-MS

- **Advantages**
  - Provides compensation for a variety of physical and chemical interferences
  - Compensates for the analyte loss during sample preparation (there is no need for 100% recovery)
  - Internal standardization

Isotope Dilution ICP-MS

Selected Stable Isotopes:

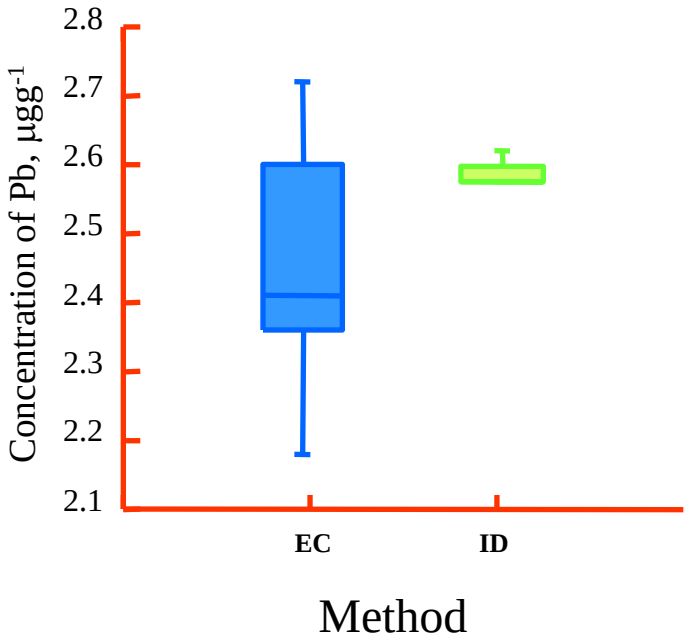
- ^{25}Mg, ^{26}Mg
- ^{86}Sr, ^{88}Sr
- ^{90}Zr, ^{91}Zr
- ^{121}Sb, ^{123}Sb
- ^{137}Ba, ^{138}Ba
- ^{149}Sm, ^{152}Sm
- ^{179}Hf, ^{180}Hf
- ^{206}Pb, ^{208}Pb



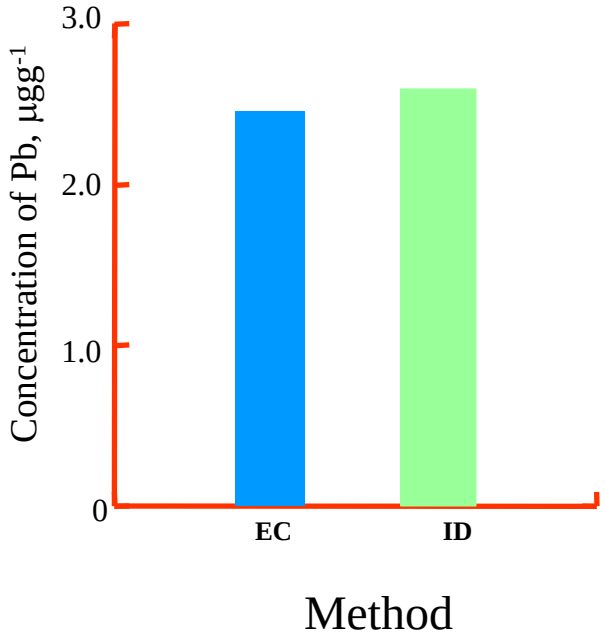
Digestion Scheme 2. Isotope dilution procedure

Comparison of Data for SRM NIST 614
(EC vs. ID)

Measure of precision for [Pb]



Comparison of means for [Pb]



[Pb] is ~3 $\mu g g^{-1}$ in the glass and ~ 1.5 $\mu g L^{-1}$ in solution

Isotope Dilution ICP-MS

element	EC-ICP-MS		ID-ICP-MS	
	average[a], μg g^{-1}	rsd, %	average, μg g^{-1}	rsd, %
Mg	26635	14	23354	0.7
Sr	74.62	2.4	67.94	0.8
Zr	46.91	2.2	42.82	1.7
Sb	-	-	0.07	1.3
Ba	15.22	8.0	13.81	1.3
Sm	0.261	9.6	0.219	7.8
Hf	1.129	10	0.978	6.3
Pb	1.231	8.1	1.382	1.7

[a] Sb values were below detection limit < 0.02 ng L^{-1}

Conclusions

- A method for the elemental analysis of glass fragments by ICP-MS with external calibration and internal standardization was developed and validated. This method proved to be rugged for the selected elements and matrices. This method is now the ASTM standard E2330

- ICP-MS, LAICPMS and isotope dilution ICPMS have shown to be excellent techniques for distinguishing between different glass samples.

- Isotope dilution was shown to provide better precision but at a cost of increased sample preparation and analysis time.