Examination and Comparison of Glass Evidence

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**
Isotopes and isobars

• Isotopes
  – Atomic number (number of protons) is the same, but number of neutrons is different (e.g. Pb\textsubscript{204} & Pb\textsubscript{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. Pb\textsubscript{204} & Hg\textsubscript{204})
  – 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. $\text{Ba}^{138}$ and $\text{La}^{138}$)
- **Polyatomic**
  - Argides
  - Oxides (i.e. $\text{Fe}^{56}$ and $\text{Ar}^{40}\text{O}^{16}$)
  - Other (i.e. Chlorides, Hydrides, etc.)
- **Doubly-charged** (i.e. $\text{Ba}^{++}$ and $\text{Ga}^{69}$)
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

$^{40}\text{Ar}^+ + \text{NH}_3 = \text{NH}_3^+ + ^{40}\text{Ar}$

$^{40}\text{Ca}^+ + \text{NH}_3 = \text{NH}_3^+ + ^{40}\text{Ca}$

- 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.

Diagram courtesy of Perkin Elmer
High Resolution SF-ICP-MS

Diagram courtesy of Thermo Scientific
<table>
<thead>
<tr>
<th>Mass</th>
<th>Formula</th>
<th>Relative Intensity</th>
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<tbody>
<tr>
<td>55.45209</td>
<td>111Cd++</td>
<td></td>
</tr>
<tr>
<td>55.93494</td>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td>55.95138</td>
<td>112Cd++</td>
<td></td>
</tr>
<tr>
<td>55.95241</td>
<td>112Sn++</td>
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</tr>
<tr>
<td>55.95729</td>
<td>40Ar16O</td>
<td></td>
</tr>
<tr>
<td>55.95750</td>
<td>40Ca16O</td>
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<td>113In++</td>
<td></td>
</tr>
<tr>
<td>56.45220</td>
<td>113Cd++</td>
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</table>
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


Standard Test Method for
the Automated Determination of Refractive Index of Glass
Samples Using the Oil Immersion Method and a Phase
Contrast Microscope¹

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.

Wash Samples (meOH, 10 min, 10% HNO₃, 30 min)

Rinse and dry (DI H₂O, dry overnight)

Crush and weigh 2-5 mg

Dissolve in 600 µL of 2:1:1 HF/HNO₃/ HCl

Dry 16-24 hr (block heater 80-85°C)

Add 800 µL of HNO₃ 0.8M, 20 µL of Rh 10ppm and 680 µL of H₂O

Vortex, leave overnight and bring into 4 mL with H₂O

Dilute an aliquot of 50 µL to 5 ml in HNO₃ 0.8 M, add 30 µL of Sc 10ppm

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
    • Intra-laboratory variations
      – Day-to-day
      – Dissolution
      – Calibration
      – Instrumental
    • Inter-laboratory variations
      – FIU-ORNL-FBI
<table>
<thead>
<tr>
<th>Days</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tr>
<td>etc.</td>
<td>Dissolution</td>
<td>etc.</td>
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<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>etc.</td>
<td>Calibration</td>
<td>etc.</td>
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<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>etc.</td>
<td>Instrument</td>
<td>etc.</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

$$[M]_{ijkl} = \text{Mean} + T_i + D_{j(i)} + C_{k(ij)} + I_{l(ijk)}$$
ICP-MS Relative Standard Deviation Versus Ranking In NIST SRM 612

RSD Rank (Lowest to Highest)

RSD (%)
# Element Classification by Accuracy and Precision

<table>
<thead>
<tr>
<th>Precision</th>
<th>Accuracy</th>
<th>Quadrant 1</th>
<th>Quadrant 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSD &lt; 10% and SD &lt; 3 ppm</td>
<td></td>
<td>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</td>
<td>Quadrant 2</td>
</tr>
<tr>
<td>RSD &gt; 10% or SD ≥3 ppm</td>
<td>Quadrant 3</td>
<td>24&amp;26Mg, 49Ti, 60Ni, 64Zn, 65Cu, 66Zn, 73Ge, 82Se, 88Sr, 107Ag, 108Pd, 109Ag, 195Pt</td>
<td>Quadrant 4</td>
</tr>
</tbody>
</table>
ANOVA Within A Sheet

Location on Sheet

1 2 3 4 5
etc. etc. Sample/Dissolution etc. etc.

1 2 3
etc. Instrument etc.

1 2 3
### Variance Components For Elements Within a Sheet

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

() 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 \((V_{\text{population}}, V_{\text{dissolution}}, V_{\text{instrument}})\)

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

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

- Ba 137,138
- Rb 85
- Sr 88
- Sr 86
- Zr 91,90
- Ga 69
Manganese & Barium -- Variance Components

Source of Variation

- Sample
- Dissolution
- Instrument

Percentage of Variation (%)

- Manganese
- Barium
### ANOVA Results: Auto Side Windows

<table>
<thead>
<tr>
<th>Element</th>
<th>Population Average (µg/g), (n=684)</th>
<th>Standard Deviation (µg/g)</th>
<th>Population Variance (Vp)</th>
<th>Dissolution Variance (Vd)</th>
<th>Instrument Variance (Vi)</th>
<th>Ratio (V_p/(V_d+V_i))</th>
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</thead>
<tbody>
<tr>
<td>55Mn</td>
<td>37.2</td>
<td>72.5</td>
<td>1648.8</td>
<td>3633.3</td>
<td>1.6</td>
<td>0.5</td>
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<tr>
<td>149Sm</td>
<td>0.4</td>
<td>0.3</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>1.6</td>
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<td>121Sb</td>
<td>15.0</td>
<td>17.4</td>
<td>239.0</td>
<td>73.2</td>
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<td>29.7</td>
<td>210.3</td>
<td>38966.5</td>
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<td>90Zr</td>
<td>96.3</td>
<td>52.9</td>
<td>2753.1</td>
<td>76.1</td>
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<td>69Ga</td>
<td>1.9</td>
<td>3.0</td>
<td>8.9</td>
<td>0.2</td>
<td>0.0</td>
<td>39.1</td>
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<tr>
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<td>50.2</td>
<td>27.5</td>
<td>748.4</td>
<td>13.9</td>
<td>1.4</td>
<td>48.8</td>
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<td>59.7</td>
<td>1.0</td>
<td>0.0</td>
<td>57.9</td>
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<tr>
<td>138 Ba</td>
<td>39.8</td>
<td>64.9</td>
<td>4206</td>
<td>51.9</td>
<td>1.2</td>
<td>79.1</td>
</tr>
</tbody>
</table>

**Discriminating Power (Ratio \(V_p/(V_d+V_i)\)):**

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

Ratio = 5.0
## Koons vehicle glass study

<table>
<thead>
<tr>
<th>Comparison parameter and criteria</th>
<th>Number of indistinguishable pairs</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $n_D \pm 0.0002$</td>
<td>648</td>
<td>1:5.0</td>
</tr>
<tr>
<td>(2) $n_D \pm 0.0001$</td>
<td>418</td>
<td>1:7.8</td>
</tr>
<tr>
<td>(3) (1) and $n_C \pm 0.0004$ and $n_F \pm 0.0004$</td>
<td>487</td>
<td>1:6.7</td>
</tr>
<tr>
<td>(4) (2) and $n_C \pm 0.0002$ and $n_F \pm 0.0002$</td>
<td>178</td>
<td>1:18.2</td>
</tr>
<tr>
<td>(5) EDXRF</td>
<td>305</td>
<td>1:10.6</td>
</tr>
<tr>
<td>(6) (5) and (3)</td>
<td>81</td>
<td>1:40</td>
</tr>
<tr>
<td>(7) (5) and (4)</td>
<td>33</td>
<td>1:98</td>
</tr>
<tr>
<td>(8) ICP-AES</td>
<td>3</td>
<td>1:1080</td>
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<td>(9) (8) and (3)</td>
<td>3</td>
<td>1:1080</td>
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<td>(10) (8) and (4)</td>
<td>2</td>
<td>1:1620</td>
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</tbody>
</table>

3240 possible comparisons

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

<table>
<thead>
<tr>
<th>experiment</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
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<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>sample</th>
<th>A (min)</th>
<th>B (%)</th>
<th>C (mg)</th>
<th>D (min)</th>
<th>E (min)</th>
<th>F (%)</th>
<th>G (days)</th>
<th>Results (µgg$^{-1}$)</th>
<th>Results (µgg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>10</td>
<td>2-4</td>
<td>90</td>
<td>90</td>
<td>13</td>
<td>0</td>
<td>41.62</td>
<td>40.35</td>
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<td>2</td>
<td>30</td>
<td>10</td>
<td>8-10</td>
<td>90</td>
<td>180</td>
<td>25</td>
<td>2</td>
<td>44.31</td>
<td>45.19</td>
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<td>3</td>
<td>30</td>
<td>50</td>
<td>2-4</td>
<td>180</td>
<td>90</td>
<td>25</td>
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<td>41.62</td>
<td>40.76</td>
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<td>5</td>
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<td>2-4</td>
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<td>13</td>
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<td>42.17</td>
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<td>2-4</td>
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<td>180</td>
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<td>40.12</td>
<td>40.28</td>
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<tr>
<td>8</td>
<td>90</td>
<td>50</td>
<td>8-10</td>
<td>90</td>
<td>90</td>
<td>13</td>
<td>2</td>
<td>44.63</td>
<td>44.92</td>
</tr>
</tbody>
</table>
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 μgg⁻¹)
  • 614 (trace metal ~ 1-10 μgg⁻¹)
  • 621 (soda-lime container)
  • 1831 (soda-lime sheet)

♦ FIU, FBI, ORNL, BKA
Results of the Round Robin for SRM NIST 612

![Graph showing concentrations of isotopes for SRM NIST 612]
Round Robin Results:
Pb in SRM NIST 612

Concentration of lead in glass, $\mu$g/g

Laboratory

1  2  3  4

38.57 ppm
Round Robin Results:

Pb in NIST SRM 614

Concentration of Lead in glass, \( \mu g g^{-1} \)

- Laboratory 1: 2.32 ppm

2.32 ppm
Round Robin Results:
Pb in NIST SRM 1831

Concentration of Lead in glass, \( \mu \text{gg}^{-1} \)

Laboratory

Concentration range: 1.97 ppm
Round Robin: Reproducibility of the Method

Isotopes

- Ti47
- Mn55
- Ga71
- Rb85
- Sr86
- Sr88
- Zr90
- Zr91
- Sb121
- Ba137
- Ce140
- Sm147
- Hf178
- Pb

RSD, %

- NIST 612
- NIST 614
- NIST 621
- NIST 1831

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Isotope Dilution ICP-MS

\[
C_x = \frac{C_s}{\frac{W_s}{W_x} \cdot \frac{A_s}{RB_x - Ax}}
\]

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:

- $^{25}\text{Mg}$, $^{26}\text{Mg}$
- $^{86}\text{Sr}$, $^{88}\text{Sr}$
- $^{90}\text{Zr}$, $^{91}\text{Zr}$
- $^{121}\text{Sb}$, $^{123}\text{Sb}$
- $^{137}\text{Ba}$, $^{138}\text{Ba}$
- $^{149}\text{Sm}$, $^{152}\text{Sm}$
- $^{179}\text{Hf}$, $^{180}\text{Hf}$
- $^{206}\text{Pb}$, $^{208}\text{Pb}$
Wash samples (1.6 molL⁻¹ HNO₃); Rinse; Air Dry

Crush Samples, Weigh 2-4 mg (±0.1 mg or better)

Digest in 2:1:1 HF/HNO₃/HCl

Dry 24-36 h (block heater 80-85 °C)

Bring to 1.5ml (.8 ml HNO₃ 4 molL⁻¹ + .7 ml H₂O)
Vortex, Sonicate, Vortex

Make a dilution bringing to 4 ml with H₂O

**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 μgg⁻¹ in the glass and ~ 1.5 μgL⁻¹ in solution
### Isotope Dilution ICP-MS

<table>
<thead>
<tr>
<th>element</th>
<th>EC-ICP-MS</th>
<th>ID-ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average, ( \mu g \ g^{-1} )</td>
<td>rsd, %</td>
</tr>
<tr>
<td>Mg</td>
<td>26635</td>
<td>14</td>
</tr>
<tr>
<td>Sr</td>
<td>74.62</td>
<td>2.4</td>
</tr>
<tr>
<td>Zr</td>
<td>46.91</td>
<td>2.2</td>
</tr>
<tr>
<td>Sb</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>15.22</td>
<td>8.0</td>
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<tr>
<td>Sm</td>
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<td>9.6</td>
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<tr>
<td>Hf</td>
<td>1.129</td>
<td>10</td>
</tr>
<tr>
<td>Pb</td>
<td>1.231</td>
<td>8.1</td>
</tr>
</tbody>
</table>

\( ^a \) 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.