Improved Antimony Recoveries in Soil Matrices by 3050B/6010B

DataChem Laboratories, Inc.
Robert P. Di Rienzo
Jeffery S. Ward
John T. Kershisnik
Agenda

- Past Method Performance for Antimony
- Current Method Performance for Antimony
- Method 3050B and procedure change
- Method 3050B effect on other elements
- Conclusions
Past LCS Performance

Antimony Soil LCS Recovery
3050 Before May 4, 2004

Past LCS Performance

Antimony Soil LCS Recovery
3050 Before May 4, 2004
Past MS/MSD Performance

Antimony Soil Matrix Spike Recovery
3050 Before May 4, 2004

<table>
<thead>
<tr>
<th>Percent Recovery</th>
<th>Date Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>1/28/2002</td>
</tr>
<tr>
<td>110</td>
<td>3/28/2002</td>
</tr>
<tr>
<td>90</td>
<td>5/28/2002</td>
</tr>
<tr>
<td>70</td>
<td>7/28/2002</td>
</tr>
<tr>
<td>50</td>
<td>9/28/2002</td>
</tr>
<tr>
<td>30</td>
<td>11/28/2002</td>
</tr>
<tr>
<td>40</td>
<td>1/28/2003</td>
</tr>
<tr>
<td>60</td>
<td>3/28/2003</td>
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<td>80</td>
<td>5/28/2003</td>
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<tr>
<td>160</td>
<td>1/28/2004</td>
</tr>
<tr>
<td>180</td>
<td>3/28/2004</td>
</tr>
</tbody>
</table>

Legend:
- Green line: Recovery
- Blue line: Mean
- Dashed line: LCL
- Dash-dotted line: UCL
# INORGANIC REFERENCE MATERIAL
## SOLID LABORATORY CONTROL SAMPLE
### LCS (0996)

The solid laboratory control sample, LCS (0996) was prepared by the UNLV Quality Assurance Laboratory, and is being distributed by IT Corporation, under contract to the EPA. The "True Value" concentrations were derived from the results of an EPA multi-laboratory analysis of the solid material by Contract Laboratory Program procedures. The "True Value" concentrations are listed in Table 1.

## TABLE 1: "TRUE VALUE" CONCENTRATIONS AND CONTROL LIMITS FOR THE ELEMENTS IN THE SOLID LABORATORY CONTROL SAMPLE, LCS (0996)

<table>
<thead>
<tr>
<th>Element</th>
<th>&quot;True Value&quot; (mg/kg)</th>
<th>Control Limits (mg/kg)</th>
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</thead>
<tbody>
<tr>
<td>Al</td>
<td>309</td>
<td>193.1</td>
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<tr>
<td>Sb</td>
<td>213</td>
<td>129.4</td>
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<tr>
<td>As</td>
<td>930</td>
<td>613.6</td>
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<tr>
<td>Ba*</td>
<td>5.3</td>
<td>2.5</td>
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<tr>
<td>Be</td>
<td>18.8</td>
<td>15.3</td>
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<tr>
<td>Cd</td>
<td>41.6</td>
<td>32.1</td>
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<tr>
<td>Ca</td>
<td>184000.5</td>
<td>142933.0</td>
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<tr>
<td>Cr</td>
<td>96.5</td>
<td>77.8</td>
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<td>Co</td>
<td>140</td>
<td>115.4</td>
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<td>Cu</td>
<td>6680</td>
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<td>Fe</td>
<td>21000</td>
<td>16831.3</td>
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<td>Pb</td>
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<td>Mg</td>
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<td>97493.0</td>
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<td>Mn</td>
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<td>Hg</td>
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<td>Ni</td>
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<tr>
<td>K*</td>
<td>[102.4]</td>
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<tr>
<td>Ag</td>
<td>20.9</td>
<td>13.2</td>
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<td>Se</td>
<td>37.0</td>
<td>17.6</td>
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<td>Na*</td>
<td>[92.8]</td>
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<tr>
<td>Ti</td>
<td>38.1</td>
<td>24.6</td>
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<td>V</td>
<td>65.8</td>
<td>53.0</td>
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<tr>
<td>Zn</td>
<td>175</td>
<td>127.7</td>
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</tbody>
</table>
Current LCS Performance

Antimony Soil LCS Recovery
3050 After May 4, 2004

Date Analyzed

Percent Recovery

Recovery
Mean
LCL
UCL

5/4/2004
5/9/2004
5/14/2004
5/19/2004
5/24/2004
5/29/2004
6/6/2004
6/13/2004
6/18/2004
6/23/2004
6/28/2004
7/3/2004
7/8/2004
7/13/2004
7/18/2004
Current MS/MSD Performance

Antimony Soil Matrix Spike Recovery

3050 After May 4, 2004

Date Analyzed

Percent Recovery

40

60

80

100

120

4/5/2004

5/9/2004

5/14/2004

5/19/2004

5/24/2004

5/29/2004

6/3/2004

6/8/2004

6/13/2004

6/18/2004

6/23/2004

6/28/2004

7/3/2004

7/8/2004

7/13/2004

7/18/2004

Recovery

Mean

LCL

UCL
Overall LCS Performance

Antimony Soil LCS Recovery

Date Analyzed

Percent Recovery

Recovery
Mean
LCL
UCL
Overall MS/MSD Performance

Antimony Soil Matrix Spike Recovery

Percent Recovery vs Date Analyzed

- Recovery
- Mean
- LCL
- UCL
Method 3050B
Procedure

Start

7.1 Mix sample, weigh a 1-g portion of each sample for preparation.

7.2 Add HNO₃ and reflux; repeat.

7.2 Evaporate solution to ~5 mL.

7.3 Add ASTM Type II water and H₂O₂; warm for peroxide react.

7.4 Add H₂O₂ and warm until effervescence is minimal

A
Method 3050B
Procedure

A

ICP analysis of As and Se, flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Cr, Co, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Tl, V, and Zn

Furnace analysis of As, Be, Cd, Cr, Co, Pb, Fe, Mo, Se, Tl, and V

Type Analysis

7.5

Cool; dilute with ASTM Type II water; allow particulates in the digestate to settle

7.6

Continue heating and reduce volume

7.6

Cool; dilute with ASTM Type II water; allow particulates in the digestate to settle

7.6

Add concentrated HCl and ASTM Type II water; reflux

7.5

Digestate now ready for analysis
Method 3050B Options

NOTE: Section 7.5 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.

7.5 Add 2.5 mL conc. HNO and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.
Method 3050B Options

7.5.1 Filter the digestate and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask.
Method 3050B Options

7.5.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.
Method 3050B Options

7.5.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by FLAA or ICP-AES.
New Procedure

Start

Mix sample, weigh a 1-g portion of each sample for preparation.

Add 2.5 mL HNO₃ and 10 mL HCL and reflux for 15 minutes.

Prewet filter paper in funnel with several mLs of Hot ASTM Type II water. Filter digest into 100 mL volumetric flask.

Rinse the digestion vessel and wash filter paper using 5 mL Hot HCl and 20 mL of Hot ASTM Type II water. Collect washing in same 100 mL volumetric flask.

Bring to Volume with ASTM Type II water

Analysis by ICP
New Procedure
New Procedure
New Procedure
New Procedure
New Procedure
New Procedure
New Procedure
New Procedure
New Procedure
Change in Performance – All Elements

All Elements LCS Average Recovery

Average Recovery

Element

- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Magnesium
- Manganese
- Nickel
- Selenium
- Silver
- Thallium
- Vanadium
- Zinc
Change in Performance – All Elements

All Elements MS/MSD Average Recovery

Percent Recovery

Element

Antimony  Arsenic  Barium  Beryllium  Cadmium  Chromium  Cobalt  Copper  Lead  Manganese  Nickel  Selenium  Silver  Vanadium  Zinc
Conclusions

Everything should be made as simple as possible, but not simpler.

--- Albert Einstein
Conclusions
Conclusions

A new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it.

--- Max Planck
Thank You

Questions???

DataChem Laboratories, Inc.
Robert P. Di Rienzo
Jeffery S. Ward
John T. Kershisnik
(801) 266-7700