ICP-MS Method for Pb and Other Metals in TSP/PM10

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Overview of Presentation

- Complexity of sample matrix.
- Data from ERG’s experiments with NIST 1648a.
- Improving total metals recoveries for the EPA national contract and NATTS sites using a modified hot acid extraction of the Compendium Method IO-3.1.
- Spinel oxides and their recoveries.
- Analytical limitations can impact choice of extraction technique.
- Bio-accessibility of metals in ambient particulate matter (APM).
- The future of APM extraction and analysis.
- Conclusions
Sample Matrix Complexity

Percent Composition of the National Institute of Standards & Temperature (NIST) 1648a

- Silicon (12.8)
- Carbon (12.7)
- Calcium (5.84)
- Sulfur (5.51)
- Iron (3.92)
- Aluminum (3.43)
- Water Moisture (2.3)
- 27 Other Known Elements (2.1)
- Potassium (1.056)
- Magnesium (0.813)
- Lead (0.655)
- Unknown (48.876)
Improving the Hot Acid Extraction of the Compendium Method IO-3.1

Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

Compendium Method IO-3.1

SELECTION, PREPARATION AND EXTRACTION OF FILTER MATERIAL

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268
June 1999
NIST 1648a Percent Recoveries for HotBlock™ and Ultrasonication Method

- HB 0.5 mg in 5% HNO3 for 1 hr. 20 min. %Rec. (n = 4)
- UE 0.5 mg in 4% HNO3 for 3 hr. Rec. (n = 4)

<table>
<thead>
<tr>
<th>Element</th>
<th>Antimony</th>
<th>Arsenic</th>
<th>Cadmium</th>
<th>Chromium</th>
<th>Cobalt</th>
<th>Lead</th>
<th>Manganese</th>
<th>Nickel</th>
<th>Selenium</th>
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<tbody>
<tr>
<td>Recovery</td>
<td>64.5</td>
<td>59.4</td>
<td>81.2</td>
<td>81.4</td>
<td>76.7</td>
<td>14.6</td>
<td>84.1</td>
<td>82.2</td>
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<td>66.4</td>
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<td></td>
<td></td>
<td>47.9</td>
<td>45.5</td>
<td>73.0</td>
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<td>70.8</td>
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</table>
NIST 1648a Recoveries for 10% Nitric vs IO3.1 Method

- HB ~5 mg for 1 hr. with 10% HNO3 %Rec. (n = 4)
- HB ~5 mg for 3 hr. with 10% HNO3 %Rec. (n = 4)
- HB ~5 mg for 6 hr. with 10% HNO3 %Rec. (n = 4)
- HB ~5 mg for 0.5 hr. with 5.55% HNO3 & 16.75% HCl %Rec. (n = 4)

Antimony
Arsenic
Cadmium
Chromium
Cobalt
Lead
Manganese
Nickel
Selenium
Modified IO3.1 with H$_2$O$_2$ and/or HF

- NIST ~ 5-7 mg for 3 hr. HB with 0.5% HF 5.55% HNO$_3$ 16.75% HCl % Rec. (n = 4)
- NIST ~ 5-7 mg for 2.5 hr. HB with 0.5% HF 5.55% HNO$_3$ 16.75% HCl & H$_2$O$_2$ % Rec. (n = 4)

- Antimony
- Arsenic
- Cadmium
- Chromium
- Cobalt
- Lead
- Manganese
- Nickel
- Selenium
Comparison of ERG Method Development Results

- HB 5% HNO₃ for 1 hr. 20 min. %Rec.
- HB 1 hr. with 10% HNO₃ %Rec.
- HB 6 hr. with 10% HNO₃ %Rec.
- HB 3 hr. with 0.5% HF 5.55% HNO₃ 16.75% HCl % Rec.
- US 4% HNO₃ for 3 hr. Rec.
- HB 3 hr. with 10% HNO₃ %Rec.
- HB 0.5 hr. with 5.55% HNO₃ & 16.75% HCl %Rec.
- HB 2.5 hr. with 0.5% HF 5.55% HNO₃ 16.75% HCl & H₂O₂ % Rec.
Many elements that are in PM are bound in spinel oxides (see Butler & Howe, 1999 and Yamashige, et al., 1989), which are in the general chemical formula of \( \text{A}^{2+}\text{B}^{3+}\text{O}_{4}^{2-} \).

The A and B cations are elements like Mg, Al, Cr, Mn, Fe, Co, Ni, Cu and Zn.

For example: an aluminum spinel \( \text{MgAl}_2\text{O}_4 \), \( \text{FeCr}_2\text{O}_4 \) known as chromite, or ilmenite as \( \text{FeTiO}_3 \).

Chromium can not only be a component of spinel oxides but it can form insoluble oxides under acid conditions (see Ashley et al., 2001 and references therein).

These elements associated with spinel oxides have proven to be difficult to extract through conventional means and in particular Cr has a long history of being difficult.

The reason for this is that these spinel oxides are refractory – meaning: difficult to fuse, corrode, or draw out; especially: capable of enduring high temperature (definition from Merriam-Webster dictionary).

These refractory compounds have demonstrated their resistance to even concentrated acids such as \( \text{HNO}_3 \), \( \text{HCl} \) and even HF (see Butler & Howe, 1999; Jalkanen & Häsänen, 1996 and Yamashige, et al., 1989).

One study suggested that the difficulty of extracting Cr was due to the soot content or organic material (see Jalkanen and Häsänen, 1996).
Comparison of Major Spinel Element Recoveries from Literature

- Aluminum
- Iron
- Magnesium

Data sources:
- UE with 25% HNO₃: Ashley et al., 2001
- UE with HNO₃-HCl: Ashley et al., 2001
- UE with concentrated HNO₃: Ashley et al., 2001
- HP with HNO₃-HCl: Yamashigae et al., 1989
- HP with HNO₃-HClO₄: Yamashigae et al., 1989
- UE with HNO₃-HF: Jalkamäki & Hasman, 1996
- MW with HNO₃-HCl: HF Wang et al., 1995
- MW with HNO₃-HF: H₂O₂: Pekeny & Davidson, 2005
- MW with HNO₃-HClO₄: Fuku et al., 2007
- MW with HNO₃-HF: H₃PO₃: Danilov et al., 2011
- HP with HF-HNO₃-HCl: Yamashigae et al., 1989
- HP with HNO₃-HClO₄: Yamashigae et al., 1989
- HP with HNO₃-H₂O₂: Yamashigae et al., 1989
Improved Recoveries of Spinels and Other Elements in NIST 1648a with H$_2$O$_2$ and/or HF

*The values for these elements are not included with NIST 1648a; the barium reference value taken from Yamashige et al., 1989 and the uranium value was taken from a study done at Iowa State University in 2005 (see: http://www.osti.gov/bridge/servlets/purl/882989-wfWShW/882989.pdf)
Comparison of IO-3.1 to UE with HF and HB with HF and H$_2$O$_2$

- HB 3 hr. IO-3.1, 16.75% HCl & 5.55% HNO$_3$ (n=1)
- UE 3 hr. 0.5% HF, 16.75% HCl & 5.55% HNO$_3$ (n=4)
- HB 3 hr. 0.5% HF, 16.75% HCl & 5.55% HNO$_3$ + H$_2$O$_2$ (n=4)

*The values for these elements are not included with NIST 1648a; the barium reference value taken from Yamashige et al., 1989 and the uranium value was taken from a study done at Iowa State University in 2005 (see: http://www.osti.gov/bridge/servlets/purl/882989-wfWSHw/882989.pdf)
Analytical Limitations Impact Extraction

• After establishing an improved method of extracting NIST 1648a some analytical limitations were discovered.
• NIST 1648a samples were initially extracted without matrix of quartz or Teflon filters.
• An ELAN 9000 ICP-MS that does not have a DRC was used for all analytical determinations.

  ➢ With the quartz filter extracted using HF an unknown matrix interference was created causing the lower mass internal standards to recover poorly, which may be due to the high [Si] or maybe SiF$_6$.
  ➢ A final concentration of 3.35% HCl in the extract proved difficult to maintain acceptable MDL’s for As and Se.
Reasons and Resolutions for Analytical Limitations

• An ICP-MS without DRC or CCT cannot eliminate polyatomic interferences and instead are handled with tune conditions and correction equations.
  ➢ (i.e. 40Ar + 35Cl interferes with 75As)

• Large quantities of 40Ar35Cl creates a relatively more unstable background making MDLs higher.
  ➢ Decreased [HCl] until As MDL was acceptable.

• The large quantity of Si in the extracts of quartz filters with HF could cause a physical interference great enough to have low internal standard recoveries.
  ➢ Removed HF from Quartz extractions.
  ➢ Future experiments may find a way to eliminate this problem.
Comparison of Old, Current and “Best” Extraction Methods

- **US 3 hr. 4% HNO3 Old Method**
- **HB 2.5 hr. 1.5% HCl 5.55% HNO3 + H2O2 Current Quartz Extraction Method**
- **HB 2.5 hr. 0.17% HF 0.5%HCl 1.85% HNO3 + H2O2 Current Teflon Extraction Method**
- **HB 2.5 hr. with 0.5% HF 5.55% HNO3 16.75% HCl & H2O2 "Best" Method**
ERG’s Expansion of Elements for Analysis

- Aluminum
- Barium
- Copper
- Iron*
- Magnesium*
- Molybdenum
- Rubidium*
- Strontium*
- Thallium
- Thorium
- Uranium
- Zinc

* Elements not listed in the IO-3.5 Method that could also be used for source apportionment studies.
Because of the new NAAQS rule for lead (2008), ERG has proposed a new FEM for analysis by ICP-MS.

- Reagents used:
  - HNO3
  - HCl
  - HF
  - H$_2$O$_2$

- HotBlock™ (not ultrasonic extraction)

- Recoveries for NIST 1648a Pb with new method ~90%.

- With the use of the additional acids this method also provides improved data for other elements of the EPA national contract and NATTS sites.
Range and Mean of Bio-accessible Trace Metals Fractions from Mukhtar & Limbeck, 2011

<table>
<thead>
<tr>
<th></th>
<th>Low Range Bio-accessibility (%)</th>
<th>Mean Bio-accessible (%)</th>
<th>High Range Bio-accessibility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium</td>
<td>33</td>
<td>78</td>
<td>97</td>
</tr>
<tr>
<td>Cobalt</td>
<td>24</td>
<td>38</td>
<td>65</td>
</tr>
<tr>
<td>Copper</td>
<td>27</td>
<td>80</td>
<td>96</td>
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<tr>
<td>Manganese</td>
<td>31</td>
<td>55</td>
<td>81</td>
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<tr>
<td>Nickel</td>
<td>9</td>
<td>32</td>
<td>53</td>
</tr>
<tr>
<td>Lead</td>
<td>43</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
The Future of APM Analysis

• Do we really want a total digestion of the sample for total elemental concentrations or are we really interested in bio-accessible trace metal fractions as studied by Mukhtar and Limbeck, 2011?
  ➢ The answer to this question probably depends on the end use of the data.

• If it’s only the bio-accessible composition then the remaining undigested APM is perhaps more of a physical concern and not necessarily the total elemental composition.

• For the purpose of source apportionment studies it may be best to completely digest the APM.
Conclusions

- Lead is not difficult to extract from APM but many other metals are and the recovery of lead may be impacted when attempting multi-element extractions using an ultrasonic bath or HotBlock™.
- The extraction procedure chosen to analyze APM is dependent upon which elements are more important for data end use.
- Other types of extraction techniques such as microwave and alkali fusion may prove to be the favored methods of the future when total elemental concentrations are required.
- Risk assessment of metal toxicity should focus on bio-accessible concentrations and not total concentrations.
- Bio-accessible concentrations are best obtained through dissolution techniques like those described in this study utilizing ultrasonication or HotBlocks™ because techniques and instrumentation used for total elemental concentrations cannot quantitate bio-accessible metals.
- The literature and ERG experiments of NIST 1648(a) demonstrate that while total recoveries for certain metals are best with some methods you may negatively impact the recovery of other metals.
- We were able to improve upon our UE method by modifying the acid concentrations and switching to a HotBlock™, which improved total recoveries of many metals in APM.
References


Acknowledgments

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  ➢ Mike Jones, OAQPS – delivery order manager.
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