What’s new and what’s coming in EPA ICP-MS methods?

200.8

The Saga Continues…
Important US Environmental Legislation Pertaining to Environmental Monitoring

1963  Clean Air Act – reduce smog and air pollution

1970  EPA created by fusing several other federal agencies (Richard Nixon)
      Goal - repairing the damage already done and work to prevent further damage to the environment

1972  Water Pollution Control Act (later superseded by CWA)

1974  Safe Drinking Water Act – established National Primary Drinking Water Regulations (NPDWRs) and Maximum Contaminant Levels (MCLs)

1976  Resource Conservation and Recovery Act (RCRA) – to manage waste disposal and encourage recycling (methods published as SW-846)

1977  Clean Water Act (CWA) – established the National Pollution Discharge Elimination System (NPDES) to control point source discharges into surface waters

1980  Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) more commonly knows as “Superfund” – designed to protect the public from abandoned, highly contaminated waste sites
Federal Register

All Environmental Acts and associated requirements are published in the Federal Register as a Code of Federal Regulations (CFR) under Title 40 (Protection of the Environment)

Various subsections (parts) are related to different programs

- Water Programs (Parts 100 - 149)
- Solid Waste Programs (Parts 239 – 282)

etc…
EPA Methods

All of these acts establish goals to limit pollutants and to provide for analytical methodologies to be used for monitoring.

Overseen by different Program Offices within EPA

- Office of Air and Radiation
- Office of Prevention, Pesticides, and Toxic Substances
- Office of Research and Development
- Office of Resource Conservation and Recovery (formerly Office of Solid Waste)
- Office of Water
- ...

There are also 10 EPA Regional Laboratories.
The main focus of the Regional Laboratories is to apply scientific principles to support regulatory and monitoring programs. This is accomplished through direct implementation with EPA program offices and through partnerships with state, local and tribal governments, private industry, academia, and the public.
Office of Solid Waste Reorganizes to Become Office of Resource Conservation and Recovery*

On January 18, 2009, the Office of Solid Waste (OSW) was reorganized and changed its name to the Office of Resource Conservation and Recovery (ORCR). The name change reflects the breadth of the responsibilities/authorities that Congress provided to EPA under the Resource Conservation and Recovery Act (RCRA), the primary authorizing statute. ORCR has three divisions, which consolidate the operations of the six divisions under the OSW structure. This reorganization will create a more efficient structure, consistent with current program priorities and resource levels, and will enable EPA to better serve the needs of the public and its key stakeholders over the next 5-10 years. EPA has increased focus on resource conservation and materials management; it is expected that focus on this important aspect of the RCRA program will continue, while maintaining a strong waste management regulatory and implementation program. EPA is taking final action to amend the Code of Federal Regulations (CFR) to reflect the reorganization and name change of the Office of Solid Waste.

NEMI is an online database that allows users to search and compare the performance and relative cost of regulatory and non-regulatory environmental monitoring methods.
General Search for all ICP-MS Methods

Can specify search filters
- Media
  - water
  - air
  - tissue
  - soil etc.
- Source
  - EPA
  - ASTM
  - Standard Methods etc.
- Method Number
- Instrumentation
  - just about everything
- Method Subcategory
  - inorganic
  - organic
  - physical
  - acute toxicity etc.
ICP-MS Methods

Quick search for ICP-MS Methods results in 23, but only two are commonly used for regulatory compliance:

- 200.8 for water and wastewater
- 6020A for solid waste

Both have been recently updated or are in the process of updating.

[Image of ICP-MS methods search results]

[Agilent Technologies logo]
## Comparison of 200.8 and 6020A

### 200.8 Rev 5.4 – 1994 (waters)
- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Chromium
- Cobalt
- Copper
- Lead
- Manganese
- Mercury
- Molybdenum
- Nickel
- Selenium
- Silver
- Thallium
- Thorium
- Uranium
- Vanadium
- Zinc

### 6020A Rev 1 - 2007 (wastes)
- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Magnesium
- Manganese
- Mercury
- Nickel
- Potassium
- Selenium
- Silver
- Sodium
- Thallium
- Vanadium
- Zinc

**No minerals (Na, K, Ca, Mg, Fe)**

**Minerals, Se, V, and Hg have been added since the original revision**

**Elements in red are not included in other method**
## Comparison of 200.8 and 6020A

### 200.8 Rev 5.4 – 1994 (waters)

- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Chromium
- Cobalt
- Copper
- Lead
- Manganese
- Mercury
- Molybdenum
- Nickel
- Selenium
- Silver
- Thallium
- Thorium
- Uranium
- Vanadium
- Zinc

**Primary drinking water MCLs established**

### 6020A Rev 1 - 2007 (wastes)

- Aluminum
- Sodium
- Antimony
- Thallium
- Arsenic
- Vanadium
- Barium
- Zinc
- Beryllium
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Magnesium
- Manganese
- Mercury
- Nickel
- Potassium
- Selenium
- Silver
- Thallium
- Thorium
- Uranium
- Vanadium
- Zinc

Elements in red are not included in other method.
Comparison of 200.8 and 6020A

200.8 Rev 5.4 – 1994 (waters)

Aluminum
Antimony
Arsenic
Barium
Beryllium
Cadmium
Chromium
Cobalt
Copper
Lead
Manganese
Mercury
Molybdenum
Nickel
Selenium
Silver
Thallium
Thorium
Uranium
Vanadium
Zinc

Primary drinking water MCLs established

Secondary drinking water standards established (+ Fe)

No standards for Co, Mo, Ni, or V

6020A Rev 1 - 2007 (wastes)

Aluminum
Antimony
Arsenic
Barium
Beryllium
Cadmium
Chromium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Mercury
Nickel
Potassium
Selenium
Silver
Zinc
Sodium
Thallium
Vanadium
Zinc

Elements in red are not included in other method
A “Universal Method” Would Include:

- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Magnesium
- Manganese
- Mercury
- Nickel
- Potassium
- Selenium
- Silver

- Sodium
- Thallium
- Thorium
- Uranium
- Vanadium
- Zinc

plus appropriate internal standards
Some Other Important Differences

6020A is a performance based method – for example

Section 1.3  “If this method is used to determine any analyte not listed in Sec. 1.2, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Sec. 9.0). Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest in the same manner as the listed elements and matrices (see Sec. 9.0).”

Also-

“In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application”.

200.8 is a prescriptive method that can not be deviated from and is generally required for regulatory compliance with drinking water and waste water monitoring - more on this is a minute
Specific Changes to Method 6020A* (2/07)

6020A is different from 6020 and from the draft version of 6020A

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ISTD recoveries (samples)</td>
<td>30 – 120 %</td>
<td>&gt; 30%</td>
<td>&gt; 70%</td>
</tr>
<tr>
<td>ICV</td>
<td>Near midpoint, not a point on curve</td>
<td>Near midpoint, not a point on curve</td>
<td>Near midpoint</td>
</tr>
<tr>
<td>Low level ICV (LLICV) at reporting limit</td>
<td>N/A</td>
<td>N/A</td>
<td>+/- 30%</td>
</tr>
<tr>
<td>Low level CCV (LLCCV) at reporting limit</td>
<td>N/A</td>
<td>N/A</td>
<td>+/- 30%</td>
</tr>
<tr>
<td>Calibration curve fit</td>
<td>Not specified</td>
<td>Not specified</td>
<td>Linear or 2nd order if corr coef &gt; .998</td>
</tr>
<tr>
<td>Matrix spike (MS)</td>
<td>+/- 25%</td>
<td>+/- 25%</td>
<td>+/- 25%</td>
</tr>
<tr>
<td>Matrix duplicate</td>
<td>&lt;20% RPD (if &gt; 100x IDL)</td>
<td>&lt;20% RPD (if &gt; 100x IDL)</td>
<td>&lt;20% RPD</td>
</tr>
<tr>
<td>Matrix spike duplicate (MSD) for low level samples</td>
<td>N/A</td>
<td>N/A</td>
<td>&lt; 20% RPD</td>
</tr>
</tbody>
</table>

* Not all inclusive
What About 200.8?

The current revision, 5.4 dates back to 1994.

The scope is as follows:

“This method provides procedures for determination of dissolved elements in ground waters, surface waters and drinking water. It may also be used for determination of total recoverable element concentrations in these waters as well as wastewaters, sludges and soils samples.”

200.8 is specified for regulatory compliance for the analysis of drinking waters and wastewaters under the Safe Drinking Water Act and the Clean Water Act (NPDES)
200.8 and Collision Reaction Cell Technology

The use of CRC technology is generally considered the most reliable method for removing polyatomic interferences in ICP-MS (even by EPA).

CRC technology did not exist in 1994, therefore 200.8 does not specify its use for interference removal.

In July, 2006, the EPA Office of Water issued a memo prohibiting the use of CRC ICP-MS for Drinking Water Compliance Monitoring pending further investigations.

Those investigations are continuing and the EPA has completed the round robin phase of the investigation. Based on the initial round robin results, EPA ORD is currently writing an updated method based on He collision mode.

Until the updated version of 200.8 is released or a statement from EPA specifically rescinds the prohibition, drinking water analysis for Compliance Monitoring must still be performed without the use of CRC technology or with the collision/reaction cell unpressurized.
What About CRC and 6020A?

6020A does not specifically mention the use of CRC technology

However in answer to an email from Agilent to EPA Office of Solid Waste in June, 2007, Shen-yi Yang – Inorganic Methods Program Manager at the EPA Office of Solid Waste in Washington DC, stated the following:

“… reaction cell or collision cell technologies are not specifically outlined in the current version of Method 6020A, it is understood their application may have profound effects on eliminating interferences for trace level analyses, and this would be considered as an acceptable modification to Method 6020A as long as it can be demonstrated to be able to determine the analytes of concern in the matrix of concern at the level of concern to meet project-specific DQOs.”
Interim Solutions for Busy Environmental Labs

Since the element lists for 6020 and 200.8 are nearly the same, most labs use a single set of calibration standards that include all elements in both methods.

The QA/QC requirements are also similar and can be combined to meet both method requirements.

The biggest difficulty in combining 200.8 and 6020A is the prohibition on the use of the collision cell in 200.8 for drinking water compliance.
Choices for Dealing with the Collision Cell Issue When Running 200.8 for Drinking Water Compliance

1. Run the methods separately with the cell turned off and using interference equations for drinking water (200.8)

2. Combine the methods and add alternate isotopes (where available) with the cell turned on for these as confirmations – only report element isotopes measured under non-cell conditions for drinking water. Provides excellent confirmation of presence or absence of unexpected interferences.

- For example, Se is normally measured at m/z 77 or 82 without the cell. Both are subject to intense interferences that must be corrected mathematically. 78Se, when measured in collision mode has virtually no interferences and can be used to confirm the result for 77 and 82 AND provide the correct result for samples run according to method 6020A

- Where alternate isotopes are not available (Arsenic for example), the Agilent ICP-MS system allows a single isotope to automatically be measured in multiple modes (cell on and off) and reported independently.

It is ALWAYS advantageous to have a collision cell available for confirmation and eventually EPA will finish the updated version of 200.8 – then it will be essential
Non-Drinking Water Uses of 200.8

The restriction applies ONLY to Drinking Water Compliance Monitoring


May one use collision cell technology with EPA 200.8 for CWA (wastewater) uses?

Yes, provided that you document that the method performance specifications relevant to ICP/MS measurements in the collision mode are met. To answer this question, we considered our experience with CWA methods and problems with matrix interferences, and information that use of a collision cell improved the accuracy of analyses in some wastewater samples. Thus, use of collision cells with EPA Method 200.8 for CWA purposes falls within the scope of the explicit flexibility described at 40 CFR Part 136.6. This regulation, which was promulgated on March 12, 2007, allows, without EPA review, many modifications that improve the performance of CWA (Part 136) methods.
Summary

6020A is new as of 2/07 and has some significant new requirements

   does not specify use of CRC, but allows it due to built-in flexibility

200.8 is still in the update stage with respect to use of CRC technology for Drinking Water Compliance Monitoring

CRC use is specifically approved for Clean Water Act compliance using 200.8 under 40CFR Part 136.6
The New Agilent 7700x ICP-MS and Environmental Monitoring
The Agilent 7700x ICP-MS
Smaller, simpler, faster, more sensitive, more robust than ever

The 7700x was designed for environmental analysis without the need for any reactive gases. It can run everything in He mode or He plus no gas mode.

Completely redesigned Octopole Reaction System (ORS³) eliminates the need for hydrogen reaction mode for most typical applications – Se detection limit in He mode ~ 20ppt

The 7700x was specifically designed for analyzing high matrix, unknown samples with the simplest setup and highest achievable data quality

The proprietary HMI (high matrix introduction accessory) is standard permitting analysis of samples containing % level dissolved solids while also permitting ppt or sub ppt detection limits for trace elements (under the same hardware configuration)
Superior Interference Removal Under Generic, Universal Conditions (3 sigma MDLs in 1% nitric / 0.5% HCl)

4 tough elements over entire mass range.

Difficult Cl based interferences completely removed.

High and low mass sensitivity in no gas mode preserved.
Drinking Water Detection Limits – 3 sigma of 7 replicates

<table>
<thead>
<tr>
<th>Mass</th>
<th>Element</th>
<th>MDL (ppt)</th>
<th>Cell mode</th>
<th>Mass</th>
<th>Element</th>
<th>MDL (ppt)</th>
<th>Cell mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Be</td>
<td>5.2</td>
<td>No gas</td>
<td>66</td>
<td>Zn</td>
<td>14.0</td>
<td>He</td>
</tr>
<tr>
<td>11</td>
<td>B</td>
<td>5.0</td>
<td>No gas</td>
<td>75</td>
<td>As</td>
<td>11.9</td>
<td>He</td>
</tr>
<tr>
<td>23</td>
<td>Na</td>
<td>58.5</td>
<td>No gas</td>
<td>78</td>
<td>Se</td>
<td>17.6</td>
<td>He</td>
</tr>
<tr>
<td>24</td>
<td>Mg</td>
<td>2.8</td>
<td>No gas</td>
<td>88</td>
<td>Sr</td>
<td>2.1</td>
<td>He</td>
</tr>
<tr>
<td>27</td>
<td>Al</td>
<td>7.9</td>
<td>No gas</td>
<td>95</td>
<td>Mo</td>
<td>6.9</td>
<td>He</td>
</tr>
<tr>
<td>39</td>
<td>K</td>
<td>76.9</td>
<td>He</td>
<td>107</td>
<td>Ag</td>
<td>2.3</td>
<td>He</td>
</tr>
<tr>
<td>42</td>
<td>Ca</td>
<td>57.8</td>
<td>He</td>
<td>111</td>
<td>Cd</td>
<td>2.9</td>
<td>He</td>
</tr>
<tr>
<td>51</td>
<td>V</td>
<td>14.3</td>
<td>He</td>
<td>121</td>
<td>Sb</td>
<td>6.1</td>
<td>He</td>
</tr>
<tr>
<td>52</td>
<td>Cr</td>
<td>4.3</td>
<td>He</td>
<td>137</td>
<td>Ba</td>
<td>5.7</td>
<td>He</td>
</tr>
<tr>
<td>55</td>
<td>Mn</td>
<td>8.5</td>
<td>He</td>
<td>202</td>
<td>Hg</td>
<td>1.2</td>
<td>He</td>
</tr>
<tr>
<td>56</td>
<td>Fe</td>
<td>14.8</td>
<td>He</td>
<td>205</td>
<td>Tl</td>
<td>2.4</td>
<td>He</td>
</tr>
<tr>
<td>59</td>
<td>Co</td>
<td>4.4</td>
<td>He</td>
<td>208</td>
<td>Pb</td>
<td>1.3</td>
<td>He</td>
</tr>
<tr>
<td>60</td>
<td>Ni</td>
<td>14.7</td>
<td>He</td>
<td>232</td>
<td>Th</td>
<td>1.8</td>
<td>He</td>
</tr>
<tr>
<td>63</td>
<td>Cu</td>
<td>2.7</td>
<td>He</td>
<td>238</td>
<td>U</td>
<td>1.7</td>
<td>He</td>
</tr>
</tbody>
</table>

3 sigma method detection limits in parts per trillion (ppt) for trace elements in drinking waters. Note Fe and Se detection limits are less than 20ppt in helium mode.
ISIS-DS High Speed Discrete Sampling for the 7700 ICP-MS

Fully integrated, Agilent supported discrete sampling for the 7700

Requires 1 ISIS peripump and 6-port valve
**ISIS-DS configuration**

**Load Loop**
- Sample loop to nebulizer
- 6-port valve
- ISIS P1
- P2
- Carrier to waste
- ISTD mixing "tee"
- Load Loop sample ISTD

**Inject Sample**
- Sample loop to nebulizer
- 6-port valve
- ISIS P1
- P2
- Carrier to waste
- ISTD mixing "tee"
- Inject Sample sample ISTD
ISIS-DS High Speed Discrete Sampling for the 7700 ICP-MS

ISIS-DS uses steady state spectrum mode acquisition exactly like traditional ICP-MS acquisition, allowing as many elements and replicates as needed for the application.

The sample loop size determines the available acquisition time.

Only the uptake and rinseout are changed.
Faster

Eliminating the need for H2 mode results in faster acquisition which when coupled with ISIS-DS results in the fastest collision cell ICP-MS ever.

31 elements including internal standards, 3 reps, EPA compliant analysis in **75.6 seconds** run to run.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma</td>
<td>Robust mode – 1550 Watts</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>Glass concentric (standard)</td>
</tr>
<tr>
<td>Number of elements (including internal standards)</td>
<td>31</td>
</tr>
<tr>
<td>ORS Mode</td>
<td>He - 4 mL/min (single mode)</td>
</tr>
<tr>
<td>Integration time per point</td>
<td>0.1 seconds (all elements)</td>
</tr>
<tr>
<td>Points per peak</td>
<td>1</td>
</tr>
<tr>
<td>Replicates</td>
<td>3</td>
</tr>
<tr>
<td>Total acquisition time (3 reps)</td>
<td>26 seconds</td>
</tr>
<tr>
<td>Loop volume</td>
<td>300µL</td>
</tr>
<tr>
<td>Loop rinse and fill time</td>
<td>8-10 seconds</td>
</tr>
<tr>
<td>Acquisition delay (after valve rotation to inject)</td>
<td>15 seconds</td>
</tr>
<tr>
<td>Steady state signal time (before valve rotation to fill again)</td>
<td>30 seconds</td>
</tr>
</tbody>
</table>
**Excellent Washout – even at ultra high speed analysis**

Washout is always a concern with high speed analysis.

Here, a sequence containing 216 samples including 26 replicates each of EPA ICS-AB followed by a blank was analyzed and the mean reduction in concentration calculated.

Washout, even for difficult elements like Ag, Sb, Mo and Tl is equivalent to or better than standard system using much longer rinse times.

<table>
<thead>
<tr>
<th>Element</th>
<th>ICS-AB spike mean</th>
<th>Blank mean</th>
<th>% reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 Be</td>
<td>94.9315</td>
<td>0.0199</td>
<td>99.979%</td>
</tr>
<tr>
<td>23 Na</td>
<td>9670.6923</td>
<td>19.6032</td>
<td>99.980%</td>
</tr>
<tr>
<td>24 Mg</td>
<td>79238.8462</td>
<td>14.2332</td>
<td>99.982%</td>
</tr>
<tr>
<td>27 Al</td>
<td>75758.0769</td>
<td>11.7913</td>
<td>99.984%</td>
</tr>
<tr>
<td>39 K</td>
<td>82694.2308</td>
<td>17.6441</td>
<td>99.979%</td>
</tr>
<tr>
<td>43 Ca</td>
<td>9092.8462</td>
<td>1.4105</td>
<td>99.984%</td>
</tr>
<tr>
<td>53 Cr</td>
<td>95.7327</td>
<td>0.0419</td>
<td>99.956%</td>
</tr>
<tr>
<td>55 Mn</td>
<td>94.8977</td>
<td>0.0132</td>
<td>99.986%</td>
</tr>
<tr>
<td>56 Fe</td>
<td>77021.9231</td>
<td>12.5122</td>
<td>99.984%</td>
</tr>
<tr>
<td>57 Fe</td>
<td>75266.5385</td>
<td>12.0863</td>
<td>99.984%</td>
</tr>
<tr>
<td>59 Co</td>
<td>106.8577</td>
<td>0.0140</td>
<td>99.987%</td>
</tr>
<tr>
<td>60 Ni</td>
<td>101.3692</td>
<td>-0.0161</td>
<td>100.016%</td>
</tr>
<tr>
<td>63 Cu</td>
<td>98.5700</td>
<td>0.0163</td>
<td>99.984%</td>
</tr>
<tr>
<td>66 Zn</td>
<td>99.9350</td>
<td>0.0055</td>
<td>99.994%</td>
</tr>
<tr>
<td>75 As</td>
<td>95.8615</td>
<td>0.0290</td>
<td>99.970%</td>
</tr>
<tr>
<td>78 Se</td>
<td>94.0162</td>
<td>0.0841</td>
<td>99.911%</td>
</tr>
<tr>
<td>95 Mo</td>
<td>1862.3077</td>
<td>1.4281</td>
<td>99.923%</td>
</tr>
<tr>
<td>107 Ag</td>
<td>96.8769</td>
<td>0.0181</td>
<td>99.981%</td>
</tr>
<tr>
<td>111 Cd</td>
<td>104.0538</td>
<td>0.0134</td>
<td>99.987%</td>
</tr>
<tr>
<td>121 Sb</td>
<td>109.1346</td>
<td>0.2629</td>
<td>99.759%</td>
</tr>
<tr>
<td>205 Tl</td>
<td>93.4731</td>
<td>0.0339</td>
<td>99.964%</td>
</tr>
<tr>
<td>208 Pb</td>
<td>92.4704</td>
<td>-0.0175</td>
<td>100.019%</td>
</tr>
</tbody>
</table>
Questions?
Thank You