EPA Methods Update

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

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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1972	Water Pollution Control Act (later superseded by CWA)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 offices within EPA

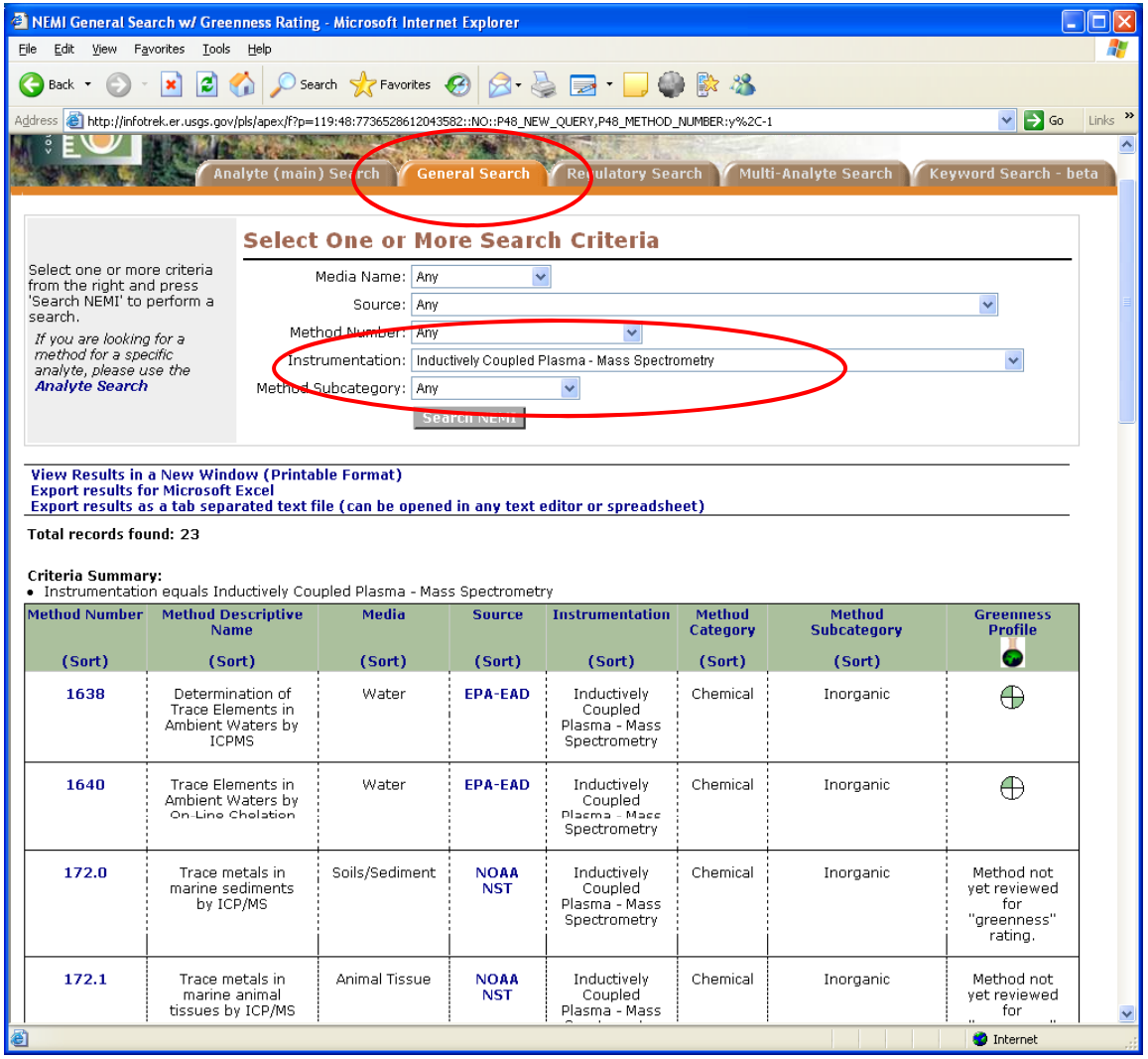
- Office of Air and Radiation
- Office of Prevention, Pesticides, and Toxic Substances
- Office of Research and Development
- Office of Solid Waste and Emergency Response
- Office of Water
- …

NEMI.GOV (National Environmental Methods Index)

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.



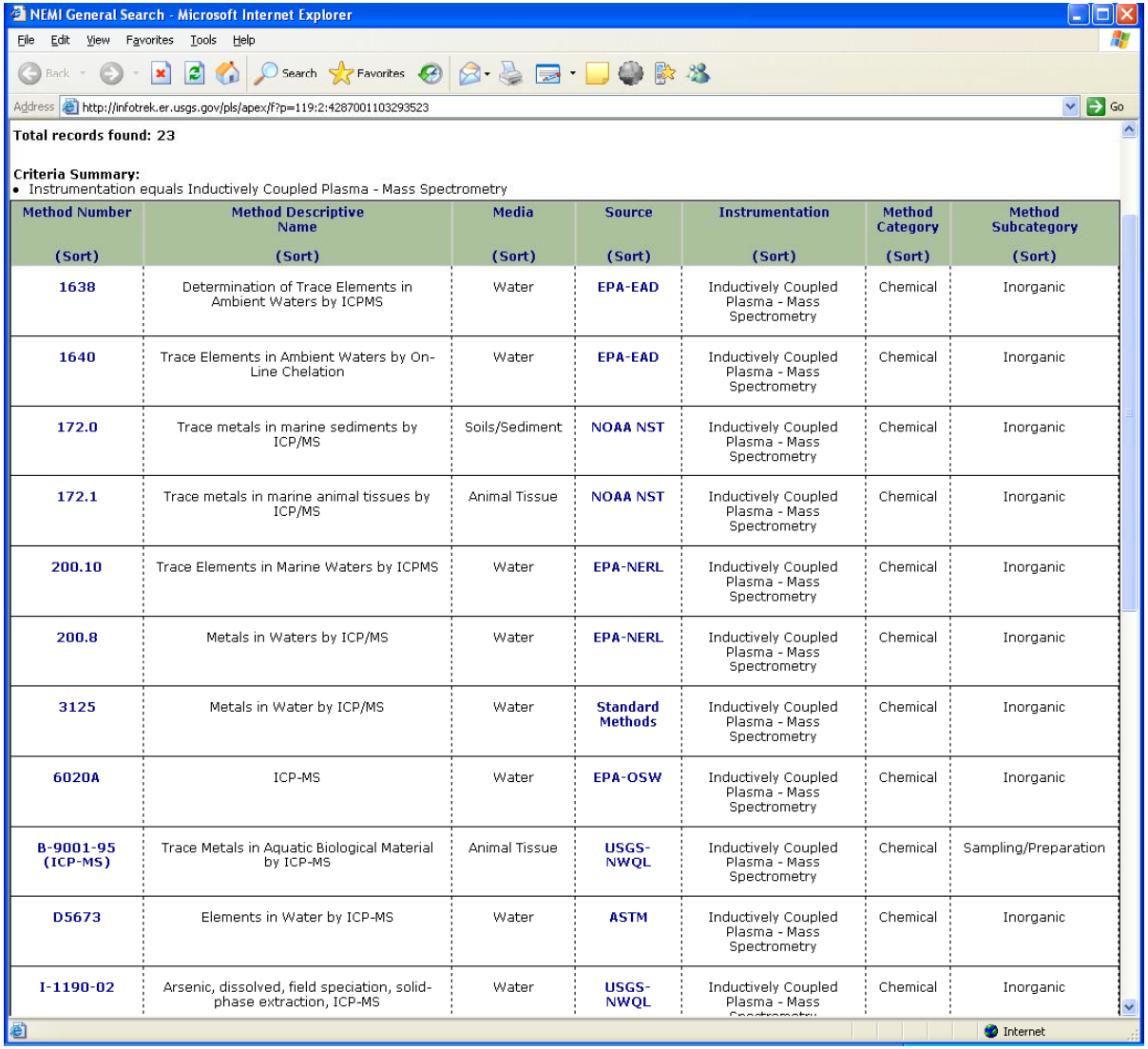
ICP-MS Methods

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



NEMI General Search - Microsoft Internet Explorer

File Edit View Favorites Tools Help

Address http://infotrek.er.usgs.gov/pls/apex/f?p=119:2:4287001103293523

Total records found: 23

Criteria Summary:

- Instrumentation equals Inductively Coupled Plasma - Mass Spectrometry

Method Number (Sort)	Method Descriptive Name (Sort)	Media (Sort)	Source (Sort)	Instrumentation (Sort)	Method Category (Sort)	Method Subcategory (Sort)
1638	Determination of Trace Elements in Ambient Waters by ICPMS	Water	EPA-EAD	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Inorganic
1640	Trace Elements in Ambient Waters by On-Line Chelation	Water	EPA-EAD	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Inorganic
172.0	Trace metals in marine sediments by ICP/MS	Soils/Sediment	NOAA NST	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Inorganic
172.1	Trace metals in marine animal tissues by ICP/MS	Animal Tissue	NOAA NST	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Inorganic
200.10	Trace Elements in Marine Waters by ICPMS	Water	EPA-NERL	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Inorganic
200.8	Metals in Waters by ICP/MS	Water	EPA-NERL	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Inorganic
3125	Metals in Water by ICP/MS	Water	Standard Methods	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Inorganic
6020A	ICP-MS	Water	EPA-OSW	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Inorganic
B-9001-95 (ICP-MS)	Trace Metals in Aquatic Biological Material by ICP-MS	Animal Tissue	USGS-NWQL	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Sampling/Preparation
D5673	Elements in Water by ICP-MS	Water	ASTM	Inductively Coupled Plasma - Mass Spectrometry	Chemical	Inorganic
I-1190-02	Arsenic, dissolved, field speciation, solid-phase extraction, ICP-MS	Water	USGS-NWQL	Inductively Coupled Plasma - Mass	Chemical	Inorganic

Internet

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

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

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

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
Antimony
Arsenic
Barium
Beryllium
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Mercury
Nickel
Potassium
Selenium
Silver
Sodium
Thallium
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
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Mercury
Nickel
Potassium
Selenium
Silver
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 in a minute

Specific Changes to Method 6020A* (2/07)

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

Criteria	6020 (1994)	6020A draft (1998)	6020A final (2007)
ISTD recoveries (samples)	30 – 120 %	> 30%	> 70%
ICV	Near midpoint, not a point on curve	Near midpoint, not a point on curve	Near midpoint
Low level ICV (LLICV) at reporting limit	N/A	N/A	+/- 30%
Low level CCV (LLCCV) at reporting limit	N/A	N/A	+/- 30%
Calibration curve fit	Not specified	Not specified	Linear or 2nd order if corr coef > .998
Matrix spike (MS)	+/- 25%	+/- 25%	+/- 25%
Matrix duplicate	<20% RPD (if > 100x IDL)	<20% RPD (if > 100x IDL)	<20% RPD
Matrix spike duplicate (MSD) for low level samples	N/A	N/A	< 20% RPD

* 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 is preparing for the round robin phase of the investigation. They are working with Agilent's full support.

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

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

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. ^{78}Se, 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 ChemStation 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

More recently – taken from EPA Q&A website:
http://www.epa.gov/waterscience/methods/update/questions.html

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.

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*."

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 review 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


Thank You

Upcoming ICP-MS eSeminar

ICP-MS – The Role of Elemental Mass Spectrometry in Life Sciences Research

Presenter: Dr. Joseph Caruso,
University of Cincinnati

May 8, 2008 – 1:00pm EDT