Auditing ICP Methods EPA 200.7, Rev. 4.4 SW-846 6010B

Assessment Forum

Winter 2008

Inductively Coupled Plasma

- Commonly used for metals minimizing the use of flame AA technology.

- Current approved EPA method revisions:
  - 200.7, Rev. 4.4 for DW and WW
  - 6010B for Solid Waste
  - SM 3120 not commonly used

Initial Demonstration of Performance

- Initial Demonstration of Performance (6010B, 7.2.1 & 200.7, 9.2)
  - Inter-element corrections and background corrections
  - Linear Dynamic Ranges
  - Method Detection Limit Studies
  - Quality Control Sample Analysis

Instrument Set-up for Inter-Element and Background Corrections

- AQ- Must record the need for IEC annually. Analyze Spectral Interference Check either way. Verification may not be required daily.
  - Needed if ±3-sigma control limits of cal blank.
  - Needs updating if a 10% change has occurred. (200.7, 4.1, 7.13 & 10.4)
- SW - Verified every 6 mo.
  - no major instrument change, for example the nebulizer flow rate must be <2% change (maintenance log info).
  - Needed if greater than IDL, or less than lower control limit of cal blank.
  - Needs updating if >10% change. (6010B, 3.1 & 7.2).

Linear Dynamic Range

- Both methods allow for calibration with a blank and 1 standard, but must verify each wavelength used at higher end of the LDR (200.7, 9.2.2 & 6010B, 7.2.4).
  - Calibrate as usual.
  - Analyze succeeding higher standards (min. of 3).
  - Recovery must be at least 90% of the true value.
  - Verification done annually (200.7), semiannually for analytes that approach LDR (6010B) or if had significant change in instrument response.
  - Any sample value higher than 90% of the determined LDR must be diluted.
  - SOP must specify calibration curve type and LDR specifics (5.5.4.1.2.b. & 5.5.5.2.2.1)

Method & Instrument Detection Limit Studies

- AQ-Annually or new analyst (200.7, 9.2.4).
- SW-MDLs on ea. instrument, for each wavelength (6010B, 7.2.5.1).

Important that the established LOQ is above the LOD (D.1.2.2.1).

Recommend:

MDLs be done over three nonconsecutive days, making it more representative (DW Manual, Chapter IV, Section 7.11 & 40 CFR, Part 136, Appendix B).

If more replicates run use all, unless a very well documented (statistical) reason to drop, but ensure appropriate Student-T is used.

Quality Control Sample vs Daily Initial Calibration Check

- A second source (independent lot ok) check to verify the calibration curve standard preparation (5.5.5.2.2.1).
  - AQ - QCS req. quarterly within ±5% recovery (200.7, 9.2.3).
  - SW - The ICV is the daily second source check (6010B, 5.4).
- Standard analyzed immediately after calibration.
  - AQ - IPC is midlevel std within ± 5% recovery & <3% rsd from replicate integrations (200.7, 9.3.4).
  - SW - ICV is second source within within ±10% recovery and <5% rsd from 2 integrations (6010B, 5.6 & & 7.4).

Most laboratories combine the methods running the Initial IPC (200.7) or ICV (6010B) as a second source to be within ±5% recovery.

Interelement Interference Check

- Interelement interference check standard:
  - AQ - At minimum annually (dw w/ interferent < 10 mg/L), daily for serious interferences, or weekly if 5 consecutives days within ±10% (200.7, 7.13).
  - SW - beg of each run w/in ±20%, if 5 consecutive days acceptable, can do weekly (6010B, 3.1.9, 5.8 & 8.6.2).

Most labs use the ICSA (interferents)/ICSAB (interferents and trace elements) standards daily and require the recovery to be within ± 20% recovery.

Continuing Calibration Check

- Calibration check standard analyzed at a 10% frequency and end of run (5.5.5.2.2. & 5.5.5.10):
  - AQ – Continuing IPC is same source, within ±10% (200.7, 9.3.4).
  - SW - CCV is mid level standard or can be second source within ±10% (6010B, 7.4, 5.7 & 8.6.1).

Can immediately reanalyze the failing CCV once, then if fails again follow with two acceptable CCVs or recalibrate. NDs can be reported following a high bias CCV and samples exceeding regulatory limits can be reported if following a low bias CCV as long as it's qualified (5.5.10.e).

Continuing Calibration Blank

- Calibration Blank analyzed at a 10% frequency (usually before or after ea. instrument check standard) and at the end:
  - AQ - less than analyte IDL but > lower 3 sigma of cal blank (200.7, 9.3.4).
  - SW - 3 times the IDL or 3 sd of the background mean or recalibrate if blank is >1/10 conc. of action level and sample w/in 10% of action limit (6010B, 5.5.1, 7,4 & 8.6.1.3).

Method Blank

- Method Blank (D.1.1.1) (Digested reagent blank):
  - AQ – When LRB constitute 10% or more of the analyte level determined for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again.
  - SW - Method Blank per sample batch (6010B, 5.5.2/8.3). Should not be higher than the highest of either:
    - MDL, or
    - 5% of the regulatory limit for that analyte, or
    - 5% of the measured concentration in the sample.
  - Most States simply require the Method Blank to be <RL, otherwise a qualified final report is required.
  - In addition, NELAC std requires that the criteria that the MB result is < than 1/10 of the amount in any sample (D.1.1.1.d.1).

Laboratory Control Sample

- Spiked blank (same or second source), carried thru entire sample prep (digestion) and analysis with each batch (5.4.4.2.2):
  - AQ - LFB within ±15% (200.7, 9.3.2.).
  - SW - LCS (SW-846, Chapter 3, rev. 3, 12/96 & Digestion procedures 3***). Limits not specified.

All components should be spiked for ICP analysis (D.1.1.2.1.c)

An LFB at the MRL should be analyzed with each batch (DW Manual, 5th ed., Chapter IV, Section 7.2.12) . Most laboratories follow a ±50% recovery for the LFB at the MRL or establish historical limits.

Duplicates

- Duplicates for every 20 samples or per analytical batch (D.1.1.3):
  - AQ - suggested, but limits and frequency not specified (200.7, 3.8/9.4.1).
  - SW - MS dups within ±20 RPD or control limits for each matrix (6010B, 8.4).

Digested Matrix Spike

- Digested Matrix spike (D.1.1.3):
  - AQ - LFM at 10% frequency or one per set (±30%), same source as LFB (200.7, 9.4.2/9.4.3).
  - SW - MS and MS dup per matrix batch. Spike recovery within ±25% or control limits for ea. matrix (6010B, 8 .4.1.2).

To meet the 200.7 (10%) frequency requirement an MS/MSD pair per batch of 10 samples would be required.

Additional QC Checks for New or Unusual Matrices

- Dilution test :
  - AQ - 1:4 dilution within 10% of original (200.7, 9.5.2).
  - SW - 1:5 dilution within 10% of original (6010B, 8.5.1).
- Post-digestion spike for new or unusual matrix:
  - AQ - within ±15% (200.7, 9.5.1).
  - SW - within ±25% (6010B, 8.5.2).
- Method of Standard Additions:
  - AQ - when serial dilution or post spike have failed, can use single addition method (200.7, 9.5/11.5).
  - SW - can use single addition method (6010B, 7.7).

Maintenance Logs

- Instrument Maintenance Logs (5.5.5.5.5).
  - When was the last documented entry and what does the laboratory normally record? i.e. nebulizer flow rate, tracking of intensity count of profiling standard, troubleshooting and resolution information.
  - Several Items listed in 2003 NELAC checklist.

Recommend:

Service Reps record maintenance or attach a copy of the work order to the maintenance log.

Preparation Procedures

- If > 1 NTU, must be digested:
  - AQ-Turbidity must be checked 16 hours after preservation (200.7, 11.2.1). Must be preserved within two weeks of sampling (200.2, 8.1).
  - SW-All samples (water & soil) must be digested for total metals unless reported as dissolved (filtered groundwater) or undigested if matrix matched to standards or IS used (6010B, 1.1).

pH checks and turbidity results with time of analysis must be documented (5.5.8.3.1.b).

MUR – For CWA, acid preservation not done immediately (within 15 min.) the acid contact time must be for at least 24 hours before analysis (40 CFR, Part 136 Table II, Footnote 19).

Preparation Procedures

- Approved digestion procedures:
  - AQ - 200.2 & 200.7, section 11.2. Silver should be digested (200.7, 1.7)
  - WW-CEM Microwave digestion for some wastewater analytes.
  - DW-Microwave digestion/heating allowed by EPA maintaining method heating temperatures in referenced method.
  - SW-aqueous; 3005A, 3010A, 3015A, soils/sludges 3050B, 3051, 3052; soils 3031, 3041.

*Lab needs to reference and follow the methods and applicable preparations within same programs.

*Digestion records to include for each batch (5.4.12.2.5.3):

date/time, temperature, traceability of standards, reagents and hotblock digestion tubes, if used & mechanical pipet volume verification (5.5.5.2.1)

Current Developments

- Collision Cell Technology
  - Approved for CWA and SW-846 analyses.

    Rationale for allowing CWA use is addressed in the following FAQ website http://www.epa.gov/waterscience/methods/update/

    Currently not approved for SDW referencing 200.7.

- Use of internal standard allowed in both methods but no implementation specifics in either method. Laboratory needs to establish criteria and use in SOP.

Current Developments

- CWA EPA has recommended (Memo from Richard Reding dated 11/7/07) allowing the addition of metals listed in the 200.7 method but not included in the MUR, however each Region must be consulted prior to allowing in each State accreditation program.

- Common finding; ICP instruments that do not show raw intensity counts on the print-out if providing the concentration value, therefore the raw counts are not saved. Many laboratories do not store the data electronically (5.4.7.2 & 5.5.5.2.2.1).

References

- AQ -"Methods for the Determination of Metals in Environmental Sample," Supplement 1, EPA/600/R-94/111, May 1994. EPA 200.7, Revision 4.4 May 1994, & 200.2, rev. 2.8 (Drinking Water & Wastewater).
- SW -6010B, SW-846, Revision 2, December 1996 (Hazardous Waste).
- MUR – Method Update Rule 40 CFR, Parts 136 & 121, 3/12/07. http://www.epa.gov/fedrgstr/EPA-WATER/2007/March/Day-12/w1073.htm
- DW - "Manual for the Certification of Laboratories Analyzing Drinking Water," EPA-815B-97-001, March 1997.
- NELAC 2003 Standards – http://www.nemc.us/epa12/2003standards.html
- ORELAP website for list of method specific checklists shared by several States: http://www.deq.state.or.us/lab/orelap/orelapchklist.htm

Barbara A. Escobar

AZDHS
Environmental Program Manager
250 N. 17th Ave.
Phoenix, AZ 85007
(602) 616-1945