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Forum on Environmental Measurements
U. S. Environmental Protection Agency
Office of the Science Advisor
109 T.W. Alexander Drive (E243-05)
Research Triangle Park, NC 27711

RE: Method Harmonization Update and Method Comparisons

Dear Ms. Phelps:

During the Environmental Laboratory Advisory Board (ELAB or Board) August 2014 face-to-face meeting in Washington, D.C., ELAB members discussed with EPA how the Agency's efforts to harmonize various procedures within similar EPA test methods for similar matrices might be enhanced. At that meeting, EPA recommended that ELAB compare three to five test methods from different EPA offices and suggest what procedures might be amenable to harmonization. The purpose of this letter is to provide an update on the Board's efforts to identify method procedures that can be practically harmonized.

First, ELAB would like to reiterate its appreciation of EPA's efforts in considering more efficient, effective and harmonized ways to establish new test methods or update older methods in a manner that does not jeopardize the data quality objectives of the method. ELAB's suggestions are meant to provide EPA examples as to where method harmonization may be possible.

ELAB reviewed six method categories, recognizing that there are certain restraints that hinder harmonization efforts, such as matrix issues, program data quality objectives and promulgated regulatory requirements. A brief synopsis of the Board's findings is provided in Attachment 1. Details of the comparisons are provided in Attachments 2–7. For the purpose of this evaluation, the Board only considered an aqueous matrix. Test method categories reviewed include:

- LC/MS/MS Methods (Methods 1694, 537 and 6850) (See Attachment 2).
- Chlorinated Herbicide GC Methods (Methods 615, 8151A and 515.4) (See Attachment 3).
- Ion Chromatography Methods (Methods 300.0, 300.1 and 9056A) (See Attachment 4).
- Total Organic Carbon Methods (Methods 415.3 and 9060A) (See Attachment 5).
- Metals by ICP Methods (Methods 200.7 and 6010C) (See Attachment 6).
- Metals by ICP/MS Methods (Methods 200.8 and 6020A) (See Attachment 7).

ELAB hopes you find the suggestions beneficial. When considering these suggestions, you may find historical method performance data helpful in determining whether harmonizing certain quality control criteria significantly hinders meeting method data quality objectives. The Board looks forward to receiving your thoughts on this matter.

Sincerely,

Dallas Wait

A. Dallas Wait
Chair, Environmental Laboratory Advisory Board

Attachment 1 Synopsis of Findings

1 LC/MS/MS Methods

- **Confirmatory ions –** None are provided for Methods 537 and 1694 but are provided for Method 6850.
- **Calibration standards –** Different requirements for each method (Method 537 = greater than or equal to 5 standards, Method 6850 = 6 standards, Method 1694 = 5 standards).
- **Calibration method –** Different approach for each method.
- **Continuing calibration verification (CCV) criteria –** Different approach for each method.
- **Retention time windows –** Different approach for each method.
- **Identification criteria –** Different approach for each method.
- **Method detection limit (MDL) requirements** – Different approach for each method.

2 Chlorinated Herbicide GC Methods

- **Extraction solvents –** Methods 615 and 8151A use diethyl ether, whereas Method 515.4 uses methyl tert-butyl ether (MtBE).
- **Calibration standards –** Methods 8151A and 515.4 use 5 standards, whereas Method 615 uses only 3 standards.
- **Calibration method –** Method 615 uses an external method, Method 515.4 uses an internal method, and Method 8151A allows for either an internal or external method.
- **Calibration curve relative standard deviation (RSD) criteria –** Method 615 RSD criteria = less than or equal to 10%, Method 8151 RSD criteria = less than or equal to 20%, and Method 515.4 criteria = less than 30%.
- **Retention time windows –** Same approach for Methods 615 and 515.4 but different for Method 8151A.
- **Calibration verification –** Different approach for each method.

3 Ion Chromatography Methods

- **EPA Method 300.0, Rev 2.1 (1993) Approved for DW&WW**
- **EPA Method 300.1-1 Rev 1.0 (1997) Approved for WW**
- **EPA Method 300.1, Rev 1.0 (2000) Approved for DW**
- **EPA Method 9056A**

- **Preservations –** Differences on preservation and holding times between Method 300 and Method 9056A.
- **Calibration –** Different approach to calibration curves among Methods 300.0, 300.1, and 9056A.
- **Calibration verification –** Different approach to verification standards (2nd source/same), verification concentrations, and acceptance criteria among Methods 300.0, 300.1, and 9056A.
- **Quality control (QC):**

- Batch frequency different among Methods 300.0, 300.1, and 9056A.
- QC required different among methods.
- QC acceptance criteria requirements different among methods.

- **Sensitivity:**
  - Methods 300.0 and 300.1 use MDLs and MRLs. Method 9056A uses LLOQ verifications or lower calibration standard.

4 Total Organic Carbon Methods (415.3 Rev 1.1/415.3 Rev 1.2/9060A)

- **Calibration:**

- **Method 415.3** – Very specific calibration requirements *vs.* Method 9060A, which is not specific.
- **Method 415.3 –** Calibration verification and QCS (2nd source) *vs.* Method 9060A a CCV of a 2nd source.
- **Method 415.3 –** CCC every 10 samples *vs.* Method 9060A every 15 samples.
- **Method 415.3** – CCC at rotating concentrations at low-, mid- and high-calibration range with different acceptance criteria depending on concentration *vs.* not specified in Method 9060A.
- **Field QC:**

- **Method 415.3** – Require field duplicates with specified acceptance criteria *vs.* Method 9060A, which requires none.
- **Quality Control:**

- Method 9060A requires quadruplicate analysis. Not required in Method 415.3.
- Laboratory-fortified blank required for Method 415.3 but not included in Method 9060A.
- Laboratory-fortified matrix:
  - Method 415.3 acceptance criteria of 30%. None given in Method 9060A.
  - Method 415.3 every 20 samples *vs.* Method 9060A every 10 samples.
  - Method 415.3 spike all samples sources overtime *vs.* Method 9060A not required.
- **Demonstration of Performance:**

- Method 415.3 very specific *vs.* Method 9060A not specific.

5 Metals by ICP Methods

- **Sample preparation –** Method 200.7 allows for direct analysis if pH is less than 2 and turbidity less than 1. Method 6010C requires digestion.
- **Interelement correction tables –** Updated annually for Method 200.7 and every 6 months for Method 6010C, assuming daily verification is acceptable and there have been no changes in instrument operating conditions.
- **Spectral interference checks –** Method 200.7 recovery range of 90-110%, and 80-120% for Method 6010C.
- **Calibration verification –** Method 200.7 recovery range of 95-105%, and 90-110% for Method 6010C.
- **Method blank –** Method 200.7 less than 10% of analyte level for sample or is less than 2.2 times than the analyte MDL. Method 6010C less than 10% of analyte level of sample or less than 10% of regulatory limit.
- **Method spike –** Method 200.7 recovery range of 85-115%, and 80-120% for Method 6010C.
- **Matrix spike** – Method 200.7 recovery range of 70-130%, and 75-125% for Method 6010C.

6 Metals by ICP/MS Methods

- SW846 Methods are performance based, whereas Method 200.8 and CLP Methods are prescriptive.
- Method 6020A requires curve correlation of 0.998, but Methods 6020 and 200.8 require correlation of 0.995.
- Method 6020A requires the low level check be +/- 30%, whereas Methods 6020 and 200.8 require +/- 50%.
- Prep blank limits are consistent for Methods 6020A and 200.8 (acceptable if sample concentration is greater than 10x PB). Method 6020 requires greater than 20x PB.
- Methods 6020 and 6020A require LCS/LCSD to be +/- 20%, but Method 200.8 requires LCS to be +/- 15% if statistical limits are not available.
- Methods 6020 and 6020A require MS to be +/- 25%, but Method 200.8 requires LCS to be +/- 30% if statistical limits are not available.
- Internal Standards…For Method 6020: 30%–120% for samples 80%–120% for ICV, CCVs, ICB, and CCBs. 30%-120% for LLC, ICSA, and ICSAB. For Method 6020A: 70–130% for samples. 200.8: Must be 60%–125% of the calibration blank.

Attachment 2 LC/MS/MS Methods

Method Number	EPA Method 537	EPA Method 1694	EPA Method 6850
	LC/MS/MS SRM Perfluorinated Alkyl Acids in Drinking Water	LC/MS/MS SRM Pharmaceuticals in Water, Soil, Sediment and Biosolids	LC/MS and LC/MS/MS SRM Perchlorate in Water, Soils and Solid Wastes
Parameters			
Confirmatory Ion	No	No	Yes
Calibration	- Internal Calibration - $\geq$ 5 ICAL standards, forced through zero - The highest and lowest internal area response of all ICAL standards should have a RPD of < 20% - Each ICAL standard concentration calculated from curve should be within 30% of true value, except low ICAL should be within 50% - Linear or quadratic regression - CCV criteria should be within 30% or within 50% for Low standards; Surrogates should be within 30%. - Peak Symmetry should be 0.8 to 1.5	- Internal Calibration - 5 ICAL standards - Average relative response factor for isotope dilution of % RSD <20% or regression analysis - Average response factor (RF) for internal standard technique % RSD <35% or regression analysis - CCV criteria – Signal/Noise ratio>10 and meets acceptance criteria specified in Table 12 of Method	- Internal Calibration - 6 ICAL standards are recommended - Linear calibration $R^2 \geq 0.995$. - Quadratic calibration $R^2 \geq 0.995$ - ICV +/- 15% - CCV every 10 Samples and before and after each batch of samples
Retention Time (R.T.) Windows	- Within a retention time window defined as +/- 3 Standard Deviations of the average RT of the ICAL standards	+/-15 seconds of Mid-level ICAL	- Retention times of perchlorate and its isotope should be within 0.2 minutes
Qualitative	- RT (+/- 3 Standard Deviation)	- RT (+/-15 seconds) -Signal/Noise ratio $\geq$ 2.5	- RT +/-0.2 minutes - mz 83 to 85 ratio should be +/-30% for LC/MS
MDL	DL (MDL) is optional Verification of Minimum Reporting Limit (MRL) is required (7 standards at MRL) Lowest ICAL standard $\leq$ the MRL The Lowest Concentration MRLs (LCMRL) are in Table 5 of Method	MDL is listed in Tables, 3,5, 7 and 9 of Method Minimum Level of Quantitation (ML) in Tables, 3,5,7 and 9 of Method	RL is the Lowest Level Calibration Standard

Method Number	EPA 300.0	EPA 300.1	EPA Method 9056 A
	PART A. – Bromide, Nitrite, Chloride Ortho-Phosphate-P, Fluoride, Sulfate, Nitrate PART B. – Bromate, Chlorite, Chlorate. Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids after extraction, leachates (when no acetic acid is used).	PART A.-- Common Anions: Bromide Nitrite Chloride ortho-Phosphate-P,Fluoride Sulfate Nitrate PART B.-- Inorganic Disinfection By-products: Bromate, Chlorite, Bromide, Chlorate In reagent water, surface water, ground water, and finished drinking water	Chloride, Fluoride, bromide, nitrate, nitrite, phosphate, sulfate in aqueous, DW, WW, and extracts of other matrices.
Parameters			
Preservation, holding time	4 °C H_2SO_4 for NO_3+NO_2 and EDA for chlorite. Nitrate, Nitrite, and orthophosphate within 48 hrs. All others within 28 days.	4 °C H_2SO_4 for NO_3+NO_2 and EDA for chlorite. Nitrate, Nitrite, and orthophosphate within 48 hrs. All others within 28 days.	6 °C Nitrate, Nitrite, and orthophosphate within 48 hrs. All others more than 48 hrs but not specified.
Calibration	3 calibration standards and a blank	3 calibration standards are required for a curve that extends over a single order of magnitude and a minimum of 5 calibration standards are required if the curve covers two orders of magnitude. Acceptable if calibration verifications pass or use <15% RSD.	Blank and 3 standards Least square regression and r ≥ 0.995 or weighted least squares 1/conc or 1/con2 and r≥ 0.995
Calibration verification	The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are still more than ±10%, a new calibration curve must be prepared for that analyte.	ICV – Same source as cal std. CCV – Same source as cal std. After 10 field samples and end of the run. Verification criteria 75-125% from MRL- 10xMRL and 85-115% from 10xMRL to highest cal point. If MRL is not established within a factor of 10, then criteria is 85-115%.	ICV – Independent source. ±10% CCV – Same source as cal std. Each day and every 10 samples. ±10%

Method Number	EPA 300.0	EPA 300.1	EPA Method 9056 A
Quality Control	Batch – All calibration verification every 20 samples. LRB – One per batch. Less than the MDL. If outside criteria must correct before continuing analysis. LFB – One per batch. 90- 110%. LFM. Every 20 samples. Must correct before continuing analysis. Initially 90-110%. Later moves to 80-120% for Part A and 75-125% for Part B. IPC. Mid-range check std and a cal blank after each "daily" calibration and after every 10 samples.	Batch – All calibration verification QC is batch every 10 field samples that includes matrix duplicates and matrix spikes (LFM). Analysis batch is every 20 samples. LRB – One per analysis batch of 20 field samples. Less than the MDL. If outside criteria must correct before continuing analysis. LFB – One per analysis batch of 20 field samples. LFM – With each group of 10 field samples. Must correct before continuing analysis. Criteria 75-125% from MRL- 10xMRL and 85-115% from 10xMRL to highest cal point. If MRL is not established within a factor of 10, then criteria is 85-115%. Has requirements on how to spike based on sample concentration. Duplicates – With each group of 10 field samples. Criteria 20% from MRL- 10xMRL and 10% from 10xMRL to highest cal point. Reanalysis of samples required. IPC – Calculate Peak Gaussian Factor Surrogate – samples must be reanalyzed if %R are outside 90-115%.	Batch – 20 samples of one matrix type Method blank – One per batch. <10% of LLOQ or <10% of regulatory limit or <10% of lowest sample concentration. If outside criteria, allows to rerun once and allows reporting analytical results if ND or according to DQO, or AL. LCS – one per batch. 80 – 120%. Matrix Spike – One per batch. 80-120%. Duplicates – One per batch. If conc near or above mid calibration use 15%, if conc in the low calibration range use 50% ICP – No Surrogate - No
Sensitivity (MDL, MRL, LLOQ)	MDL determination initially, every 6 months, changes in analyst and significant changes in background, or instrument response.	MDL determination initially, every 6 months, changes in analyst and significant changes in background, or instrument response.	LLOQ verification of the LLOQ by spiking at that level and %R within 50% or by using as lowest level calibration standard.
Demonstration of performance	IDP – LCR Use of a QCS with results within 10% and MDL.	IDP – LCR Use of a QCS with results within 15% and MDL.	IDP – See Method 8000

Attachment 3 Chlorinated Herbicide GC Methods

Method	EPA Method 615[a]	EPA Method 8151A[b]	EPA Method 515.4[c]
Description:	The Determination of Chlorinated Herbicides in Municipal and Industrial Wastewater.	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization.	Determination of Chlorinated Acids in Drinking Water by Liquid-Lquid Microextraction, Derivatization, and Fast Gas Chromatography with Electron Capture Detection.
Year:	2007	1996	2000
Office:	Office of Waste Water.	Office of Solid Waste and Emergency Response (OSWER).	Office of Ground Water and Drinking Water.
Parameters			
Matrix	**Wastewater**	**Water, soil, and waste samples.**	**Drinking water**
GC Column (recommended)	Column 1 - 180 cm long, 4 mm ID **glass packed** with 1.5% SP-2250/1.95%, SP-2401 or equivalent; Column 2 - 180 cm long, 4 mm ID **glass packed** with 5% OV-210, Gas Chrom Q, or equivalent; Column 3 - 180 cm long, 2 mm ID **glass packed** with 0.1% SP-1000, Carbopac C, or equivalent.	**Narrow bore columns** [t]- Primary column 1 - 30 m x 0.25 mm, **5% phenyl/95% methyl silicone** 0.25 µm film thickness. - Confirmation column - 30 m x 0.25 mm, **14% cyanopropyl phenyl silicone**, 0.25 µm film thickness. **or wide bore columns** - Primary Column - 30 m x 0.53 mm DB-608 with 0.83 µm film thickness. - Confirmation Column - 30 m x 0.53 mm, **14% cyanopropyl phenyl silicone,** 1.0 µm film thickness.	Column 1 - Fused silica **capillary,** RTX-1701 or equivalent Column 2 (confirmation) - Fused silica **capillary,** DB-5 or equivalent.
Extraction Method - Waters	- Separatory funnel technique - Acidify to pH < 2 with sulfuric acid.	- Separatory funnel technique - Acidify to pH < 2 with sulfuric acid.	- **Glass extraction vials (micro-extraction) in sodium hydroxide basic solution (pH ≥ 12).** - **Add hexane:MTBE (90:10 v/v**) to remove interferences, and discard top phase. - Acidify to pH < 2 with sulfuric acid. - **Add 2 g copper II sulfate pentahydrate, and 16 g sodium sulfate.** (This aids in distinguishing phases and increases ionic strenth of the aqueous phase to drive analytes into the organic phase.)
Extraction Method - Soils	NA	**Ultrasonic extraction system or shaker (Erlenmeyer flask)** - Acidify to pH to 2 with hydrochloric acid.	NA
Extraction Solvent - Waters	**Ethyl ether**	**Methylene chloride, then diethyl ether.**	**Methyl tert butly ether (MTBE).**
Extraction Solvent - Soils	NA	**- Ultrasonic method: Methlyene chloride/acetone (1:1 v/v), then diethyl ether.** **- Shaker method: Acetone, then diethyl ether.**	NA
Extraction Solvent Concentration	**Ethyl ether (1 mL)**	During nitrogen blow-down, **dilute with isooctane and methanol**. Dilute to final volume **(4 mL) with diethyl ether.**	**Methyl tert butly ether (4 mL).**
Esterification	Convert to methyl esters with diazomethane.	Convert to methyl esters by derivatization with either **diazomethane or pentafluorobenzyl bromide (PFB).**	Convert to methyl esters with diazomethane.

Method	EPA Method 615[a]	EPA Method 8151A[b]	EPA Method 515.4[c]
Final Extract Solvent	Hexane	Hexane	**MTBE**
Internal Standard	**No**	Yes	Yes
Surrogate	**No**	Yes	Yes
Calibration Method	- **External calibration** - Standards must be treated like samples (i.e. derivatized to methyl esters).	- **External or Internal Calibration** - Refers to Method 8000[d] - Standards must be treated like samples (i.e. derivatized to methyl esters).	- **Internal Calibration** - Standards must be treated like samples (i.e. derivatized to methyl esters).
Calibration Curve	- **3 calibration standards**; low standard near, but above MDL; high standard should define the working range of the detector. - Tabulate on peak height or response *vs.* analyte mass of 2-5 ul injection; **- RSD of ≤ 10%.**	- **5 calibration standards**; Low standard - near, but above the MDL. - Linear or quadradic regression; $r^2 \geq 0.99$ - **RSD of ≤ 20%**	- ICAL with minimum of **5 standard** concentrations; low standard at or below the minimum reporting limit, high standard should define the working range of the detector. - Linear regression or quadradic (best fit); - **RSD of < 30%**
Retention Time (R.T.) Windows	- Within a RT window of ± 3 standard deviation of the daily calibration standard variation. - Analyst experience should weigh heavily on interpretation.	Refers to Method 8000[d] **± 3 standard deviation (of mean RT) or 0.03 minutes, whichever is greater.**	- Within a RT window of ± 3 standard deviation of the daily calibration standard variation. - Analyst experience should weigh heavily on the determination of RT window size.
Quality Control	Defined in the **text of the method** as an initial demonstration of capability and spiked samples as an ongoing laboratory capability.	**Refers to Method 8000[d]**	**Summarized in Table 14** of the Method.
Calibration Verification (ICV/CCV)	**ICV/CCV every work shift; ±10 % of expected value of the standard.**	ICV/CCV **recovery between 80-120%** of true value of the standard.	- Initial Calibration Check (ICAL) mid-point standard recovery **between 70-130%**, and **low standard 50--150%** of true value. - Continuing Calibration Check (CCC) recovery **between 70-130%**, and lowest standard 50--150% of true value; **- Low CCC - near MRL** **- Mid CCC - near mid-point of calibration curve** **- High CCC- near highest calibration standard**
Method Blank	Reagent Blanks, 1/batch.	Method Blank, 1/batch.	Reagent Blank - **peaks below 1/3 of the reporting limit (RL)** or calibration low standard.
Laboratory control sample (LCS/LFB)	LCS 1/batch, spike concentration within **control limits of ±3s of true value** of the standard.	LCS 1/batch; **recovery of 70-130%** of true value of the standard.	Laboratory Fortified Blank (LFB), 1/batch; **recovery of 70-130%** of true value.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	MS **every 10 samples**, or **1 per month**, whichever is greater. Spike concentration within **control limits of ±3s of true value.**	MS 1/batch**; recovery 70-130% or UCL, LCL ±3s; MS/MSD pair RPD 30%.**	LFM 1/batch; r**ecovery of 70-130%** of true value **(or 50-150% if fortified near or at the minimum reporting limit**).
Sample Duplicate (Field Duplicate)	**As needed** (according to the needs of the laboratory).	Duplicate (or MS/MSD pair) 1/batch; RPD 30%.	Field Duplicate 1/batch; RPD ± 30% (applies to sample duplicate pair and LFM/LFMD pair).
Surrogate	**The use of a surrogate is not indicted with this method.**	Surrogate Recovery of 70-130% of true value of the standard; or **UCL, LCL ±3s.**	Surrogate **Recovery of 70-130%** of true value of the standard.
Internal Standard (IS Calibration Method)	**NA (External Calibration Method)**	Internal standard **within 50-200% of calibration standard**; relative retention time **(RRT) range of 0.080 to 1.20.**	Internal standard **wiithin 50-150%** of average peak area calculated during the initial calibration.

Method	EPA Method 615[a]	EPA Method 8151A[b]	EPA Method 515.4[c]
Sample Collection	Collect water samples in a glass container and **extracted within 7 days.**	Collect water samples in a glass container (1L); **hold time estimated to be 7 days.**	- Collect water samples in an amber glass container (40 mL) with PTFE lined cap, and sodium sulfite reagent (to eliminate residual chlorine) in the sample. - Water samples should be **extract within 14 days,** and **extracts stored at ≤ 0 deg. C.;** protected from light in glass vials with PTFE lined cap.
Sample Preservation	Samples must be **refrigerated at 4 deg. C.**	Samples must be **refrigerated at 4 deg. C.**	**Samples iced at ≤ 10 deg. C. during transport to the lab.** **At the lab, samples should be stored at ≤ 6 deg. C. , but not frozen.**
Analysis	**Analyze within 40 days of extraction.**	**Analyze immediately following esterification.**	**Analysis within 21 days of extraction.**

Notes:

(a) US EPA. November 2007. "EPA Method 615: The Determination of Chlorinated Herbicides in Municipal and Industrial Wastewater." 21p. [215-3358]

(b) US EPA. December 1996. "EPA Method 8151A: Chlorinated Herbicides by GC Using Methylation or Pentafluorbenzylation Derivatization (Revision 1)." 31p. [215-3359]

(c) US EPA. April 2000. "Method 515.4: Determination of Chlorinated Acids in Drinking Water by Liquid-Liquid Microextraction, Derivatization and Fast Gas Chromatography with Electron Capture Detection (Revision 1.0)." 48p. [215-3360]

(d) US EPA. March 2003. "Method 8000C: Determinative Chromatographic Separations. (Revision 3)." 66p. [208-2011]

Attachment 4 Ion Chromatography Methods

Method Number	EPA 300.0, Rev 2.1 (1993) Approved for DW&WW	EPA 300.1-1 Rev 1.0 (1997), Approved for WW EPA 300.1, Rev 1.0 (2000) Approved for DW	EPA Method 9056 A
	PART A. – Bromide, Nitrite, Chloride Ortho-Phosphate-P, Fluoride, Sulfate, Nitrate PART B. – Bromate, Chlorite, Chlorate. Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids after extraction, leachates (when no acetic acid is used).	PART A.-- Common Anions: Bromide Nitrite Chloride ortho-Phosphate-P,Fluoride Sulfate Nitrate PART B.-- Inorganic Disinfection By-products: Bromate, Chlorite, Bromide, Chlorate In reagent water, surface water, ground water, and finished drinking water	Chloride, Fluoride, bromide, nitrate, nitrite, phosphate, sulfate in aqueous, DW, WW, and extracts of other matrices.
Preservation, holding time	4 ^{o}C H2SO4 for NO3+NO2 and EDA for chlorite. Nitrate, Nitrite, and orthophosphate within 48 hrs. All others within 28 days.	4 ^{o}C H2SO4 for NO3+NO2 and EDA for chlorite. Nitrate, Nitrite, and orthophosphate within 48 hrs. All others within 28 days.	6 ^{o}C Nitrate, Nitrite, and orthophosphate within 48 hrs. All others more than 48 hrs but not specified.
Calibration	3 calibration STDs and a blank	3 calibration STDs are required for a curve that extends over a single order of magnitude and a minimum of 5 calibration standards are required if the curve covers two orders of magnitude. Acceptable if calibration verifications pass or use <15% RSD.	Blank and 3 STDs Least square regression and r ≥ 0.995 or weighted least squares 1/conc or 1/con2 and r≥ 0.995
Calibration verification	The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are still more than ±10%, a new calibration curve must be prepared for that analyte.	ICV – Same source as cal STD. CCV – Same source as cal STD. After 10 field samples and end of the run. Verification criteria 75-125% from MRL- 10xMRL and 85-115% from 10xMRL to highest cal point. If MRL is not established within a factor of 10, then criteria is 85-115%.	ICV – Independent source. ±10% CCV – Same source as cal STD. Each day and every 10 samples. ±10%
Quality Control	Batch – All calibration verification every 20 samples. LRB – One per batch. Less than the MDL. If outside criteria must correct before continuing analysis. LFB – One per batch. 90- 110%. LFM. Every 20 samples. Must correct before continuing analysis. Initially 90-110%. Later moves to 80-120% for Part A and 75-125% for Part B. IPC. Mid-range check STD and a cal blank after each “daily” calibration and after every 10 samples.	Batch – All calibration verification QC is batch every 10 field samples that includes matrix duplicates and matrix spikes (LFM). Analysis batch is every 20 samples. LRB – One per analysis batch of 20 field samples. Less than the MDL. If outside criteria must correct before continuing analysis. LFB – One per analysis batch of 20 field samples. LFM. With each group of 10 field samples. Must correct before continuing analysis. Criteria 75-125% from MRL- 10xMRL and 85-115% from 10xMRL to highest cal point. If MRL is not established within a factor of 10, then criteria is 85-115%. Requirements on how to spike based on sample concentration. Duplicates. With each group of 10 field samples. Criteria 20% from MRL- 10xMRL and 10% from 10xMRL to highest cal point. Reanalysis of samples required. IPC – Calculate Peak Gaussian Factor	Reference to SW-846 8000 Batch – 20 samples of one matrix type Method blank – One per batch. <10% of LLOQ or <10% of regulatory limit or <10% of lowest sample concentration. If outside criteria, allows to rerun once and allows reporting analytical results if ND or according to DQO, or AL. LCS – one per batch. 80 – 120%. Matrix Spike – One per batch. 80-120%. Duplicates – One per batch. If conc near or above mid calibration use 15%, if conc in the low calibration range use 50% ICP – No Surrogate - No

Method Number	EPA 300.0, Rev 2.1 (1993) Approved for DW&WW	EPA 300.1-1 Rev 1.0 (1997), Approved for WW EPA 300.1, Rev 1.0 (2000) Approved for DW	EPA Method 9056 A
		Surrogate – samples must be reanalyzed if %R are outside 90-115%.	
Sensitivity (MDL, MRL, LLOQ)	MDL determination initially, every 6 months, changes in analyst and significant changes in background, or instrument response.	MDL determination initially, every 6 months, changes in analyst and significant changes in background, or instrument response.	LLOQ verification of the LLOQ by spiking at that level and %R within 50% or by using as lowest level calibration standard.
Demonstration of performance	IDP: Linear Calibration Range Use of a QCS with results within 10% and MDL.	IDP: Linear Calibration Range Use of a QCS with results within 15% and MDL.	IDP – See Method 8000

Attachment 5 Total Organic Carbon Methods

Method Number	EPA 415.3 Rev 1.1 (2005) Approved for DW	EPA 415.3, Rev 1.2 (2009) Approved for DW	EPA Method 9060 A
	TOC/DOC and also includes UV/SUVA	TOC/DOC and also includes UV/SUVA	TOC
Preservation, holding time	≤6°C, acidified ≤ 2 if not analyzed within 2 hours and hold for up to 28 days	≤6°C, acidified ≤ 2 if not analyzed within 2 hours and hold for up to 28 days	≤4°C, acidified ≤ 2 if not analyzed within 2 hours. 28 days in Chapter 3 of SW-846 but not in 9060 A.
Batch	An analysis batch is limited to 20 field samples. QC samples are not counted towards the 20 sample limit. The CCC = LFB, CCCs done every 10 samples and at the end.	An analysis batch is limited to 20 field samples. QC samples are not counted towards the 20 sample limit. The CCC = LFB, CCCs done every 10 samples and at the end.	Not specified. Chapter 1 of SW-846 is 20 samples.
Calibration	CB and 7 STDs (last two STDs optional for high concentrations). r2 = 0.993 before proceeding with analyses. Ideally the instrument calibration should be r2 = 0.9995 for best results.	CB and 7 STDs (last two STDs optional for high concentrations). r2 = 0.993 before proceeding with analyses. Ideally the instrument calibration should be r2 = 0.9995 for best results.	Follow instrument instructions. Use a series of calibration STDs to cover sample concentrations.
Calibration verification	After the instrument system has been calibrated, verify the calibration using the Continuing Calibration Check and QCS.	After the instrument system has been calibrated, verify the calibration using the Continuing Calibration Check and QCS.	CCV from 2nd source after calibration and CCC every 15 samples.
CCC	The CCC = LFB, CCCs done every 10 samples and at the end. Low-CCC initially at or below MRL. One CCC every 10 samples and at end rotating concentrations. Low-CCC = ± 50%, Mid-CCC = ±20%, High-CCC = ±15%.	The CCC = LFB, CCCs done every 10 samples and at the end. Low-CCC initially at or below MRL. One CCC every 10 samples and at end rotating concentrations. Low-CCC = ± 50%, Mid-CCC = ±20%, High-CCC = ±15%.	NA
Quality Control:	-	-	Quadruplicate analysis is required. Report average and Range.
FD	Relative percent difference for field duplicates having an average concentration of > 2 mg/L OC should fall in the range of < 20% RPD. If field duplicates in this concentration range exhibit an RPD greater than 20%, results should be flagged and the cause for the greater difference (e.g. incomplete IC removal or matrix interference), investigated. NOTE: *Greater variability may be observed for samples with OC approaching the OCDL.*	Relative percent difference for field duplicates having an average concentration of > 2 mg/L OC should fall in the range of < 20% RPD. If field duplicates in this concentration range exhibit an RPD greater than 20%, results should be flagged and the cause for the greater difference (e.g. incomplete IC removal or matrix interference), investigated. NOTE: *Greater variability may be observed for samples with OC approaching the OCDL.*	NA
LRB	Every 20 samples. Results ≤0.35 mg/L	Every 20 samples. Results ≤0.35 mg/L	One per batch.
LFB	For DOC every 20 samples %R= ±20%	For DOC every 20 samples %R= ±20%	NA
LFM	Spike to result in 50-200% increase in sample concentration. Every 20 samples. %R = 70-130%. Overtime spike all sample sources.	Spike to result in 50-200% increase in sample concentration. Every 20 samples. %R = 70-130%. Overtime spike all sample sources.	One MSD every 10 samples.
QCS	During the analysis of the IDC, each time new OC-PDS solutions are prepared, or at least quarterly, analyze a QCS from a source different from the source of the calibration standards. Results with ± 20%	During the analysis of the IDC, each time new OC-PDS solutions are prepared, or at least quarterly, analyze a QCS from a source different from the source of the calibration standards. Results with ± 20%	NA
Sensitivity (MDL, MRL, LLOQ)	The greater of the (mean of LRB+3sigma) OR (LFB*2) Although the lowest calibration standard for OC may be below the MRL, the MRL for OC must never be established at a concentration lower than the lowest OC calibration standard.	The greater of the (mean of LRB+3sigma) OR (LFB*2) Although the lowest calibration standard for OC may be below the MRL, the MRL for OC must never be established at a concentration lower than the lowest OC calibration standard.	NA
Initial Demonstration of performance	5 LFB with ± 20% each and RSD ≤20%	5 LFB with ± 20% each and RSD ≤20%	NA.

Attachment 6 Metals by ICP Methods

Method	EPA Method 200.7 (Rev. 4.4)[a]	SW 846 Method 6010C[b,c]
Description:	Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)	Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)
Year:	1994	2007
Office:	Office of Water.	Office of Solid Waste and Emergency Response (OSWER).
Parameters		
Matrix:	Drinking water, Wastewater and Solids	Groundwater, Wastewater and Solids
Preparation Method (Aqueous):	**Direct analysis** (no preparation) is permitted if pH < 2 and turbidity < 1 NTUs (Nephelometric Turbidity Units).	Sample **digestion is required.** Preparation by acid digestion following an appropriate method (*e.g.* 3000 series method).
Preparation Method (Solids):	Acid digested on **hot plate.**	Sample **digestion is required.** Preparation by acid digestion following an appropriate method (*e.g.* 3000 series method).
Interferences	Interelement correction (IEC) tables verified daily, if interferences are present in the samples, otherwise **verified and updated annually**, or when there is a change in the instrument operating conditions.	IEC tables verified daily. IEC **updated every 6 months** of when an instrument change is made.
Calibration	Minimum of a blank and a high standard (Table 3 in method).	Minimum of a blank and a high standard. **A multi-point calibration is optional. Linear response with $R^2 \geq 0.998$.**
Quality Control		
- Spectral Interference Check: ICSA/ICSAB	Criterion of ± 3S control limit of the calibration blank for the anlayte. **Recovery of 90-110%** of the true value of the standard.	Criterion of ± 3S control limis of calibration blank for the analyte. **Recovery 80-120%** of true value of the standard.
- Calibration Verification (IPC, ICV)	Instrument Performance Check (IPC) **recovery of 95-105%** of true value of standard.	Initial calibration verification (ICV), concentration at the midpoint of calibration range, **recovery of 90-110%** of ture value of standard; **low-level ICV (LLICV),** concentration near the reporting limit, **recovery of 70-130%** of true value of standard.
- Calibration Blank	Run every 10 samples. **Analyte concentration <DL.**	Continuing calibration blank following CCV, **< limit of quantitation** (LOQ) for analytes.
- Method Blank: LRB/MB	Laboratory reagent blank (LRB) with every 20 or fewer samples. Value must be **<10% of analyte level for sample, or is <2.2 times the analyte MDL**.	Laboratory method blank (MB) with every 20 or fewer samples. Value must be less than the **reporting limit of target analytes**. Or **<10% of the concentration of the target analytes, or < 10% of regulatory limit.**
- Method Spike: LFB/LCS (Aqueous)	Laboratory fortified blank (LFB) **recovery of 85-115%,** or within control limits of ± 3S of true value established from 20-30 data points.	Laboratory control sample (LCS) **recovery of 80-120%.**
- Standard Reference Material (SRM, Solids)	**Not specified**	Standard Reference Material, recovery should be **within manufacturer acceptance criterion** associated with SRM lot.
- Matrix Spike/Matrix Spike Duplicate	Laboratory fortified matrix in **10% of samples**. **Recovery 70-130%** of true value of standard.	Matrix Spike/MSD **one per batch** of samples. **Recovery of 75-125%,** with relative percent difference of 20%.
Preservation - solids	Solid samples preservation of **storage at 4 deg. C**	Solid sample preservation **"None" required.** Hold time: 6 Months

Notes:

(a) US EPA. 1994. "EPA Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry (Revision 4.4)." 58p.
(b) US EPA. February 2007. "EPA Method 6010C: Inductively Coupled Plasma-Atomic Emission Spectrometry (Revision 3)." 34p.
(c) US EPA. February 2007. "EPA SW-846: Chapter Three, Inorganic Analytes (Revision 4)." 28p.
(d) US EPA. February 2007. "EPA Method 7000B: Flame Atomic Absorption Spectrophotometry (Revision 2)." 23p.

Attachment 7 Metals by ICP/MS Methods

From EAM Guide 5th Ed.

Parameter	SW-846 Method 6020A	EPA Method 200.8	CLP ILM05.2
Applicability	Groundwater, aqueous samples, industrial wastes, soils, sludges, sediments and other solid wastes. Performance based.	Groundwater, drinking water, surface water, wastewater, sludges and soils. Prescriptive.	Water samples. Prescriptive.
Number of Analytes	15 metals listed. Additional elements can be determined based upon precision and accuracy data.	21 total.	17 total.
Method Validation	Initial demonstration of performance. 1. Determine Method Detection Limit (MDL) by analyzing at least 3 portions of a solution at a concentration near 3 to 5 times the estimated MDL. 2. Determine Instrument Detection Limit (IDL) by calculating the average of the standard deviations of the 3 runs on 3 nonconsecutive days from the analysis of a reagent blank with 7 consecutive measurements per day. IDLs are determined quarterly.	Initial demonstration of performance. 1. Determination of the Linear Calibration Range. Verify linear calibration range limit by analyzing a minimum of 3 different concentration standards. Results must be within 10% of the true value. 2. A Quality Control sample (QCS), and independent standard, is prepared and analyzed 3 times at least quarterly to verify the calibration standards and instrument performance. The concentration of the analytes should be $\leq$ 100ug/L except selenium at a concentration < 500ug/L, and mercury at a concentration $\leq$ 5ug/L. If the mean value of the 3 analyses is not within $\pm$ 10% of the stated value or within the limits listed in Table 8, reanalyze QCS. If the second analysis of the QCS is not within the specified limits, determine source of problem and correct before continuing with analyses. 3. Determine MDLs by analyzing 7 replicates of laboratory fortified blanks. MDLs must be determined annually.	Perform MDL study for each instrument prior to analysis of any samples from contract. Linear dynamic range for each element on each instrument determined prior to analysis of any samples under the contract and checked quarterly thereafter.

Parameter	SW-846 Method 6020A	EPA Method 200.8	CLP ILM05.2
QC Check Standards/Samples	Verify each element calibration with an Instrument Calibration Verification (ICV) solution prepared from a source different than the calibration standard. If not within ± 10% of stated value, stop analysis, correct problem, recalibrate instrument, verify calibration and reanalyze all samples since last compliant CCV. A laboratory control samples (LCS) is analyzed for each analyte using the same sample preparation methods used for the samples at a frequency of one per 20 samples or batch. No criteria specified.	Prepare and analyze a Laboratory Fortified Blank (LFB) with each batch of samples by fortifying laboratory reagent water with multi-element stock standards. The final concentration of the spike added should range from 40ug/L to 100ug/L except for selenium and mercury. For selenium, the concentration should range from 200ug/L to 500ug/L. For mercury, the concentration should range from 2ug/L to 5ug/L. %R = 85-155. If %R for analytes is outside control limits, correct problem before continuing analyses.	LCS analyzed with each SDG, control limits 80-120% otherwise re-digest and re-analyze all samples associated with LCS.
Method Detection Limit	IDLs, sensitivities, and linear ranges will vary with the matrices, instrumentation, and operating conditions.	Estimated IDLs listed in Table 1. MDLs listed in Table 7.	MDL must be less than CRQL; Determined for each instrument immediately before start of analysis of contract samples and annually thereafter.
Standard Solution Expiration	Not specified. Calibration standards are initially verified with QC standards and monitored weekly thereafter. Working ICS solutions are prepared weekly.	Expiration date for stock solutions not specified. Calibration standards should be prepared every two weeks or as needed and verified initially with QCS and monitored weekly thereafter.	Not specified.
Pre-calibration Routine	Analyze tuning solution (10 ug/L Li, Co, In, Tl) 4 times. RSD of absolute signals ≤ 5%. Analyze tuning solution and conduct mass calibration and resolution checks in the mass regions of interest. Adjust mass calibration if it has shifted by more than 0.1 AMU from the true value, mass calibration must be adjusted to the true value. The resolution must be verified to be less than 0.9 AMU full width at 10% peak height.	Analyze tuning solution (100 ug/L Be, Mg, Co, In, Pb) 5 times. RSD of absolute signal ≤ 5%. Resolution at low mass is indicated by magnesium isotopes 24, 25, 26. Resolution at high mass is indicated by lead isotopes, 206, 207, 208. Adjust spectrometer resolution to produce a peak width of 0.75 AMU at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 AMU from unit mass.	Analyze tuning solution (100 ug/L Be, Mg, Co, In, Pb) 5 times. Peak width within 0.75 SMU at 5% peak height. Mass calibration within 0.1 AMU over 6-210 AMU range.
Initial Calibration	Per instrument manufacturer's specifications. Minimum of a blank and one standard for calibration. Use average of at least 3 integrations for calibration and sample analyses.	Per instrument manufacturer's specifications. Minimum of a blank and one standard for calibration. Use average of at least 3 integrations for calibration and sample analyses. Concentration of standards should range from 10ug/L to 200ug/L, except for mercury ≤ 5ug/L and selenium 50ug/L to 500ug/L.	At least one standard and blank used in ICAL every 24 hours or more frequency.

Parameter	SW-846 Method 6020A	EPA Method 200.8	CLP ILM05.2
Continuing Calibration	Analyze the ICV after calibrating instrument, after every 10 samples and after the last sample. If not within ± 10% of the stated value, stop analysis, correct problem, recalibrate instrument, verify calibration and reanalyze all samples since last compliant CCV.	Analyze calibration standards after calibrating instrument, after every 10 samples and at the end of the analytical run. If the recovery is not within ± 10% of the calibration, recalibrate and continue analysis. If the recovery is not within ± 15% of the calibration, recalibrate and reanalyze all samples since last compliant continuing calibration standard.	Analyze ICV solution for every mass immediately after ICAL. Results for each element within 90-110%, otherwise re-calibrate. Analyze CCV solution at beginning and end of analytical run and every 10th sample or every 2 hours whichever is more frequent. Resluts for each element within 90-110%, otherwise re-calibrate and re-analyze all samples run since last successful CCV.
Internal Standards	Recommended internal standards are ^{6}LI, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, and ^{209}Bi. Concentrations not specified. The intensity levels of the internal standard of the calibration blanks and instrument check standards must agree within ± 20% of the intensity level of the internal standard of the original calibration solution, otherwise stop the analysis, correct the problem, calibrate, and re-analyze the affected samples. If intensity levels of the internal standard for samples is not between 30-120% of the intensity level of the internal standard in the initial calibration standard, dilute fresh aliquot of sample 5 times, add internal standard, and re-analyze. Repeat procedure until sample internal standard intensities fall within the prescribed window.	Recommended internal standards are Sc, Y, In, Te and Bi. Concentration range of 20ug/L to 200ug/L. See Table 3 for the mass numbers and limitations of use. If mercury is to be determined, add an aliquot of gold to provide a concentration of 100ug/L in the final dilution of all blanks, standards and samples. The absolute respones of any internal standard must be within 60-125% of the original response in the calibration blank, otherwise flush instrument with rinse blank and monitor response of calibration blank. If response for calibration blank is within limits, dilute a fresh aliquot of sample 2 times, add internal standard, and re-analyze. If response for calibration blank is not within limits, terminate analysis and correct problem.	Choose at least 3 IS from list in Table 4. Response must be between 60-125% of the response in the original calibration blank.
Accuracy/Precision	One MS/MSD, for each batch of samples. No critera specified. Analyze 1 duplicate sample for each matrix and for every 20 samples or analytical batch, whichever is more frequent. %RPD is < 20 for analytes values > 100 times. If %RPD is not within specified limits, correct problem and re-analyze samples during out of control conditions.	1 MS for every 10 prior to sample digestion and analyze. Aqueous: Added analyte concentration should be the same as that used in the LFB. %R = 70-130%. %R is not calculated if analyte concentration added is < 30% of background concentration. If %R for analyte falls outside control limits and system is in control, notify user that analyte is suspect due to sample related effect. Laboratory duplicates. Frequency of analysis and %RPD is not specified.	One MS/MSD in each SDG. If results fall outside control limits of 75-125% then perform post dilution spike. 1 duplicate sample in each SDG.

Parameter	SW-846 Method 6020A	EPA Method 200.8	CLP ILM05.2
Blanks	One method blank per batch of samples processed at the same time. No criteria specified. Analyze calibration blank after each QCS and continuing calibration standard. If the result > ± 3 times the IDL, stop the analysis, correct the problem, and re-analyze the affected samples.	A calibration blank is analyze after every continuing calibration standard. If the recovery is not within ± 10% of the calibration, recalibrate and continue analysis. If the recovery is not within ± 15% of the calibration, recalibrate and reanalyze all samples since last compliant continuing calibration blank. A Field Reagent Blank (FRB) consisting of reagent water placed in a sample container in the laboratory and treated as a sample in all respects. Frequency of preparation and criteria not specified. A Laboratory Reagent Blank (LRB) is carried through the entire samples preparation scheme with each batch of 20 or fewer samples of the same matrix. When LRB values constitute 10% or more of the analyte level or is 2.2 times the analyte MDL, whichever is greater, fresh aliquots of the sample must be prepared and analyzed again for the affected analytes after the source of the contamination has been corrected.	One preparation blank per SDG. Calibration blanks run immediately after ICAL and Calibration Cal checks. Results for each element must be less than CRQL. Rinse blanks run after each exposure in instrument.
Preservation/Storage Conditions	Aqueous: pH < 2 with HNO3 Solid: Store at 4C.	pH < 2 with HNO3	Aqueous: pH < 2 with HNO3 Solid: Store at 4C.
Holding Times	6 months	6 months	180 days from VTSR
Field Sample Amounts Required	Aqueous: 1L Solid: 200g Polyethylene or fluorcarbon container	Aqueous: 1L Solid: 200g Polyethylene or glass container	At least 100mL
Amount for Digestion	Aqueous: 100mL Solid: 2g	Aqueous: 100mL Solid: 2g	100mL

Parameter	SW-846 Method 6020A	EPA Method 200.8	CLP ILM05.2
Other Criteria (Method Specific)	Analyze Interference Check Solution (ICS) containing known concentrations of interfering elements and the elements of interest to verify correction factors at the beginning of the run or every 12 hours, whichever is more frequent. Refer to Table 2 for the recommended components and concentrations for solutions A and AB. Test each new matrix for interference: 1. Dilution test: Perform 1:4 dilution on sample containing analytes > 100 times the reagent blank. Results of dilution should agree within ± 10% of original measurement. If not, interference must be suspect. One per 20 samples per matrix per batch. 2. Post Digestion Spike (PDS): Spike level based on the indigenous element concentration. If the recovery is within 85-115%, perform Dilution test or MSA may be used to compensate for this effect. Results of dilution should agree within ± 10% of original sample concentration. Sample calculations should include interference corrections, internal standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead. Dilute and re-analyze samples that are more concentrated than the linear range for analyte or measure an alternate less-abundant isotope.	All masses which might affect data quality must be monitored. See Table 4 for recommended analytical isotopes and additional masses. Isobaric polyatomic ion interference must be recognized and appropriate corrections made to the data. See Table 2 for the more common interferences and the elements affected. Elemental equations for sample data calculations are listed in Table 5. Dilute and re-analyze samples that are more concentrated than the linear range or measure an alternate less-abundant isotope.	Analyze ICSA, ICSAB and CRI solutions at a frequency of not greater than 20 analytical samples. Must be followed immediately by CCV/CCB pair. 1. ICSA: For target analytes with CRDL < 10ug/L, results should fall within ± 2 times the CRDL of the analyte's true value (true value = 0 unless otherwise stated), otherwise use the alternate method to quantify results for affected analytes. 2. ICSAB: If results are not within ± 20% of the stated value, terminate analysis, correct problem, re-calibrate instrument, and re-analyze all samples since last compliant ICS. 3. To verify linearity at the CRDL, analyze CRI standard at beginning and end of each analytical sequence, and after every 20 samples; 70-130% control limits (50-150% for Co, Mn, Zn); if outside control limits re-analyze; if still outside control limits re-calibrate. 4. 1 serial dilution per sample delivery group or per matrix type, whichever is more frequent. If analyte concentration >50 times the IDL in original sample for that analyte, the serial dilutions (5 times dilution) must agree within 10% of the original determination for that analyte.