Section A

LABORATORY
QUALITY ASSURANCE/QUALITY CONTROL

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SECTION A   Laboratory Quality Assurance/Quality Control Guidelines

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LABORATORY QA/QC GUIDELINES

1.0   INTRODUCTION

This chapter specifies essential QA/QC activities to enable laboratories to achieve reproducible results on an ongoing basis. The first part of Section E 'Microbiological Examination' discusses QA/QC as they pertain to microbiological methods.

Guidelines alone cannot guarantee high quality results. Common sense steps to avoid contamination, ongoing programs of staff training, and proactive method improvement procedures are also essential.

All laboratories should regularly participate in cooperative inter-laboratory studies, and standard reference materials should be analyzed frequently, preferably on a blind or semi-blind basis. Large laboratories should have a full time QA Officer.

The procedures for determining method detection limits and for handling blank corrections are controversial. Different procedures and calculation algorithms are being used by various laboratories.

2.0   GENERAL GUIDELINES

2.1   Quality Manual

A Quality Manual shall be set up that documents all resources, policies and procedures making up the Quality System. The Quality Manual is to include detailed descriptions of the topics outlined in this section and clearly define the responsibilities of management, supervisory staff, and laboratory staff with respect to the quality systems. It shall be reviewed and updated regularly.

2.2   Laboratory Record Keeping

The laboratory record system shall be designed to ensure sample, analytical data, and analyst traceability, including dates and analysts' initials or signatures. Dated and signed material shall include forms, instrumental records and printouts, as well as notebooks.

The sample numbering system of the laboratory must be designed to eliminate the possibility of a sample mix-up.

The record storage system should be designed for easy retrieval. A policy on the length of storage and disposal of records should be established.

2.3   Sample History Requirements

Documentation and procedures on sample history shall be maintained, including:
- sample collection
- field sample preparation
- chemical preservation
- sample containers
- holding times
- storage conditions
- condition of samples on receipt at laboratory

Potential deficiencies in sample history requirements shall be monitored and noncompliance must be identified and any affected analytical data flagged.

a. **Sample collection**

Documentation accompanying all samples should include a test requisition form, or should comply with chain of custody requirements.

b. **Sample containers**

Sample containers may be purchased pre-cleaned from commercial suppliers. Alternatively, sample containers may be cleaned and prepared by the laboratory using documented procedures. Contaminants or interferences in sample containers and preservatives should be monitored by the analysis of container blanks on a per-batch basis. Results of this monitoring should be documented. Container blanks may be prepared by leaching or rinsing containers with reagent water and performing analyses for the parameters of interest. It is recommended that the monitoring of sample containers for cleanliness be focused on 'low level' studies; i.e., where analytical results are anticipated to be <10 times MDLs (e.g., trace metals, dioxins).

2.4 **Sample Collection and Preservation**

a. **Sample condition on receipt**

Inspect sample containers for damage; record and report temperature on receipt where appropriate. Where critical, temperature limits should be established and maximum/minimum thermometers should accompany the samples to document compliance with the limits.

b. **Storage conditions**

Temperatures of refrigerated and frozen storage facilities shall be monitored and recorded daily.

c. **Sample Pre-treatment**

Documentation on sample preparation and pre-treatment procedures shall be maintained, including:

- drying or removal of moisture
- determination of moisture content
- sub-sampling
- preparation of geological samples including splitting, sieving, grinding, pulverizing
- preparation of biological tissue samples
- homogenization
- filtration

Complete records shall be maintained to ensure that potential problems, including cross-contamination, are traceable.

d. **Hold Times and Preservation**

The hold times and preservation listed below in Table 1 will take precedent over the hold times and preservation criteria listed in the individual methods. The intent of this table is to ensure that hold times, sample containers and preservation practices reflect the most current and approved treatment.

Table 1. Summary of sample preservation and hold time requirements

BC MOE SAMPLE PRESERVATION & HOLDING TIME REQUIREMENTS[1,2]				Version: 06-Nov-2015	
Parameter Name	**Sample Container**	**Storage Temp[3]**	**Preservation**	**Holding Time[4] (days)**	**References**
Water					
Physical & Aggregate Properties					
Acidity	Plastic, Glass	≤6ºC	none	14 days	APHA
Alkalinity	Plastic, Glass	≤6ºC	none	14 days	APHA
Colour	Plastic, Glass	≤6ºC	none	3 days	APHA / BC MOE
Conductivity	Plastic, Glass	≤6ºC	none	28 days	APHA
pH	Plastic, Glass	≤6ºC	none	15 minutes	APHA
Solids (Total, TSS, TDS, Fixed, Volatile, etc.)	Plastic, Glass	≤6ºC	none	7 days	APHA
Turbidity	Plastic, Glass	≤6ºC	none	3 days	EPA 40CFR 2012 / BC MOE
UV Transmittance	Plastic, Glass	≤6ºC	none	3 days	APHA / BC MOE
Inorganic Non-metallics					
Bromide	Plastic, Glass	no requirement	none	28 days	EPA 300.1
Chloride	Plastic, Glass	no requirement	none	28 days	APHA / EPA 300.1
Chlorate, Bromate	Plastic, Glass	≤6ºC	50 mg/L EDA	28 days	EPA 317.0
Chlorine, Total Residual (Free Chlorine)	Plastic, Glass	none	none	15 minutes	APHA
Chlorite	Plastic, Amber Glass	≤6ºC	50 mg/L EDA	14 days	EPA 317.0
Cyanide (SAD, WAD)	Plastic, Glass	≤6ºC	field NaOH, store in dark	14 days	APHA
			none	24 hours	APHA
Dissolved Oxygen (Winkler Method)	Glass BOD bottle	≤6ºC	Winkler kit, store in dark	8 hours	APHA
Fluoride	Plastic	no requirement	none	28 days	APHA / EPA 300.1
Nitrogen, Nitrate + Nitrite	Plastic, Glass	≤6ºC	H2SO4	28 days	APHA
			none	3 days	BC MOE
Nitrogen, Ammonia	Plastic, Glass	≤6ºC	H2SO4	28 days	APHA
			none	3 days	BC MOE
Nitrogen, Nitrate	Plastic, Glass	≤6ºC, do not freeze	none	3 days	APHA / BC MOE
Nitrogen, Nitrite	Plastic, Glass	≤6ºC, do not freeze	none	3 days	APHA / BC MOE
Nitrogen, Total Kjeldahl	Plastic, Glass	≤6ºC	H2SO4	28 days	APHA
			none	3 days	BC MOE
Nitrogen, Total, Persulfate Method	Plastic, Glass	≤6ºC	H2SO4	28 days	APHA
			none	3 days	BC MOE
Nitrogen, Total, Combustion Method	Plastic, Glass	≤6ºC	HCl	28 days	APHA
			none	3 days	BC MOE
Phosphorus, Dissolved (Orthophosphate)	Plastic, Glass	≤6ºC	filter (field or lab)	3 days	EPA 40CFR 2012 / BC MOE
Phosphorus, Total Reactive (Orthophosphate)	Plastic, Glass	≤6ºC	none	3 days	APHA / BC MOE
Phosphorus, Total Dissolved	Plastic, Glass	≤6ºC	filter, H2SO4	28 days	APHA
			none	3 days	BC MOE
Phosphorus, Total	Plastic, Glass	≤6ºC	H2SO4	28 days	APHA
			none	3 days	BC MOE
Silica, Reactive	Plastic	≤6ºC, do not freeze	none	28 days	APHA
Sulfate	Plastic, Glass	≤6ºC	none	28 days	APHA / SW846 Ch3 2007
Sulfide	Plastic, Glass	≤6ºC	ZnAc / NaOH to pH >9	7 days	APHA
Metals					
Hexavalent Chromium	Plastic, Glass	≤6ºC	1 mL 50% NaOH per 125 mL	30 days	EPA 1669
			none	24 hours	APHA
Metals, Total	Plastic, Glass	no requirement	HNO3 [7]	180 days	APHA / EPA 200.2
Metals, Dissolved	Plastic, Glass	no requirement	field filter 0.45 um + HNO3, qualify if lab-filtered [7]	180 days	APHA
Mercury, Total	Glass, PTFE	no requirement	HCl or BrCl [8]	28 days	APHA / EPA 1631E
Mercury, Dissolved	Glass, PTFE	no requirement	field filter 0.45 um + HCl or BrCl, qualify if lab-filtered [8]	28 days	APHA / EPA 1631E
Aggregate Organics					
Adsorbable Organic Halides (AOX)	Amber Glass	≤6ºC	HNO3, store in dark, sodium sulfite if chlorinated, collect with no headspace	14 days	APHA 5320
Biochemical Oxygen Demand (BOD)	Plastic, Glass	≤6ºC, do not freeze	none	3 days	APHA / BC MOE
Carbonaceous Biochemical Oxygen Demand (CBOD)	Plastic, Glass	≤6ºC, do not freeze	none	3 days	APHA / BC MOE
Carbon, Dissolved Organic	Plastic, Glass	≤6ºC	filter, H2SO4 or HCl	28 days	APHA
				3 days	BC MOE
Carbon, Dissolved Inorganic	Plastic, Glass	≤6ºC	field filter	14 days	APHA (alkalinity)
Carbon, Total Organic	Plastic, Glass	≤6ºC	H2SO4 or HCl	28 days	APHA
Carbon, Total Inorganic	Plastic, Glass	≤6ºC	none	14 days	APHA (alkalinity)
Chemical Oxygen Demand (COD)	Plastic, Glass	≤6ºC	H2SO4 (field or lab)	28 days	APHA
			none	3 days	BC MOE
Chlorophyll a and Phaeophytin	Filter	Filters: freeze	field filter, store in dark	Filters: 28 days	APHA
	Dark Plastic, Amber Glass	≤6ºC	unfiltered, store in dark	2 days	
Surfactants (Methylene Blue Active Substances)	Plastic, Glass	≤6ºC	none	3 days	APHA / BC MOE
Total Phenols (4AAP)	Plastic, Glass	≤6ºC	H2SO4	28 days	APHA
Extractable Hydrocarbons					
Extractable Hydrocarbons (LEPH, HEPH, EPH)	Amber Glass	≤6ºC	NaHSO4, HCl, or H2SO4	14 / 40 days	EPA 3511
			none	7 / 40 days	SW846 Ch4 2007
Oil and Grease / Mineral Oil and Grease	Amber Glass	≤6ºC	HCl or H2SO4	28 days	EPA 40CFR 2012
Waste Oil Content	Amber Glass	≤6ºC	none	28 days	BC MOE

BC MOE SAMPLE PRESERVATION & HOLDING TIME REQUIREMENTS[1,2]
Version: 04-Jan-2016

Parameter Name	Sample Container	Storage Temp[3]	Preservation	Holding Time[4] (days)	References
Individual Organic Compounds					
Carbamate Pesticides	Amber Glass	≤6ºC	Potassium Dihydrogen Citrate (solid), ~pH 3.8, 9.2-9.5 g/L, + 100 mg/L Na2S2O3 if chlorinated	28 days	EPA 531.2, APHA 6610B
			ChlorAC buffer, ~pH 3, 1.8mL / 60 mL sample, + 100 mg/L Na2S2O3 if chlorinated	28 days	EPA 531.1
			none, 100 mg/L Na2S2O3 if chlorinated	7 days	EPA 8321A
Chlorinated and Non-chlorinated Phenolics	Amber Glass	≤6ºC	0.5g Ascorbic Acid / L + NaHSO4 or H2SO4	14 / 40 days	Alberta Env AE130
			none	7 / 40 days	SW846 Ch4 2007
Dioxins / Furans	Amber Glass	≤6ºC	none	unlimited	SW846 Ch4 2007
Glyphosate / AMPA	Amber Glass or Polypropylene	≤6ºC	100 mg/L Na2S2O3 if chlorinated	14 days	APHA 6651B
Glycols	Glass	≤6ºC	NaHSO4, HCl, or H2SO4	14 / 40 days	EPA 3511
			none	7 / 40 days	SW846 Ch4 2007
Halogenated Hydrocarbons (Semi-Volatile)	Amber Glass	≤6ºC	100 mg/L Na2S2O3 if chlorinated	7 / 40 days	SW846 Ch4 2007
Herbicides, Acid Extractable	Amber Glass	≤6ºC	HCl (optional), store in dark, 50 mg/L Na2SO3 if chlorinated	14 / 21 days	APHA 6640A APHA 6640A
Paraquat / Diquat	Dark Plastic (protect from light)	≤6ºC	100 mg/L Na2S2O3 if chlorinated	7 / 21 days	EPA 549.2
Pesticides (NP, OP, OC)	Amber Glass	≤6ºC	none	7 / 40 days	SW846 Ch4 2007
Polychlorinated Biphenyls (PCBs)	Amber Glass	≤6ºC	none	unlimited	SW846 Ch4 2007
Polycyclic Aromatic Hydrocarbons (PAHs)	Amber Glass	≤6ºC	NaHSO4, HCl, or H2SO4	14 / 40 days	EPA 3511
			none	7 / 40 days	SW846 Ch4 2007
Resin Acids, Fatty Acids	Amber Glass	≤6ºC	(0.5g Ascorbic Acid + 0.4g NaOH) / L	14 / 40 days	Alberta Env AE129
			none	7 / 40 days	SW846 Ch4 2007
Volatile Organic Compounds (Trihalomethanes)	43mL Glass VOC Vials (2-3)	≤6ºC	3 mg Na2S2O3 (see BC Lab Manual method for more details)	14 days	BC MOE
Volatile Organic Compounds (VOC, BTEX,VH)	43mL Glass VOC Vials (2-3)	≤6ºC	200 mg NaHSO4, or 3 mg Na2S2O3 if chlorinated (see BC Lab Manual method for other options and details)	14 days	BC MOE
Microbiological Parameters					
Coliforms, Total, Fecal, and Ecoli	Sterile Glass or Plastic	<8ºC, do not freeze	Na2S2O3	30 hours [5]	BC CDC / APHA 9060B
Cryptosporidium, Giardia	Sterile Glass or Plastic	<8ºC, do not freeze	Na2S2O3	96 hours	EPA 1623 / APHA 9060B
Enterococcus	Sterile Glass or Plastic	<8ºC, do not freeze	Na2S2O3	30 hours [5]	APHA 9060B
Heterotrophic Plate Count	Sterile Glass or Plastic	<8ºC, do not freeze	Na2S2O3	24 hours	APHA 9215
Toxicity					
Daphnia, Chronic 21day / Chronic EC25	Plastic, Glass (non-toxic)	4±2ºC	collect with no headspace	5 days	EC EPS 1/RM/14 & 11
Daphnia, LC50 / LT50	Plastic, Glass (non-toxic)	4±2ºC	collect with no headspace	5 days	EC EPS 1/RM/14 & 11
Microtox	Plastic, Glass (non-toxic)	4±2ºC	collect with no headspace	3 days	EC EPS 1/RM/24
Trout, LC50	Plastic, Glass (non-toxic)	4±2ºC	collect with no headspace	5 days	EC EPS 1/RM/13 & 9
Trout, LT50	Plastic, Glass (non-toxic)	4±2ºC	collect with no headspace	5 days	EC EPS 1/RM/13 & 9

Soil and Sediment

Parameter Name	Sample Container	Storage Temp[3]	Preservation	Holding Time[4] (days)	References
Inorganics					
Bromide / Chloride / Fluoride	Plastic, Glass	no requirement	none	unlimited	Carter (Table 4.1)
Cyanide (WAD / SAD)	Plastic, Glass	≤6ºC	store in dark, field moist	14 days	SW846 Ch3 2007
Hexavalent Chromium	Plastic, Glass	≤6ºC	store field moist	30 / 7 days	SW846 Ch3 2007 / EPA 3060A
Metals, Total	Plastic, Glass	no requirement	none	180 days	SW846 Ch3 2007
Mercury, Total	Plastic, Glass	no requirement	none	28 days	SW846 Ch3 2007
Moisture	Plastic, Glass	≤6ºC	none	14 days	Puget Sound Protocols
pH	Plastic, Glass	no requirement	none	365 days	Carter
Sulfide	Plastic, Glass	≤6ºC	store field moist	7 days	Puget Sound Protocols
TCLP - Mercury	Plastic, Glass	no requirement	sample: none TCLP extract: HNO3, HCl, or BrCl	28 / 28 days	EPA 1311
TCLP - Metals	Plastic, Glass	no requirement	sample: none TCLP extract: HNO3	180 / 180 days	EPA 1311
Organics					
Carbons (TC, TOC)	Plastic, Glass	≤6ºC	none	28 days	SW846 Ch3 2007
	Plastic, Glass	no requirement	dried state	unlimited	Carter (Table 4.1)
Chlorinated and Non-chlorinated phenolics	Glass	≤6ºC	none	14 / 40 days	SW846 Ch4 2007
Dioxins / Furans	Glass	≤6ºC	none	unlimited	SW846 Ch4 2007
Extractable Hydrocarbons (LEPH, HEPH, EPH)	Glass	≤6ºC	none	14 / 40 days	SW846 Ch4 2007
Glycols	Glass	≤6ºC	none	14 / 40 days	SW846 Ch4 2007
Herbicides, Acid Extractable	Glass	≤6ºC	none	14 / 40 days	SW846 Ch4 2007
Oil and Grease / Mineral Oil and Grease / Waste Oil Content	Glass	≤6ºC	none	28 days	SW846 Ch3 2007, Puget Sound Protocols
Pesticides (NP, OP, OC)	Glass	≤6ºC	none	14 / 40 days	SW846 Ch4 2007
Polychlorinated Biphenyls (PCBs)	Glass	≤6ºC	none	unlimited	SW846 Ch4 2007
Polycyclic Aromatic Hydrocarbons (PAHs)	Glass	≤6ºC	none	14 / 40 days	SW846 Ch4 2007
Resin Acids, Fatty Acids	Glass	≤6ºC	none	14 / 40 days	SW846 Ch4 2007
TCLP - Volatile Organic Compounds	Glass	≤6ºC	sample: none TCLP extract: NaHSO4, HCl, or H2SO4	14 / 14 days	EPA 1311
TCLP - Semi-Volatile Organic Compounds	Glass	≤6ºC	none	14 / 7 / 40 days	EPA 1311
Volatile Organic Compounds (VOC, BTEX, VH, THM)	Pre-weighed sealed glass vial charged with methanol preservative + glass soil jar for moisture	≤6ºC	methanol (exact volume, e.g. 10.0 mL)	40 days	EPA 5035A / CCME
	Hermetic sampler + glass soil jar for moisture[6]	≤6ºC	none	48 hours [6] / 40 days	EPA 5035A / CCME / ASTM D6418-09

BC MOE SAMPLE PRESERVATION & HOLDING TIME REQUIREMENTS[1,2] — Version: 04-Jan-2016

Parameter Name	Sample Container	Storage Temp[3]	Preservation	Holding Time[4] (days)	References
Biota					
Inorganics					
Metals, Total	Plastic, Glass	freeze (≤ -18C)	none	2 years [9]	Puget Sound Protocols
Mercury, Total	Plastic, Glass	freeze (≤ -18C)	none	1 year [9]	EPA 1631 Appendix
Organics					
Semi-Volatile Organic Compounds	Glass, PTFE	freeze (≤ -18C)	none	365 / 40 days	Puget Sound Protocols
Volatile Organic Compounds	Glass, PTFE	freeze (≤ -18C)	none	14 days	Puget Sound Protocols
Air (Vapours)					
VOCs by Canister Sampling	SS canister	ambient	none	30 days	EPA TO15
VOCs by Thermal Desorption	thermal desorption tube	≤6ºC	none	30 days	EPA TO17
VOCs and other Volatile Substances by Charcoal and Miscellaneous Collection Media	see BC Lab Manual Method	≤6ºC (or as per applicable reference method)	none	30 days	see BC Lab Manual Method

1. A Director or an Environmental Management Act permit may specify alternate requirements.

2. Refer to applicable BC Environmental Laboratory Manual methods for additional detail. Where differences exist between Lab Manual methods and this table, this table takes precedence.

3. Storage temperature applies to storage at the laboratory. For all tests where refrigeration at ≤ 6°C is required at the laboratory, samples should be packed with ice or cold packs to maintain a temperature of ≤10°C during transport to the laboratory. The storage of <8°C for microbiological samples applies during storage at the laboratory and during transport to the laboratory. To prevent breakage, water samples stored in glass should not be frozen. Except where indicated by "do not freeze", test results need not be qualified for frozen samples. Labs may apply a "Cooling Initiated" qualifier on reports to indicate where samples were received above specified storage temperature, but where sampling occurred < 8 hours before arrival at the lab, and where samples were packed appropriately in coolers with ice or cold packs to initiate the cooling process.

4. Hold Times: Single values refer to hold time from sampling to analysis. Where 2 values are given, the first is hold time from sampling to extraction, and the second is hold time from extraction to analysis. 3 values are given for TCLP semi-volatiles (1st is from collection to TCLP extraction; 2nd is from TCLP extraction to preparative extraction; 3rd is from preparative extraction to analysis).

5. Samples received from remote locations more than 48 hours after collection must not be tested.

6. Methanol extracts are stable for 40 days from sampling. Hermetic samples must be methanol-extracted within 48 hours of sampling or may be frozen at ≤ -7°C within 48 hours of sampling to extend hold time to 7 days from sampling. Frozen hermetic samples must be extruded into methanol while still predominantly or partially frozen.

7. If not field-preserved, water samples for metals analysis must be acidified at the lab in their original containers by addition of HNO3 (within 14 days of sampling), then equilibrated at least 16 hours prior to sub-sampling or analysis (otherwise, qualify as "received unpreserved"). This approach is also applicable to dissolved metals if field filtered. Not applicable to mercury.

8. Use only glass or PTFE containers to collect water samples for total or dissolved mercury. For total mercury, field-preserve with HCl or BrCl. For dissolved mercury, field filter and then preserve with HCl or BrCl. Adding BrCl to original sample container at the laboratory within 28 days of sampling is an acceptable alternative for total mercury and for dissolved mercury (if field-filtered). if samples are oxidized for 24 hours prior to sub-sampling or analysis. Dissolved mercury should not be lab-filtered. Qualify lab-filtered results for dissolved mercury as "lab-filtered".

9. Freezing is optional for freeze dried tissue samples and for vegetation that is dried prior to digestion and reported on a dry weight basis; in these cases, samples may be stored at ambient temperature, with a hold time of 28 days for mercury and 6 months for other metals (based on BC MOE soil guidelines).

Effective Date of this revision: January 4, 2016

List of References:

Alberta Env AE129	Resin and Fatty Acids in Pulp Mill Effluents and Receiving Waters, Method AE129.0, Alberta Environment, August 1990.
Alberta Env AE130	Chlorinated Phenolic Compounds in Bleached Kraft Mill Effluents and Receiving Waters, Method AE130.0, Alberta Environment, April 1991.
APHA	Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF). Primary reference is Section 1060, Collection and Preservation of Samples, Table 1060:I, Summary of Special Sampling and Handling Requirements, 2011.
APHA 5320	Dissolved Organic Halogen, Method 5320, APHA Standard Methods, 1997.
APHA 6610B	Carbamate Pesticides, Method 6610B, High Performance Liquid Chromatography Method, APHA Standard Methods, 2004.
APHA 6640A	Acidic Herbicide Compounds, Method 6640A, Introduction, APHA Standard Methods, 2001 (HCl preservation, 14 day hold time).
APHA 6640A	Acidic Herbicide Compounds, Method 6640A, Introduction, APHA Standard Methods, 2001 (reference does not use HCl preservation, but recommends extraction as soon as possible, up to 14 days, cautions about potential analyte degradation).
APHA 6651B	Glyphosate Herbicide, Method 6651B, Liquid Chromatographic Post-Column Fluorescence Method, APHA Standard Methods, 2000.
APHA 9060B	Microbiological Examination Section, Samples, Method 9060B, Preservation and Storage, APHA Standard Methods, 2006.
APHA 9215	Heterotrophic Plate Count, Method 9215, APHA Standard Methods, 2004.
ASTM D6418-09	Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis.
BC CDC	British Columbia Centre for Disease Control.
BC MOE	British Columbia Ministry of Environment (British Columbia Environmental Laboratory Manual).
Carter	Carter, Martin R. and Gregorich, E. G., Soil Sampling and Methods of Analysis, Canadian Society of Soil Science, 2008.
CCME	Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method, ISBN 1-896997-01-5, Publication No. 1310, Canadian Council of Ministers of the Environment Inc., 2001.
EC EPS 1/RM/24	Biological Test Method: Toxicity Test Using Luminescent Bacteria, Environment Canada, Report EPS 1/RM/24, November 1992.
EC EPS 1/RM/11	Biological Test Method: Acute Lethality Test Using Daphnia spp., Environment Canada, Report EPS 1/RM/11, July 1990 (with May 1996 amendments).
EC EPS 1/RM/14	Biological Test Method: Biological Test Method: Reference Method for Determining Acute Lethality of Effluents to Daphnia magna, Environment Canada, Report EPS 1/RM/14 second edition, December 2000.
EC EPS 1/RM/13	Biological Test Method: Reference Method for Determining Acute Lethality of Effluents to Rainbow Trout, Environment Canada, Report EPS 1/RM/13, second edition, December 2000 (with May 2007 amendments).
EC EPS 1/RM/9	Biological Test Method: Acute Lethality Test Using Rainbow Trout, Environment Canada, Report EPS 1/RM/ 9, July 1990 (with May 1996 and May 2007 amendments).
EPA	United States Environmental Protection Agency.
EPA 1311	Toxicity Characteristic Leaching Procedure, SW 846 Method 1311, Revision 0, US EPA Office of Solid Waste, July 1992.
EPA 1631E	Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, US EPA Office of Water, August 2002.
EPA 1669	Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, Method 1669, US EPA Office of Water, July 1996.
EPA 200.2	Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, Method 200.2, Revision 2.8, US EPA Office of Research and Development, 1994.
EPA 300.1	Determination of Inorganic Anions in Drinking Water by Ion Chromatography, Revision 1.0, US EPA Office of Research and Development, 1997.
EPA 3060A	Alkaline Digestion for Hexavalent Chromium, SW846 Method 3060A, Revision 1, US EPA Office of Solid Waste, December 1996.
EPA 317.0	Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis, Revision 2.0, US EPA Office of Research and Development, July 2001.
EPA 3511	Organic Compounds in Water by MicroExtraction, SW 846 Method 3511, Revision 0, US EPA Office of Solid Waste, Nov 2002.
EPA 40CFR 2012	Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures, Final Rule, 40 CFR Parts 136, 260, et al, Table II - Required Containers, Preservation Techniques, and Holding Times, US EPA , May 18, 2012.
EPA 5035A	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, SW 846 Method 5035A, Draft Revision 1, US EPA Office of Solid Waste, July 2002.
EPA 531.1	Measurement of N-MethylCarbamoyloximes and N-MethylCarbamates in Water by Direct Aqueous Injection HPLC with PostColumn Derivatization, Revision 3.1, US EPA Office of Ground Water and Drinking Water, 1995.
EPA 531.2	Measurement of N-MethylCarbamoyloximes and N-MethylCarbamates in Water by Direct Aqueous Injection HPLC with PostColumn Derivatization, Revision 1.0, US EPA Office of Ground Water and Drinking Water, September 2001.
EPA 549.2	Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection, Method 549.2, Revision 1.0, US EPA Office of Research and Development, June 1997.
EPA 8321A	Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography / Thermospray / Mass Spectrometry (HPLC/TS/MS) or Ultravioloet (UV) Detection, Revision 1, US EPA Office of Solid Waste, Dec 1996.
EPA TO15	Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), Compendium Method TO-15, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, US EPA Office of Research and Development, January 1999.
EPA TO17	Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes, Compendium Method TO-17, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, US EPA Office of Research and Development, January 1999.
Puget Sound Protocols	Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound, Puget Sound Water Quality Action Team, prepared for U.S. Environmental Protection Agency (Region 10) and U.S. Army Corps of Engineers, July 1996.
SW846 Ch3 2007	Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, Final Update IV, Chapter 3, Inorganic Analytes, Revision 4, US EPA Office of Solid Waste, February 2007.
SW846 Ch4 2007	Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, Final Update IV, Chapter 4, Organic Analytes, Revision 4, US EPA Office of Solid Waste, February 2007.

2.5   Test Methods, Existing

An inventory of methods shall be maintained that will include:

- all current methods
- all previous methods
- date of transition

Test method and procedures documentation should include:

- analysis procedure in sufficient detail such that an experienced analyst, unfamiliar with the specific test procedure, should be able to perform the analysis
- procedures for the preparation of reagent solutions and calibration standard solutions
- operating instructions for instrumentation, which are supplemental to the manufacturer operating manuals
- requirement for quality control sample preparation and analysis
- current quality control criteria (i.e., acceptable limits)

Where data are kept on computer files, changes to methodology should be reflected by changes in related computer codes. A system should be established to review methods and documentation on an annual basis; the system should include periodic re-validation of methods when warranted, such as when personnel or equipment are changed.

2.6   Test Methods, New

Methods should be periodically reviewed to ensure that the most up-to-date methods are being used. Test methods that are new to the laboratory, methods that have been developed in-house, and changes and modifications to existing methods must be validated. Validation should include determination of method detection limits, linear range, precision, recoveries, interference checks, and performance of equivalency testing where required.

2.7   Equipment

Equipment logs shall specify:
- manufacturer, model, serial number
- significant modifications
- repair and maintenance history
- calibration history
- performance history

Routine maintenance should be performed according to manufacturers' instructions and schedules.

Log books or other records shall be kept which record daily operating, calibration, and setup parameters.

Instrument operating procedures that supplement instructions given in the manufacturer's operating manuals should be documented.

2.8   Analyst Qualifications

Records of qualifications and experience shall include:
- copy of current resume
- records of training in new laboratory operations
- records of attendance at technical meetings and seminars
- records of completion of relevant courses (including in-house courses, night school classes, and courses sponsored by instrument manufacturers)

Initially, proficiency in the performance of an analysis new to the analyst should be demonstrated by the successful analysis of known samples, standards or certified material prior to the analyst being assigned routine analysis.

Continuing proficiency may be monitored through the analysis of routine quality control samples, certified materials, and performance evaluation samples, and also by participation in inter-laboratory studies and blind audits.

2.9   Reagents and Standard Solutions

All chemicals shall be reagent grade or better, and must meet specifications identified in the test methods. Procedures for the preparation of reagent solutions and calibration standard solutions shall be included as part of the applicable analysis method.

Establish and maintain logs that document the preparation of reagents and standard solutions specifying:

- supplier, grade, batch number
- if applicable, details on drying, mixing, etc.
- record of all laboratory operations performed and record of weights and volumes
- all calculations
- identity of analyst preparing the reagent or standard solution

A file of certificates of standard solutions that have been obtained from commercial suppliers shall be kept.

Prior to routine use, and periodically throughout its shelf life, performance of a reagent or standard shall be verified. Compare performance of standard solutions by analysis of old and new solutions consecutively. Set criteria for the response of new versus old standard solutions.

All reagent solutions and standard solutions must be properly labelled. Labels shall identify material, concentration, date prepared and expiry date. Expiry dates will vary depending upon the solution and concentration. A general guideline for concentrated stock standard solutions is an expiry date of one year.

2.10   Reagent Water

Reagent water shall comply with ASTM D 1193-77, Standard Specification for Reagent Water, Type I, Type II, or Type III, or Standard Methods 18th Edition (1992), Section 1080 Reagent-Grade Water, Type I or Type II.

Reagent water must be free from chemical and microbiological substances that interfere with analytical methods. The presence of contaminants may be monitored for each test by the analysis of blank reagent water with each batch of samples. Microbiological evaluation may be performed by using a Total Plate Count.

The conductivity of reagent water should be recorded daily.

2.11   Gravimetric Measurement

Accuracy of gravimetric measurements shall be ensured by referencing calibrations to class S or S-1 weights. Annual balance calibration and daily calibration checks are required and records must be kept. ("S" and "S-1" are terms defined in NIST (formerly NBS) Circular 547).

2.12   Volumetric Measurement

The use of class A glassware will ensure accuracy of volumetric measurement.

Delivery volumes of automatic pipettes and diluters shall be checked on a routine basis and records of results maintained.

2.13   Glassware Cleaning

Up-to-date documentation shall be kept on all glassware cleaning procedures and requirements.

The effectiveness of cleaning may be monitored by the analysis of blanks using randomly selected glassware.

2.14   Contamination Control

Effective separation between laboratory areas of incompatible activity must be ensured.

Tests in progress and other laboratory operations should not interfere with or lead to contamination of other tests in progress. Scheduling of tests, and scheduling the use of fume hoods and other apparatus and facilities may be required.

The identity of samples and the order in which samples are analyzed on each instrument must be recorded, so that problems such as cross-contamination may be identified.

2.15   Calibration Practices

The accuracy and stability of calibrations is established by setting requirements for the following, as appropriate:

- equivalent standard/sample reagent backgrounds
- sufficient number of standards
- low standards (less than ten times the detection limit)
- reagent blanks used to zero response
- appropriate curve fit
- internal standards
- normalization standards
- control and verification standards to verify accuracy and stability
- associated control limits and specified corrective action

2.16   Quality Control Approaches

Appropriate quality control techniques applied to each batch of samples shall be recorded and documented. QC data must be made available to the client and it is encouraged that batch QC results be included in reports.

The type and number of quality control samples to be analyzed should be stated in the analysis method, or in a section in the overall Quality Manual.

Quality Control samples include:

- method blanks to monitor possible contamination
- duplicates to monitor precision (both inter- and intra-laboratory)
- certified reference samples to monitor accuracy
- internal reference samples to monitor accuracy
- analyte spikes to monitor recoveries
- surrogate spikes to monitor recoveries

Due to the diversity of tests and QC sample requirements, it is not possible to define overall requirements. However, based on an arbitrary sample batch size of ten samples, two examples (not recommendations) are:

a.   Analysis of pH of water:

QC approach: run one sample in duplicate per batch

b.   Analysis of copper in water:

QC approach: run one method blank per batch
run one sample in duplicate per batch
run one certified reference sample per batch

In general a level of QC in the range of 10-30% is considered appropriate.

2.17   Control Limits

Control charts for QC samples must be established. Control Limits may be statistically derived based on data generated from QC samples within each laboratory, but must not exceed Data Quality Objective values as defined in the individual test methods within this manual. Commonly used statistically derived limits are ±2s (for warning limits) and ±3s (for control limits) around the mean. Statistical limits are recommended for use in trend monitoring if not used directly as Control Limits.

Corrective action must be taken when control limits are exceeded, and records of out-of-control events and actions taken must be maintained. Test results associated with Quality Control data that does not meet minimum BC MOE Data Quality Objectives must be appropriately qualified in laboratory reports.

Multi-Element Scan (MES) Qualifiers: As the number of analytes in a test method increases, so does the chance of a DQO exceedance by random chance as opposed to a legitimate method problem. Thus, in multi-element test methods (also known as Multi-Element Scans), for Laboratory Control Samples, Matrix Spikes, or Reference Materials, it is considered acceptable to exceed quoted DQOs by up to 10% (absolute), for up to 10% of the total number of analytes (rounded down) included within the method. For example, in a PAH scan of seventeen analytes with LCS acceptance limits of 60-130%, 10% of the analytes reported by the method (*i.e.* <u>one</u> analyte) may have a recovery exceeding 60-130% by up to 10% absolute (*i.e.* recovery of 50-140%). Recurring non-random issues with specific parameters <u>must</u> be addressed, and will be highlighted by ongoing re-validation assessments. Where applicable exceedances occur, a suitable qualifier (*e.g. "MES"*) may be applied to test results.

2.18   Recommended Data Quality Objectives for Laboratory Duplicates

Table 2 presents BC MOE recommended Data Quality Objectives for laboratory duplicates. These DQOs are applicable to duplicates where at least one of the duplicate results exceeds five times the Laboratory's detection limit. These DQOs were derived from Measurement Uncertainty (MU) estimates obtained from four BC Laboratories represented on the BC Environmental Laboratory Technical Advisory Committee (BCELTAC).

Laboratory duplicate values that meet these DQOs may be considered acceptable, falling within the expected range of variability for the indicated parameter. Duplicate values that exceed these DQOs should be investigated by the laboratory to ensure validity. Where no issues are identified, duplicate results that exceed DQOs should be quantified to indicate potential heterogeneity issues with the sample. Table 2 supersedes laboratory duplicate DQO values from within specific BC Lab Manual Methods.

Table 2. Recommended data quality objectives for laboratory duplicates

Parameter Category	Recommended Lab Duplicate DQO (as RPD) Applicable at Concentrations > 5x MDL
Organics in Soil and Sediment	
Polycyclic Aromatic Hydrocarbons (PAH)	50%
Volatile organics (including BTEX and VH)	40%
Extractable Petroleum Hydrocarbons (EPH)	40%
Most other typical organic parameters[1]	40%
Organics in Water[2]	
Volatile organics (including BTEX and VH)	30%
Most other typical organic parameters[1]	30%
Metals in Soil and Sediment	
High variability metals: Ag, Al, Ba, Hg, K, Mo, Na, Pb, Sn, Sr, Ti	40%
Other metals	30%
Metals in Water[1]	20%
General Inorganics in Soil and Sediment[1]	30%
General Inorganics in Water[1]	20%

[1]. Represents a default DQO for most common parameters in this category. Higher values may be appropriate for some tests.

[2]. Where applicable. Many tests for organics in water consume the entire sample, so lab duplicates are not possible.

2.19   Expression of Results in the Final Report

It is good practice to report measurement uncertainty along with measurement results. When measurement uncertainty is reported, it should be as the 95% confidence interval.

$$Result \pm 95\% \ CI$$

Many laboratories prefer to report results following the significant figures convention. When that convention is employed, the previous estimates should be based on its 95% confidence interval where practical.

Rounding of results should be deferred until the final calculation for reporting purposes. The ability to store data, to one more significant figure than would normally be the case, is of benefit to those undertaking statistical studies of data and its provision is encouraged.

The reporting convention of the analyte must be stated in unambiguous terms, but "+" and "-"symbols for ions need not be shown unless speciation has been effected. For example:

Copper	Cu
Nitrate	as N
Ortho-phosphate	as P
Silica	SiO_2
Sulfate	SO_4

Units must also be expressed in unambiguous terms, for example:

mg/L   µg/g (dry weight)   % (w/v)
                              µg/g (wet weight)   % (w/w)% (v/v)

2.20   Guidelines for Analytical Parameters Determined by Calculation (Ver.: Jan. 8, 2004)

The BC Ministry of Environment has several numerical criteria that incorporate calculated parameters. Calculated parameters are those that require mathematical operations to be performed on one or more measured parameter results in order to determine their value. The most common examples, which are dealt with in this document, are parameters that are calculated by addition or subtraction from pre-requisite component results.

This document outlines proposed general guidelines for calculating and reporting these calculated parameters. These rules may be superseded by specific instructions within individual published BC Environment laboratory methods.

General Guidelines for All Calculated Parameters:

1.   For calculation purposes, use a value of zero for any component result that is reported as less than a detection limit.

2.   Wherever possible, calculations shall be done using raw, un-rounded results.

3.   For parameters that involve both additions and subtractions, a combination of the rules for both addition and subtraction should be applied.

4.   Detection limits for both calculated and directly analyzed parameters (whether MDL's, RDL's, LOQ's, or otherwise) should generally be provided to two significant digits. Analytical results should be provided to the same level of significance. This prevents the introduction of rounding error that may be significant at low levels.

5.   These guidelines define procedures for calculation of Method Detection Limits (MDL's). Limits of Reporting (reported detection limits) may be higher, for example if based on Level of Quantitation (LOQ) or Practical Quantitation Limit (PQL).

Examples of parameters for which these guidelines are applicable include:

Parameters Determined by Addition:
- Total PAH's, Total Light PAH's and Total Heavy PAH's
- Total Resin Acids
- Total Xylenes
- Total Trihalomethanes
- Total Nitrogen (as Total Kjeldahl Nitrogen plus Nitrate plus Nitrite)

Parameters Determined by Subtraction
- Nitrate (when determined as "Nitrite/Nitrate" minus Nitrite)
- Organic Nitrogen (as Total Kjeldahl Nitrogen minus Ammonia Nitrogen)
- Chromium III (Total Chromium minus Chromium VI)

Detection Limit Guidelines for Parameters Calculated by Addition

A summed parameter is one that is obtained by summing two or more parameters that are analyzed independently.

The Method Detection Limit for a Summed Parameter is calculated as follows:

$$\textbf{If Result}_{\textbf{summed}} = (C_1 + C_2 + C_3 \dots)$$

$$\textbf{MDL for Result}_{\textbf{summed}} = \text{sqrt} \ [\ (MDL_1)^2 + (MDL_2)^2 + (MDL_3)^2 + \dots]$$

Where:

C_x =   Concentration of parameter X.
MDL_x =   Method Detection Limit of parameter X.

Detection Limit Guidelines for Parameters Calculated by Subtraction

Special considerations are necessary to determine valid Detection Limits for parameters that are determined by subtraction. When a result being subtracted approaches the magnitude of the result it is subtracted from, the difference is subject to a high degree of uncertainty due to the uncertainty in the original two results. For subtracted parameters, an estimate of the uncertainty in the calculated result is the only reasonable measure of detection limit.

Except where methods specifically define alternate procedures, the following guidelines are recommended to determine valid Detection Limits for Subtracted Parameters. There are three different situations that require consideration:

Where Result$_{sub}$ = $C_1 - C_2$;

Case 1: C_1 is reported as less than detection limit:

Use the MDL of the larger result (C_1) as the MDL for the subtracted parameter (Result$_{sub}$). (Result$_{sub}$) would be reported as < DL.

Case 2: C_2 is less than 1/3 the magnitude of C_1:

Use the MDL of the larger result (C_1) as the MDL for the subtracted parameter (Result$_{sub}$). In this situation, the uncertainty of the difference of the two results should be acceptably low, and will not dominate the question of whether or not the subtracted parameter has been detected or not.

Case 3: C_2 is greater than 1/3 the magnitude of C_1:

In this case, the subtracted result (Result$_{sub}$) may be subject to an unacceptably high degree of uncertainty due to the uncertainty in the component results (C_1 and C_2). Where practical, it is recommended that the MDL for the subtracted parameter be determined by adding the uncertainties of the two results (in quadrature) as follows:

$$\textbf{Where Result}_{\textbf{sub}} = C_1 - C_2$$

$$\textbf{MDL for Result}_{\textbf{sub}} = \text{sqrt} \ [\ (U_{C1})^2 + (U_{C2})^2]$$

Where:

U_{C1} = The laboratory's expanded (95% confidence level) Measurement Uncertainty (MU) estimate for result C_1 (i.e. MU for parameter 1 at concentration C).

U_{C2} = The laboratory's expanded (95% confidence level) Measurement Uncertainty (MU) estimate for result C_2 (i.e. MU for parameter 2 at concentration C).

Under Case 3, if the MDL calculated above is insufficient to meet a data requirement, then an alternative measurement technique utilizing a direct measurement of the parameter should be sought.

These guidelines were developed by the BCELQAAC Technical Subcommittee, and were endorsed by the committee for inclusion in the BC Lab Manual on September 11, 2003.

2.21 Performance Audits

Where facilities permit, internal audits should be conducted. Performance audits should incorporate blind or other samples in order to check functioning of laboratory QC procedures. This action may be helpful if external audits are imposed. Records of audit results and action taken should be kept.

2.22 Inter-Lab Comparison Studies

Participation in inter-laboratory comparison studies is recommended, as appropriate (e.g., BC EDQA program leading to registration or CALA program leading to certification). Records of results and action taken should be kept.

3.0 RECOMMENDED PROTOCOL FOR ESTABLISHING METHOD DETECTION LIMITS

3.1 Introduction

Method Detection Limits (MDLs) are set at the 95% confidence level above zero (or the blank - see section 4.0). For an infinite number of replications this is:

$$MDL = 2 \times 1.645 * SD_{near\ zero}$$
$$= 3.29 \times SD_{near\ zero}$$

where SD near zero is standard deviation estimate made within a factor of 10 of the (expected) MDL.

MDL for a smaller number of replicates is

$$MDL = 2 \times t_{1,\ 0.05} \times SD_{near\ zero}$$

where $t_{1,\ 0.05}$ = the one-tailed 't' statistic at p = 0.05 (see Table 1).

The standard deviation, SD, of a low level sample may be used to produce this estimate.

The sample used should have the following characteristics:

- i) the sample must be stable
- ii) it must have an analyte concentration that minimizes the overestimation of sigma-zero ($\sigma_{\varnothing}$), (the population standard deviation at zero)
- iii) it must have an analyte concentration that is sufficient to produce a measured value that is statistically significant

A concentration in the range of 1 to 3 times the anticipated MDL is recommended.

The standard deviation used to estimate $\sigma_{\varnothing}$ may be the within-batch standard deviations provided by duplicate or replicate samples carried through the sample processing steps, or the standard deviations of between-batch replicates.

Calculation of standard deviations should be based on:

    i)   blank corrected data, if appropriate, and

    ii)   at least 7 observations of the analytical result (sample size n=7).

The 't' statistic is used to compensate for the tendency of small sample sizes to underestimate variability.

3.2 Calculation of Standard Deviation

The formulae used to calculate standard deviation, SD, are as follows:

Case 1. duplicate analyses carried out in successive batches

$$SD = sqrt\ [\ \Sigma\ (x_1 - x_2)^2\ /2n\ ]$$

where n = number of pairs of data.

Case 2. replicate analysis carried out in a single batch

$$SD = sqrt\ [\ \Sigma\ (x - x_i)^2\ /2n\ ]$$

where n = number of pairs of replicates.

Case 3. replicate analysis carried out in successive batches

$$pooled\ SD = sqrt\ [\ \{\ \Sigma\ (v_1 \times s_1{}^2) + (v_2 \times s_2{}^2) + ... (v_i \times s_i{}^2)\}\ /\ (v_1+v_2+ ..... v_i)\ ]$$

where v = degrees of freedom for each batch,
and   s = standard deviation for each batch.

Examples of methods for estimating SD for MDL calculation:

1.   Replicate analysis of a bulk sample of the desired matrix known to be homogenous and stable. Sub-sampling of the bulk sample is performed and each sub-sample is carried through the entire preparative and analytical step. Concentration is not to exceed 10 times the estimated MDL, but is preferred to be 1-3 times the estimated MDL. Estimate SD using formula case 2 for single batch analysis, and formula case 3 for multiple batch analysis.

2.   If a bulk sample is not available, prepare a composite sample in the concentration range required. Continue as in 1.

3.   If the above two are not possible, use duplicate analyses from several batches, adhering to the described concentration range. Use formula in case 1 for estimation of SD.

4.   If the above three are not available, use a spiked blank or clean matrix, to produce a large sample. Take steps to assure the spike is homogenously distributed (e.g. mixing overnight). Spike to a concentration not greater than 10 times the estimated MDL. Sub-sample this bulk spiked sample and carry each sample through all preparative and analytical steps. Use formula case 2 to estimate SD.

5.   If facilities do not allow preparation of a bulk spike sample, spike individual blank or clean matrix samples to a concentration as defined above. Take steps to assure the spike is homogenously distributed (e.g. mixing overnight). Continue as described above.

6. If no blank or clean matrix is available proceed as in 4 or 5 using pure de-ionized water as the matrix.

7. For methods which employ continuous monitoring of a detector signal, 3 times the noise in the area of the analytical peak can be used if none of the above can be used. This produces an estimate of instrument SD and does not take into account the contribution of preparative and matrix effects.

3.3   Calculation of Method Detection Limits

Section 3.2 demonstrates how method standards may be determined for three cases: from pairs of duplicates, from replicates in same batch and for pooled standard deviations from replicates in successive batches.

An example calculation of MDL is presented for each of these three cases:

EXAMPLE 1:   MDL ESTIMATION FROM DUPLICATES

EXAMPLE 2:   MDL ESTIMATION FROM REPLICATES IN SAME BATCH

EXAMPLE 3:   MDL ESTIMATION FROM POOLED STANDARD DEVIATIONS FROM REPLICATES IN SUCCESSIVE BATCHES

These appear as Tables 4, 5 and 6 respectively. For each example the data have been organized in a format convenient for spreadsheet calculation.

MDLs must be determined for each matrix type processed by the laboratory, and must reflect all steps of the applicable method.

3.4   Recorded Figures

MDLs should be recorded to one non-zero figure. The final MDL values and the data used to estimate SD should be recorded to two significant figures, to reduce rounding errors.

3.5   Limit of Quantitation

The limit of quantitation (LOQ) is normally defined as 10 times SD (at MDL). The LOQ is the concentration at which precise quantitative results are possible (precision approaches ± 30%). At the MDL, on the other hand, the presence of a detected t analyte is defined with certainty but concentration estimates are imprecise (precision approaches ±100%).

3.6   Confidence Interval Convention

The MDL definition described here uses a factor of 2 x the one sided 't' factor at p = 0.05, and is sometimes referred to as a Reliable Detection Limit (RDL). For an infinite sample size, this would be MDL = 3.29 x SD. This is the sum of two distributions: one centered on 0 (zero) has a 5% risk of declaring a null quantity as a positive amount, while the other distribution, centered above 0, involves a 5% chance of declaring a measurement as 0, when in fact, it is real (see Table 3).

The MDL definition given at the bottom of Tables 4, 5 and 6 is the USEPA convention. This definition uses the one-sided 't' factor for p = 0.01. For an infinite sample size, this would set the MDL = 3 x SD. This is derived from a single distribution, centered on 0 (zero) and having a 1% risk of declaring a null quantity as a positive amount.

The two MDLs, while derived from different theory, are in fact very close. The USEPA derived MDLs include lower and upper limits; the CAEAL value always falls within those limits.

4.0 BLANKS

While there are few situations where blank correction is appropriate, monitoring of blanks should be carried out for most samples and blanks should be controlled within defined limits for data to be acceptable.

4.1 Documentation of Blanks

Batch blank values shall be recorded on the analytical result sheet with each batch. In addition, a tabulation of day-to-day blanks shall be maintained and kept current. It will include, at a minimum, analytical date, preparative and analytical operators' initials, individual blank values, a reference to the long term blank and the date range over which it was determined, and any comments explaining unusual occurrences. If possible a control chart of batch blanks will be maintained.

4.2 Determination of Long Term Blank

The long term blank should be estimated, on at least 2 separate occasions, from replicate blank matrices which have been processed through all the preparative and analytical steps applied to a regular sample. It is suggested that 10 replicate blanks be processed on each occasion. The long term blank value should be confirmed at least once each year.

The average and standard deviations of blank readings should be calculated for each occasion. Pooled blank average and standard deviations should be calculated using the following formula (Taylor, 1987):

Pooled Standard Deviation (σ) =

$$\text{sqrt } [\Sigma \{ (v_1 \times s^2_1) + (v_2 \times s^2_2) + ... + (v_n \times s^2_n) \} / (v_1 + v_2 + ... v_n)] \qquad (1)$$

$$\text{where} \quad s_n = \text{standard deviation for } n^{th} \text{ case.}$$
$$v_n = \text{degrees of freedom, usually} = n - 1.$$

Test for outliers using the Grubbs test (Taylor, 1987). If outliers are present, remove them and recalculate the average and standard deviation as above.

4.3 Application

Blank correction should be applied to every sample for which a reliable estimate of long term blank levels has been made (i.e., the blank is in statistical control).

Blank correction should be applied to all samples where the batch method blank(s) exceeds the method detection limit (MDL), and is less than the long term blank control limits.

Samples with concentrations greater than 20x the batch blank, need not be blank corrected (US EPA, 1990).

4.4 Evaluation of batch blanks

If all batch blanks are <MDL, no blank correction is necessary.

4.4.1 <u>Where the long term average batch blank is known.</u>

If all batch blanks are greater than the MDL and less than the control blank limit, all batch samples for that parameter should be corrected by subtracting the average batch blank.

The control blank limits will be set as the long term average method blank plus 1.64 times the standard deviation of the long term average blank.

If the long term average blank is <MDL, the control blank limits will be set as MDL plus 1.64 times the standard deviation of the long term average blank.

This control limit should include approximately 95% of the blank values that will occur.

If the estimate of the long term blank is based on <100 determinations, the appropriate 't $_{0.05}$' value from the table of 't' values is substituted for 1.64.

If any batch blank exceeds the long term blank control limit, the batch must be reprocessed.

If this is not possible due, for example, to insufficient sample, or instability of the sample, the parameter results can be blank corrected, but must be flagged in the report as having "High blank, subtraction made, accuracy of results may be compromised".

If multiple parameters are analyzed for the same sample preparation batch, and if more than 5% of the parameters exceed the blank control limits, the batch must be re-processed; e.g., for ICP total metals scans (33 elements), if more than 2 parameters have blank levels greater than blank control limits, the batch must be re-processed. Otherwise the parameters greater than blank control limits can be reported with a flag stating "High blank for parameter XX, subtraction made, accuracy of results may be compromised".

Criteria Concentration	Action to take
Batch blank ≤ MDL	no correction
Batch blank > MDL	blank correct
Batch blank > long term blank control limit	reprocess batch
Sample concentration > 20 x batch blank	no correction

4.4.2   Incorporation of batch blank into calibration curve

If the batch blank is part of the calibration curve, this effectively corrects for the blank provided the linearity of the calibration curve is not destroyed.

If the batch blank deviates from the linear best fit line, calculated excluding the blank, by greater than 50%, the batch blank is too high, and the batch must be re-processed.

4.4.3   Situation where long term blank is not known:

If all batch blanks are <MDL, no blank subtraction is necessary.

If all batch blanks are greater than the MDL and less than 10X the MDL, all batch samples for that parameter may be corrected by subtracting the average batch blank.

If any batch blank exceeds 10 times the MDL, the batch must be reprocessed.

If this is not possible, due, for example, to insufficient sample, or instability of the sample, the parameter results can be blank corrected, but must be flagged in the report as having "High blank, subtraction made, accuracy of results may be compromised".

4.4.4   Readable units

Where the batch blank fails the blank control limit test by ≤ one readable unit, the batch blank shall be considered acceptable.

4.5   Documentation of Blank QC

Batch blank values are to be recorded on the analytical result sheet with each batch. In addition, a tabulation of day to day blanks shall be maintained and kept current. It will include, at a minimum, analysis date, preparative and analytical operators initials, individual blank values, a reference to the long term blank and the date range over which the long term blank was determined as well as any comments explaining unusual occurrences. If possible a control chart for batch blanks is to be established and maintained.

Analytical reports to clients must indicate whether or not data has been blank corrected. In addition, the reports must indicate batch blank levels for the data, regardless of whether blank correction has been applied.

4.6   Blank Correction Summary

Blank correction is rarely appropriate when these rules are followed, since at high analyte concentrations the correction is insignificant and at low levels (near MDL), the blank, whether subtracted or not, merely increases the uncertainty of the value.

5.0   QC FOR SMALL LABORATORIES

While all laboratories are encouraged to implement a comprehensive QA program, it is recognized that small laboratories with limited resources may find it economically necessary to implement a less comprehensive program.

This section is relevant only to small permittee laboratories that participate in the CALA laboratory proficiency-testing program and who have achieved a PE score greater than 70 for each applicable variable in the last four studies and who generally analyze only small batches of samples.

A small batch is defined as less than 11 samples analyzed at one time as a group using a common blank, standards and duplicate data. In cases where a laboratory receives only a few samples per day, and sample stability or treatment permits, it is preferable that samples be stored and run as one small batch on a weekly basis. If stability does not permit, the samples should be analyzed on a daily basis.

5.1   Small Laboratory Quality Control Level

a.   Group samples (e.g. colorimetric methods)

- one method blank per batch
- one duplicate sample per batch
- one certified reference sample per batch (internal recovery control)

b.   Individual sample (e.g. NFR, pH, BOD, AOX)

- one blank daily
- one duplicate per 10 samples (minimum 1 per week)
- one certified reference sample or internally prepared recovery control per 10 samples (minimum 1 per week)

5.2 Small Laboratory Quality Control Criteria

a. Calibration control limits of ±2s as a warning limit and ±3s as a control limit are applicable for quality control standards for most variables.

b. Method blanks

- If the batch blank is ≤MDL, no blank subtraction is necessary.
- If the batch blank exceeds the MDL, refer to sections 4.3 and 4.6 above.

c. Duplicates for water and wastewater must be within the precision limits given in Table 1020:I of Standard Methods, 18th Edition (1992).

d. Internal recovery control must be within the precision limits given in Table 1020:I of Standard Methods 18th Edition (1992).

6.0 REFERENCES

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7.0   REVISION HISTORY

February 14, 1994:	Initial publication.
December 31, 2000:	Republication: additional text added to 2.18; item 3.4 clarified; definition of 'significant figures' added to glossary. Revision history added. Several editing changes to clarify items. Rules for reporting summed parameters was added as requested and with wording approved by the BCLQAAC Technical Subcommittee. Reference to the EDQA laboratory proficiency testing was replaced by reference to the CAEAL laboratory proficiency testing program. M. Clark 2000 citation added to References.
July 8, 2009:	Revision of Sections 2.4, 2.18, 3.3, 3.4, 3.5(new), 3.6(new) and deleted Sections 3.5 and 3.8.
October 1, 2013:	Section 2.4, in ToC, changed to "Sample Collection and Preservation". Table 2 updated. Revision history added.
October 2015:	Section 2.17 updated, Section 2.4 Preservation Table updated.

Table 3. Values of the one-tailed 't' statistic at p=0.05, applied to the standard deviation, SD, appear in the following table

Degrees of Freedom	$t_{1,\ 0.05}$
7	1.90
8	1.86
9	1.83
10	1.81
15	1.75
20	1.73
25	1.71
30	1.70
40	1.68
60	1.67
infinity	1.64

For case 1, duplicates, degrees of freedom = n, the number of pairs of duplicates,

For case 2, replicates in same batch, degrees of freedom = n - 1, where n = the number of replicates,

For case 3, pooled SD from replicates in successive batches, degrees of freedom = sum of $v_1 + v_2 + ... v_i$.

Table 4. Example 1: MDL estimation from duplicates

MDL determination for Carbon in Soil Samples

Parameter:	Total Carbon, Leco	Matrix:	Soil, sediment
Sparcode:	C--T	Units:	µg/g

Procedure   Results for duplicates analyses of soil samples on different days were recorded. All data are less than 10x the MDL.

Sample #	result 1	result 2	difference	difference^2
4486	4100	4600	500	250000
262	5200	5300	100	10000
25074	2600	2200	400	160000
25080	3500	3700	200	40000
25090	1600	1500	100	10000
25099	2000	2300	300	90000
26011	2100	2100	0	0

SD dup =   sqrt [difference^2 / (2 x # of duplicates)]   200

MDL	=	SD dup x 2 x t 0.05, t (df = 7)
	=	SD dup x 2 x 1.895
	=	758

Table 5. Example 2: MDL estimation from replicates in same batch

MDL determination for BTEX in soil samples

Sparcode:	BTEXF092	Matrix: Soil	units:	µg/g
Instrument:	HP5890A/FID GC#5	Operator: ***	MDL listed =	1
Prep.	Extract 5 g with Freon	Date: 7-Jul-93		

5 g of sea sand was spiked to 10 µg/g with BTEX standard, mixed, sealed in a purge & trap vial, and retained for 2 days in freezer. The samples were then individually processed.   m,p-Xylene was spiked at 20 ug/g.

	Benzene	Toluene	m- & p-Xylene	o-Xylene
	8.978	8.936	18.182	9.130
	8.280	8.340	16.980	8.560
	7.578	7.654	16.282	8.250
	5.732	6.184	14.076	7.230
	5.428	5.662	12.960	6.682
	8.924	8.864	18.074	9.088
	6.434	6.602	14.308	7.276
	8.668	8.494	17.244	8.642
	6.624	6.896	15.318	7.804
average	7.405	7.515	15.936	8.074
std dev	1.389	1.221	1.867	0.873
count	9	9	9	9
MDL	5.1668	4.5407	6.9451	3.2464
MDL (1 sig fig)	5	5	7	3
MDL (USEPA) =2.896 x SD	4	4	5	3
LCL (USEPA) =0.72 x MDL	2.9	2.5	3.9	1.8
UCL (USEPA) =1.65 x MDL	6.6	5.8	8.9	4.2

Table 6. Example 3: MDL estimation from pooled standard deviations from replicates in successive batches

Parameter: Cd-D   **Units:** mg/L   **Instrument:**   Varian GFAA in ppb mode

Cd MDL for GFAA - attempt to achieve 0.1 ppb

Between day data.

Date	conc 1	conc 2	conc 3	conc 4	conc 5
design	0.00000	0.00050	0.00240	0.00060	0.00120
10-Sep	0.00002	0.00048	0.00238	0.00065	0.00116
14-Sep	-0.00001	0.00055	0.00256	0.00066	0.00126
15-Sep	0.00000	0.00049	0.00242	0.00065	0.00124
15-Sep	-0.00002	0.00047	0.00242	0.00069	0.00138
16-Sep	-0.00001	0.00054	0.00252	0.00067	0.00136
17-Sep	0.00000	0.00052	0.00234	0.00070	0.00124
19-Sep	0.00000	0.00049	0.00249	0.00068	0.00119
21-Sep	-0.00001	0.00052	0.00247	0.00065	0.00120
23-Sep	-0.00001	0.00053	0.00247	0.00067	0.00122
23-Sep	0.00001	0.00050	0.00235	0.00064	0.00121
24-Sep	-0.00002	0.00054	0.00246	0.00068	0.00128
25-Sep	-0.00001	0.00046	0.00255	0.00065	0.00127
28-Sep	0.00000	0.00047	0.00242	0.00057	
30-Sep		0.00046	0.00238	0.00065	
1-Oct		0.00040	0.00233	0.00068	
average	-0.000005	0.000495	0.002437	0.000659	0.001251
std dev	0.000011	0.000040	0.000074	0.000030	0.000066
count	13	15	15	15	12
MDL mg/L	0.000040	0.000141	0.000260	0.000107	0.000236
MDL µg/L	0.040	0.141	0.260	0.107	0.236

Based on a single concentration.

Design			>10x MDL		>10x MDL

Note: conc'ns. 3 & 5 are too high and not used to calculate MDL.

Pooled sd   0.00003   with 40 df for blank, 0.0005, and QCB.
The pooled standard deviation for other 3 concentrations is
Pooled sd = sqrt[((n1-1) x sd1^2+(n2-1) x sd2^2 + (n4-1) x sd4^2) / (n1-1)+(n2-1)+(n4-1)]
MDL from pooled sd: 0.00010242

MDL (CAEAL), µg/L (1 sig. fig.):   **0.1**

USEPA MDL, µg/L   **0.07**   lower control limit 0.05;   upper control limit 0.12

Note: Pooling of standard deviations is appropriate over concentrations up to 10 x the MDL,
          and over several days of data acquisition.

GLOSSARY OF STATISTICAL TERMS USED IN QUALITY ASSURANCE

Accuracy - indicates the closeness of a measured value to a true value; combines bias and precision.

Bias - consistent tendency of measured value to deviate, either positively or negatively, from a true value.

Calibration check standard - standard, usually mid-analytical range, used to monitor the validity of instrument calibration between periodic full recalibration.

Confidence coefficient - the probability, expressed as a percentage, which a measurement result will reside in the confidence interval (between the confidence limits).

Confidence interval - the set of possible values within which the true value will reside with a stated probability level.

Confidence limit - upper or lower boundary values delineating the confidence interval.

Detection limits - various limits are defined; in increasing order these are:

Instrument detection limit (IDL) - the analyte concentration that produces a response five times greater than the signal/noise ratio of the instrument. This is similar to the "criterion of detection" which is defined as 1.645 times the standard deviation, s, of blank analyses.

Lower limit of detection (LLD) - also called "detection limit" (DL) and "limit of detection" (LOD) - the analyte concentration in reagent water that produces an instrument response $2(1.645)s$ above the mean of blank analyses. This criterion sets the (maximum?) probability of both Type I and Type II errors at 5%.

Method detection limit (MDL) - the analyte concentration that, when processed through the complete method, produces an instrument response with a 99% probability that it is non-blank.

Limit of Quantitation (LOQ) - the analyte concentration that produces an instrument response sufficiently greater than the response by the blank that it can be measured within specified accuracy limits by competent laboratories in routine operation. Typically it is regarded as the analyte concentration that produces a response ten times greater than the standard deviation, s, of the reagent water blank signal.

Duplicate - least case of replicates (two); in general, while any portion of the analytical protocol can be duplicated, the term duplicate is usually applied to duplicate samples, i.e., two samples taken at the same time from the same location.

Internal standard - a pure compound different from, but similar enough to, the analyte, that, when added at a known concentration to the sample extract immediately prior to instrumental analysis, allows corrections due to instrument inefficiencies or vagaries.

Laboratory control standard - a standard, optimally certified by an outside authority, used to measure method bias.

Precision - gauge of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation.

Quality assessment - procedure for determining the quality of laboratory data using internal and external quality control measures.

Quality assurance - a system of laboratory operation that specifies the measures used to produce data of documented accuracy.

Quality control - a set of procedures applied to an analytical methodology to demonstrate that the analysis is in control.

Random error - the deviation experienced in any step of an analytical procedure that can be estimated by standard statistical techniques.

Replicate - repeated operation of part of an analytical procedure. Two or more (instrumental) analyses for the same analyte in a processed sample are termed replicate extract analyses.

Significant figures – A convention of reporting numeric results where all digits in result are known without doubt, except for the right-most figure.

Surrogate (or surrogate standard) - a pure compound different from, but similar enough to, the analyte that, when added at a known concentration to the sample prior to processing, provides a measure of the overall efficiency of the method (recovery).

Type I error - also called alpha error, is the probability of deciding an analyte is present when it actually is absent.

Type II error - also called beta error, is the probability of deciding an analyte is absent when it actually is present.