

STANDARD OPERATING PROCEDURE

For

USEPA METHOD 300.0, Rev. 2.1

THE DETERMINATION OF INORGANIC ANIONS

SOP #: EPA 300.0

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MassDEP

Massachusetts Department of Environmental Protection
Division of Environmental Analysis
Senator William X. Wall Experiment Station
37 Shattuck Street, Lawrence, MA 01843

Prepared by: <u>Maria E. Ruiz</u> Maria E. Ruiz, Chemist	Date: <u>October 2000</u>
Revised by: <u>Nina M. Duston</u> Nina M. Duston, Chemist	Date: <u>January 29, 2013</u>
Approved by: <u>James H. Sullivan</u> James Sullivan, Laboratory Supervisor	Date: <u>January 29, 2013</u>
Approved by: <u>John J. Bardzik</u> John Bardzik, Laboratory Certification/Quality Assurance Officer	Date: <u>January 29, 2013</u>
Approved by: <u>Ann Marie Allen</u> Ann Marie Allen, Acting Deputy Director and Quality Assurance Manager	Date: <u>January 29, 2013</u>
Approved by: <u>Oscar E. Pancorbo</u> Oscar Pancorbo, Director	Date: <u>January 29, 2013</u>



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LIST OF REVISIONS

Rev. #	Date	Description of Revision	Page #
0	October 2000	None	
1.0	October 2001	Section 8.2, Nitrate-N (non-chlorinated and chlorinated) was added Section 11.2 was added; the following sections were renumbered from 11.2-11.8 to 11.3-11.9 Table 1, Table 2, and Table 3 were updated Table 4 was added	11-12 18 21 & 23 24
1.1	March 2002	Table 2 and Table 3 were updated Numerous minor edits	22-23 Throughout Document
1.2	April 2003	Changes to Section 7.5.1 Section 14.3 & 14.4 added Section 15.1 rewritten Table 1 deleted Table 2 and 3 renumbered to Table 1 and Table 2 and updated Table 4 renumbered to Table 3	10 20 20 21 22 & 23 24
1.3	November 2003	Numerous minor edits	Throughout Document
1.4	April 2004	Numerous changes throughout document as corrective action to USEPA New England On-site Audit Report (March 25, 2004) – includes addition of equipment maintenance procedures in Section 6.0	Throughout Document
1.5	December 2006	Replaced old DEP Logo with state seal + MassDEP New operating system software (Sec. 6.2.10) New software operating procedures (Sec. 10.5 – 10.9) Updated chromatographic conditions (Table 1) Updated MDLs for Part A analytes (Table 2)	Title page & header 9 18 – 21 25 26



Rev. #	Date	Description of Revision	Page #
1.6	January 2008	Section 3.0 - Added definitions Minor wording changes throughout document (Sections 6.2, 7.7, 8.2, 9.2.1, 9.3.2, 11.9, 12.1, 13.2) Section 7.5.2.4 – Added factors for converting nitrate to nitrate-N, nitrite to nitrite-N, and phosphate to phosphate-P Sections 9.2.2 & 10.5.2.1 – Major wording changes Section 11.1 – Updated calibration procedure Section 11.2 – Updated analytical sequence Tables 1, 2 and 3 - Updated	5 Throughout document 14 16 23 23 27-29
1.7	March 2008	Table 3 – Revised	29
1.8	May 2008	Section 9.2.2 – Clarification of the determination of method detection limit	16 & 17
1.9	August 2009	Minor wording changes Table 2 – Updated with most recent MDL data including clarification of Chloride MDL	Throughout document 28
2.0	April 2011	Section 1.3 – Added Note Table 2 – Updated MDL data	
2.1	December 2012	Tables 1 and 2 – Updated	
2.2	January 2013	Table 2 – The spiking concentration for fluoride and the MRLs for chloride and bromide were incorrect in the earlier revision (Rev 2.1) and have been corrected.	



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1.0 SCOPE AND APPLICATION

- 1.1 This method covers the determination of the following inorganic anions:

PART A – Bromide, Chloride, Fluoride, Nitrate-N, Nitrite-N, Ortho-Phosphate-P, & Sulfate

PART B – Bromate, Chlorate, and Chlorite

- 1.2 The matrices applicable to this method are:

PART A – Drinking water, ground water, surface water, reagent water, mixed domestic and industrial wastewaters, soil and other solid matrices (after extraction – see Section 11.8), leachates (when no acetic acid is used)

PART B – Drinking water and reagent water

- 1.3 The Method Detection Limits (MDLs) for the above analytes in reagent water for our laboratory are listed in Table 2, Part A and Part B. The MDLs for a specific matrix may differ from those listed, depending upon the nature of that sample matrix.

Note

Part A: When there are no requests for analysis of field samples, MDLs must be determined every 12 months; when a new operator begins work; or whenever there is a significant change in the background or instrument response. If the laboratory receives or expects to receive field samples on a given date and the MDLs are more than 6 months old, the laboratory shall repeat the MDL determination immediately prior to receiving the samples or with the sample analysis batch.

Part B: These analytes are rarely requested; Part B MDLs will be updated when a request for analysis occurs.

- 1.4 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification will be supported by the use of a fortified sample matrix that includes the anions of interest. The fortification procedure is described in Section 9.4.1.

1.4.1 Analysts must demonstrate the ability to generate acceptable results with this method using the procedures described in Section 9.0.

2.0 SUMMARY OF METHOD

- 2.1 A small volume of sample is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

- 2.2 An extraction procedure (See Section 11.8) is performed on solid matrices prior to analysis by ion chromatography.



3.0 DEFINITIONS

- 3.1 **Laboratory Reagent Blank (LRB)** – An aliquot of reagent water that is treated exactly as a sample. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.
- 3.2 **Stock Standard Solution (SSS)** – A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.3 **Calibration Standard (Cal Std, Cal Standard, or Standard)** – A solution prepared from the dilution of stock standard solutions or from the primary dilution standard solution. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.4 **CAS** – Chemical Abstract Service.
- 3.5 **Laboratory Duplicates** – Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures.
- 3.6 **Laboratory Fortified Sample Matrix (LFM)** – An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory.
- 3.7 **Method Detection Limit (MDL)** – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.
- 3.8 **UCL** – Upper Control Limit = Mean concentration (X) + 3 standard deviation (SD)
- 3.9 **UWL** – Upper Warning Limit = X + 2 SD
- 3.10 **LCL** – Lower Control Limit = X - 3 SD
- 3.11 **LWL** – Lower Warning Limit = X - 2 SD
- 3.12 **Quality Control Sample (QCS)** – A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards.
- 3.13 **Laboratory Fortified Blank (LFB)** – An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory.
- 3.14 **Calibration Blank (CB) or Continuing Calibration Blank (CCB)** – A volume of reagent water used in the calibration curve.
- 3.15 **Initial Calibration Verification (ICV)** – One or more solution(s) of method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria. The ICV(s) is/are run after the Calibration standards. May also be called an Instrument Performance Check solution (IPC).
- 3.16 **Continuing Calibration Verification (CCV)** – One or more solution(s) of method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria. The CCV(s) is run after sample analyses and before the end of the analysis run. May also be called an Instrument Performance Check solution (IPC).



- 3.17 **Proficiency Test (PT) Sample** – Prepared by a third-party supplier acceptable to EPA. The sample's true analyte concentration is unknown to the analyst. Analyte concentrations measured and reported by laboratories throughout the U.S. and world for a PT sample are used to determine statistically the accuracy and precision that can be expected for the given analytical method when used by a competent analyst.
- 3.18 **Material Safety Data Sheet (MSDS)** – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire potential, and reactivity data, including storage, spill containment, and handling precautions.
- 3.19 **Linear Calibration Range (LCR)** – The concentration range over which the instrument response is linear.
- 3.20 **Field Duplicates (FD)** – Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
- 3.21 **Instrument Performance Check Solution (IPC)** – A solution of method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria. See Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

4.0 INTERFERENCES

- 4.1 The water dip or negative peak that elutes near, and can interfere with the fluoride peak is voided using void volume treatment for this peak (3.46 min).
- 4.2 Substances with retention times that are similar to and overlap those of the anions of interest can cause interferences. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to eliminate most interference problems associated with retention times.
- 4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.
- 4.4 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known co-elution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant.
- 4.5 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Leachates of solid matrix samples when acetic acid is used for pH adjustment are not recommended.
- 4.6 Samples that contain particles larger than 0.45 μm and reagent solutions that contain particles larger than 0.20 μm require filtration to prevent damage to instrument columns and flow systems.
- 4.7 The quantitation of un-retained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate etc.) that are conductive and co-elute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.



- 4.8 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, purge the sample with an inert gas (argon or nitrogen) for above five minutes or until no chlorine dioxide remains.

5.0 SAFETY

- 5.1 The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.
- 5.2 Standard laboratory protective clothing and eye covering is required.

6.0 EQUIPMENT AND SUPPLIES

- 6.1 **Analytical Balance** - Capable of accurately weighing to the nearest 0.0001 g; used to weigh target analyte salts for stock standard preparation.
- 6.2 **Dionex DX-120 Ion Chromatograph Components, Operation, and Maintenance**

Note: DX-120 must be turned on and eluent pumped through the system for a minimum of 4 hours once per week to prevent precipitation of carbonates. Precipitated carbonates can cause total or partial blockage of system resulting in increased system pressure, leaks in the Anion Self-Regenerating Suppressor (ASRS) and/or pump, delayed or erratic peak retention, or peak shape changes.

- 6.2.1 High-pressure pump – Single-reciprocating piston with metal-free flow path with PEEK™ (polyether ether ketone) components

Flow Range: 0.5 to 4.5 mL/min; set to 1.0-mL constant volume.

If the DX-120 is idle for 90 minutes, the pump flow automatically decreases to 1/20th of its current flow rate and the Self Regenerating Suppressor (SRS) cycles on and off. The LEDs on the **Pump** and **SRS buttons flash. Press any button to return to the last selected flow rate.**

- 6.2.1.1 **High Pressure Pump Maintenance** – The high-pressure pump is replaced when the pump leaks, the piston sticks or breaks, the flow rate is not stable or the seals leak.

- 6.2.2 Pulse Damper – Coiled restricted tubing (PEEK)™ controlled compliance.

Maximum Pressure: 4000 psi

- 6.2.2.1 **Pulse Damper Maintenance** – The pulse damper is replaced when the tubing is crimped or broken or a leak at the connection is not fixed by replacement of the connector or connector parts.

- 6.2.3 Rheodyne Injection Valve – Two-position, six-port, electrically activated valve with PEEK-wetted components. In the load position, sample is loaded into the sample loop,



where it is held until injection. In the Inject position, sample is swept to the column for analysis.

Eluent flows through one of two paths, depending on the valve position:

- In the Load position, eluent flows from the pump, through the valve, and to the column, bypassing the sample loop. Sample flows from the syringe or autosampler line, through the valve, and into the sample loop; excess sample flows out to waste.
- In the Inject position, eluent flows from the pump, through the sample loop, and on the column, carrying the contents of the sample loop with it.

6.2.4 Anion guard column – Dionex-IonPac AG9-HC- 4- x 50-mm (P/N 051791); a protector of the separator or analytical column. If omitted, the retention times will be shorter.

6.2.4.1 **Guard Column Maintenance** – The guard column is replaced when:

- Baseline becomes noisy or increases, or extraneous peaks not normally encountered in sample type appear and all other possible sources of the problem, such as eluent, leaks, valves, etc., have been ruled out.
- Sample or eluent will not flow through column but will flow to column.

6.2.5 Anion separator column – Dionex- IonPac AS9-HC- 4- x 250-mm (P/N 051786). Anion Exchange high capacity (Latex). Table 1 outlines the standard conditions and typical results using these conditions.

6.2.5.1 **Separator Column Maintenance** – The separator column is replaced when:

- Retention times shift, peak shape changes, baseline becomes noisy or increases and all other possible sources of the problem, such as eluent, leaks, valves, tubing, have been ruled out.
- Sample or eluent will flow to the column but will not flow through column.

6.2.6 Anion suppressor device – Dionex-ASRS-Ultra-4mm (P/N 53946). Anion Self-Regenerating Suppressor (ASRS) Recycle Mode set at 100 mA. The SRS neutralizes the eluent and enhances analyte conductivity. This improves sensitivity, stability, and dynamic range. For a dual-column system, order two suppressors.

6.2.7 Detector: Conductivity cell – A DX-120 heated cell (DS4 Detection Stabilizer Model DS4-1; P/N 031183); active volume, 1.25 μ L; 316 stainless steel electrodes; range, 1000 μ S, full scale. All detector cells require enough backpressure to prevent eluent in the cell from degassing. Degassing creates bubbles in the cell and disrupts detector response. The detector produces a signal based on a chemical or physical property of an analyte. The temperature compensation setting is selected with a DIP (dual in-line package) switch (SW5-5) at 1.7 % to minimize the effect of temperature fluctuations.

6.2.7.1 **Detector Maintenance** – The detector is replaced when:

- No response is found after checking all connections, including electrical, and all other possible sources of the problem including, but not limited to,



bubbles in the line, leaking connectors or tubing, no eluent leaking SRS or valves, broken tubing, and standards have been ruled out.

- Detector leaks or is cracked or broken.
- Detector response is erratic or decreases, and the problem is not fixed by cleaning the detector.
- For heated detector(s), the heating element is not functioning properly.

6.2.8 Pressurizable Regenerant Plastic Reservoir

6.2.9 Automated sampler (Dionex – AS40) with PeakNet connections to TTL (transistor-transistor logic) input and output connectors on the DX-120 rear panel. The AS40 holds 66 vials of 5-mL size. The unique PolyVial sample vial eliminates the need for an external sampling pump. The vial incorporates a cap that acts as a simple piston to force sample out of the vial and deliver it to an injection loop with backpressure up to 690 Kpa (100 psi). The caps with a 20- μ m-filter pore size are used to remove particles from the samples and reagents before injection.

6.2.10 Operation system – Windows 2000 Control Software - Chromeleon 6.6, Serial No. 47824; Dell Computer, Model OPTIPLEX GX270.

6.2.11 Printer – HP-Laser 1100

6.3 **Miscellaneous laboratory glassware** – All washed with a detergent solution and rinsed with tap water; rinsed with reagent water prior to use.

6.4 **Helium** – Compressed High Pressure Gas.

6.5 **Magnetic stirrer, with TFE-coated stirring bar.**

6.6 **Bottles, high-density polyethylene (HDPE), 125 mL; used for** samples and storage of calibration solutions.

7.0 REAGENTS AND STANDARDS

7.1 **Eluent solution** – 9.0-mM Na_2CO_3

Dilute 18 mL of 0.5-M or 1-N Na_2CO_3 solution to 1000 mL with reagent water or dissolve 1.91 g of sodium carbonate (CASRN 497-19-8) in reagent water and dilute to 2 L.

7.2 **Stock standard solutions, 1000 mg/L (1 mg/mL).**

Prepared from ACS reagent grade materials (dried at 105° C for 30 min) as listed below:

7.2.1 Bromide (Br^-) 1000 mg/L: Dissolve 0.1288 g sodium bromide (NaBr , CASRN 7647-15-6) in reagent water and dilute to 100 mL in a volumetric flask.

7.2.2 Bromate (BrO_3^-) 1000 mg/L: Dissolve 0.1180 g of sodium bromate (NaBrO_3 , CASRN 7789-38-0) in reagent water and dilute to 100 mL in a volumetric flask.



- 7.2.3 Chlorate (ClO_3^-) 1000 mg/L: Dissolve 0.1275 g of sodium chlorate (NaClO_3 , CASRN 7775-09-9) in reagent water and dilute to 100 mL in a volumetric flask.
- 7.2.4 Chloride (Cl^-) 1000 mg/L: Dissolve 0.1649 g sodium chloride (NaCl , CASRN 7647-14-5) in reagent water and dilute to 100 mL in a volumetric flask.
- 7.2.5 Chlorite (ClO_2^-) 1000 mg/L: Dissolve 0.1676 g of sodium chlorite (NaClO_2 , CASRN 7758-19-2) in reagent water and dilute to 100 mL in a volumetric flask. Or buy 1000 mg/L Chlorite standard (Cat # AS-CL029-2Y-Spex CertiPrep).
- 7.2.6 Fluoride (F^-) 1000 mg/L: Dissolve 0.2210 g sodium fluoride (NaF , CASRN 7681-49-4) in reagent water and dilute to 100 mL in a volumetric flask.
- 7.2.7 Nitrate (NO_3^- -N) 1000 mg/L: Dissolve 0.6068 g sodium nitrate (NaNO_3 , CASRN 7631-99-4) in reagent water and dilute to 100 mL in a volumetric flask.
- 7.2.8 Nitrite (NO_2^- -N) 1000 mg/L: Dissolve 0.4926 g sodium nitrite (NaNO_2 , CASRN 7632-00-0) in reagent water and dilute to 100 mL in a volumetric flask.
- 7.2.9 Phosphate (PO_4^- -P) 1000 mg/L: Dissolve 0.4394 g potassium phosphate (KH_2PO_4 , CASRN 7778-77-0) in reagent water and dilute to 100 mL in a volumetric flask.
- 7.2.10 Sulfate (SO_4^{2-}) 1000 mg/L: Dissolve 0.1814g potassium sulfate (K_2SO_4 , CASRN 7778-80-5) in reagent water and dilute to 100 mL in a volumetric flask.

NOTE: Stability of stock standards: For at least 1 month when stored at 4°C, except for the chlorite standard which is only stable for two weeks.

- 7.3 **Ethylenediamine preservation solution** – Dilute 10 mL of ethylenediamine (99%) (CASRN 107-15-3) to 200 mL with reagent water. Use 1 mL of this dilution to each 1 L of sample taken for the determination of chlorite.
- 7.4 **Reagent Water** – ASTM Type I reagent-grade water (Note: Method requires only Type II water). Water should contain particles no larger than 0.20 microns.
- 7.5 **Preparation of Calibration Standards** – Fresh calibration standards are prepared each day samples are analyzed.

From the stock solutions (7.2) prepare the following combined standards.

7.5.1 **METHOD A**

7.5.1.1 STD # 4

<u>Anion</u>	<u>Concentration, mg/L</u>
SO_4^{2-}	50
NO_2^-	10
NO_3^-	10
Br^-	10



Cl^-	10
F^-	5
PO_4^{3-}	5

Preparation: Into a 100-mL volumetric flask, pipet 5 mL of 1000 mg/L solution of sulfate (7.2.10), 1 mL of 1000 mg/L solution of each of the following: bromide, (7.2.1), nitrate (7.2.7), nitrite (7.2.8), chloride (7.2.4). Pipet 0.5 mL 1000 mg/L solution of each of the following: fluoride (7.2.6), and phosphate (7.2.9). Fill the flask to 100 mL with reagent water.

7.5.1.2 STD # 3

<u>Anion</u>	<u>Concentration, mg/L</u>
SO_4^{2-}	25
NO_2^-	5
NO_3^-	5
Br^-	5
Cl^-	5
F^-	2.5
PO_4^{3-}	2.5

Preparation: Pipet 25 mL of STD # 4 into a 50-mL volumetric flask and fill the flask to 50 mL with reagent water.

7.5.1.3 STD # 2

<u>Anion</u>	<u>Concentration, mg/L</u>
SO_4^{2-}	5
NO_2^-	2
NO_3^-	2
Br^-	2
Cl^-	2
F^-	1
PO_4^{3-}	1

Preparation: Pipet 10 mL of STD #4 into a 100-mL volumetric flask and fill the flask to 100 mL with reagent water.



7.5.1.4 STD # 1

<u>Anion</u>	<u>Concentration, mg/L</u>
SO_4^{-2}	0.50
NO_2^{-}	0.20
NO_3^{-}	0.20
Br^{-}	0.20
Cl^{-}	0.20
F^{-}	0.10
PO_4^{-3}	0.10

Preparation: Pipet 10 mL of STD # 2 into a 100-mL volumetric flask and fill the flask to 100 mL with reagent water.

7.5.2 **METHOD B**

7.5.2.1 STD # 4

<u>Anion</u>	<u>Concentration, mg/L</u>
BrO_3^{-}	5.00
ClO_3^{-}	5.00
ClO_2^{-}	5.00

Preparation: Into a 100-mL volumetric flask, pipet 0.5 mL of 1000 mg/L solution of each of the following: bromate (7.2.2), chlorate (7.2.3), and chlorite (7.2.5). Fill the flask to 100 mL with reagent water.

7.5.2.2. STD # 3

<u>Anion</u>	<u>Concentration, mg/L</u>
BrO_3^{-}	2.50
ClO_3^{-}	2.50
ClO_2^{-}	2.50

Preparation: Pipet 25 mL of STD # 4 into a 50-mL volumetric flask and fill the flask to 50 mL with reagent water.



7.5.2.3 STD # 2

<u>Anion</u>	<u>Concentration, mg/L</u>
BrO_3^-	1.00
ClO_3^-	1.00
ClO_2^-	1.00

Preparation: Pipet 20 mL of STD # 4 into a 100-mL volumetric flask and fill the flask to 100 mL with reagent water.

7.5.2.4 STD # 1

<u>Anion</u>	<u>Concentration, mg/L</u>
BrO_3^-	0.10
ClO_3^-	0.10
ClO_2^-	0.10

Preparation: Pipet 10 mL of STD # 2 into a 100-mL volumetric flask and fill the flask to 100 mL with reagent water

Alternative concentrations may be similarly prepared so long as the highest standard's concentrations do not exceed the Linear Range of the test and the lowest standard's concentrations are at or below the Minimum Reporting Level (MRL) determined for this test.

Commercially prepared single or multi-element stock or mixed standards of high quality may be substituted and appropriate alternative calibrations, as described above, made. Certain stock standards may require conversion factors as follows. Multiply nitrite by 0.3045 to obtain nitrite-N. Multiply nitrate by 0.2259 to obtain nitrate-N. Multiply phosphate by 0.3261 to obtain phosphate-P.

7.6 **Blanks**

7.6.1 Laboratory Reagent Blank (LRB). An aliquot of the reagent water used to make the calibration standards and QC elements.

7.6.2 Laboratory Fortified Blank (LFB). Fortify an aliquot of the LRB with the analytes of interest at a value at least four times the MDL but not to exceed the highest calibration standard used in the analysis. Prepare the LFB from the same stocks and standards and in the same manor as the calibration standards. For example, from the stock solutions prepare the following combined LFB for Method A.

From the stock solutions (7.2), pipet into a 100mL volumetric flask 0.5-mL sulfate (7.2.10), 0.15-mL nitrate (7.2.7), bromide (7.2.1), fluoride (7.2.6), nitrite (7.2.8), and phosphate (7.2.9). Fill the flask to 100 mL with reagent water.



- 7.7 **Initial Calibration Verification (ICV) Solution(s).** For all determinations, the laboratory must analyze one or more ICV (a mid-range check standard) prepared from the same standard stock solution used to prepare the calibration standards.
- 7.8 **Quality Control Sample (QCS).** For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solutions and prepared according to the manufacturer's instructions.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1 Samples must be collected in plastic or glass bottles.
- 8.2 Sample preservation and holding times for the anions determined by this method are as follows:

ANALYTE	PRESERVATION	HOLDING TIME
Bromide	None required	28 days
Chlorate	None required	28 days
Chloride	None required	28 days
Chlorite	Cool to 4°C	Analyze immediately; otherwise see Sec. 8.3.1
Fluoride	None required	28 days
Nitrate-N (non-chlorinated)	Cool to 4°C	48 hours
Nitrate-N (chlorinated)	Cool to 4°C	14 days
Nitrite-N	Cool to 4°C	48 hours
Combined (Nitrate/Nitrite)	Conc. H ₂ SO ₄ to a pH < 2	28 days
O-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days.

- 8.3 It is recommended that all samples be cooled to 4°C and held for no longer than 28 days for Method A and analyzed immediately when using Method B.
- 8.3.1 If the sample cannot be analyzed for chlorite within 10 minutes, it may be preserved as follows. Add 1 mL of the ethylenediamine (EDA) preservative solution (Sec. 7.3) per 1 L of sample. This will preserve the chlorite for up to 14 days without affecting the bromate or chlorate so that they can be determined in the same preserved sample. Any residual chlorine dioxide should be removed prior to sample preservation with EDA.

9.0 QUALITY CONTROL

- 9.1 The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data generated.



9.2 Initial Demonstration of Performance

9.2.1 Instrument Performance

- Determination of linear calibration ranges (LCR) and analysis of quality control samples (QCS) are required prior to samples being analyzed by this method.
- Linear calibration range (LCR) must be determined initially and verified every 12 months or whenever a significant change in instrument response is observed or expected. The verification of linearity must use a minimum of a blank and three standards.
- The QCS is analyzed at the beginning of the run. If the determined concentrations are not within $\pm 10\%$ of the stated values, performance of the determinative step of the method is unacceptable.

9.2.2 Laboratory Performance

Determination of Method Detection Limit (MDL) – MDLs are established for all analytes using reagent water fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method over at least three separate days.

$$MDL = (t) \times (S)$$

Where:

t = Students' t value for a 99 % confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

S = standard deviation of the replicate analyses.

NOTE: When there are no requests for analysis of field samples, MDLs must be determined every 12 months, when a new operator begins work, or whenever there is a significant change in the background or instrument response. If the laboratory receives, or expects to receive field samples on a given date and the MDLs are more than 6 months old, the laboratory shall repeat the MDL determination immediately prior to receiving the samples or with the sample analysis batch.

9.3 Assessing Laboratory Performance

- 9.3.1 A laboratory reagent blank (LRB) and IPC solution must be analyzed immediately following each calibration, after every tenth sample, and at the end of the run. Analysis of the IPC solution immediately following calibration must verify that the instrument is within $\pm 10\%$ of calibration. Subsequent analyses of the IPC solution must verify the instrument is still within $\pm 10\%$ of calibration. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.



9.3.2 Laboratory fortified blank (LFB) – One LFB is analyzed with each batch of samples.

Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses if possible. When this is not possible the samples will be qualified. When sufficient internal performance data become available (usually 30 analyses), control charts are made. After each five to ten new recovery measurements, new control limits can be calculated using only the 30 most recent data points. Replicate LFBs should be run to assess precision whenever samples are analyzed if sample duplicates are expected to be below the MRL.

9.4 **Assessing Analyte Recovery and Data Quality**

9.4.1 Every 10 or fewer samples, analyze a duplicate and LFM of an aliquot of a sample used for analysis. The LFM sample is spiked with at least four times the MDL; analyte concentration must be high enough to be detected above the sample's concentration but not exceed the linear range of the test. It is preferable that the same added analyte concentration be used as in the LFB. The LFM is spiked with the same stocks or standards used to generate the calibration curve; it is a duplicate of an aliquot of a sample used for analysis.

9.4.2 Recovery calculations are not required if the concentration added is less than 25 % of the unfortified sample concentration.

Calculate the percent recovery for each analyte using the following equation:

$$R = \frac{C_s - C}{S} \times 100$$

Where,

R = percent recovery.

C_s = fortified sample concentration.

C = sample background concentration.

S = concentration equivalent of analyte added to sample.

9.4.3 Percent recovery for each analyte must be in the range of 80-120 %. If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

9.4.4 When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification must be used.

9.4.5 Calculate the relative percent difference (RPD) of the initial sample concentration (I_c) and duplicate sample concentration (D_c) using the following formula.



$$RPD = \frac{|(I_c - D_c)|}{([I_c + D_c] \div 2)} \times 100$$

10.0 CALIBRATION AND STANDARDIZATION

- 10.1 Remove stock standard(s), QCS and samples from refrigerator. Prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (Sec. 7.2) or commercial stock standards to a volumetric flask and diluting to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range or a new calibration curve must be chosen. Two of the new calibration standards must bracket the concentration of the analyte of interest.
- 10.2 Fill eluent container on top of the DX-120 Chromatograph. End-line filters (P/N 045987) are installed on the end of the eluent line inside reservoir to remove small particulates that may contaminate the pump check valves and cause erratic flow rates or loss of prime. To prevent air from being drawn through the lines, make sure that the end of the filter reaches the bottom of the eluent reservoir.
- 10.3 Turn on the HELIUM gas to pressurize eluent reservoir. Verify the pressure is regulated at 300 kPa (45 psi).
- 10.4 Press the power switch below the DX-120 front control panel to turn on the system power. The DX-120 is in LOCAL mode at power-up.
 - 10.4.1 Press **Eluent Pressure** to turn on the gas pressure to the eluent reservoir(s). A regulator inside the DX-120 regulates the pressure to between 5 to 10 psi.
 - 10.4.2 Press **Pump** to turn on the pump flow.
 - 10.4.3 Press **SRS** to turn on the SRS power. The screen briefly displays the SRS current setting in mA (300).
 - 10.4.4 Press **Flow Setting** and verify that the pump flow rate is correct (1 mL/min). If necessary, pull out the knob on the front of the pump and turn it right or left to increase or decrease the flow rate. When the correct rate is displayed, push in the knob.
 - 10.4.5 Press **Offset Cond** to display the offset conductivity reading.
 - 10.4.6 Allow the system to equilibrate for 15 to 20 minutes. The screen displays the background conductivity (the conductivity of the eluent before injecting sample). Press **Auto Offset** to offset the background and zero the reading.

NOTE: If the DX-120 receives no input for 90 minutes, the pump flow is reduced to 1/20th of its current rate and the SRS cycles on and off (SW1-2). The LEDs on the Pump and SRS buttons flash when this occurs. Press any button to return to the previous flow rate.
- 10.5 Switch on the computer, monitor, printer, and auto sampler. To start the Chromeleon program, select OKAY in the "Logon to Windows" window; no password is required. Double click the Chromeleon icon.



NOTE: The Chromeleon server configuration was set during software installation. Unless the system configuration changes (e.g., additional equipment, updated equipment, or new equipment are added), you do not need to access this software. The server monitor is accessed through Chromeleon at later point.

Chromeleon uses Windows elements such as menu bars, toolbars, status bars, and folders. The first window contains a list of folders containing sample information files, program files, and method (quantitation) files.

10.5.1 Program Files (.pgm). The DX120.pgm file contains the information necessary to control the DX-120, AS-40 autosampler, and signal acquisition by the computer software. This information should not be changed unless there are changes in equipment, column or eluent type, or timing and/or duration of data acquisition. Note that there is also a shutdown program (shutdown.pgm), which allows the computer to turn off the DX-120 pump, SRS, and Eluent pressure. This file is used in a dummy sample placed at the end of the sample run to place the DX-120 in a semi-off mode. This saves eluent, eluent gas, and pump-wear. These programs are in the folder marked Program.

10.5.2 Method Files (.qnt) contain the information necessary to calibrate and quantitate samples. There are several toolbars and page tabs available. Additionally, one sample chromatogram may be displayed while in the qnt screen.

10.5.2.1 Tabs

General: Contains the global settings for the qnt editor. How to treat retention times, analyte units, and calibrations are on this tab. These settings should not need changing under normal circumstances

Detection: The detection parameters determine how peaks are recognized, classified, or suppressed as well as determining baseline contact. Once established, these parameters generally do not need to be changed unless there are changes to columns, eluent, equipment, or sample specific interferences (e.g., rider peaks, inverse peaks) occur.

Peak Table: In conjunction with the Amount Table and Peak Tracking tabs, contains the parameters required to identify peaks, perform calibrations, and convert the measured area values into amount or concentration values. This table contains the peak name, peak retention time, retention time window, calibration type, integration type, peak type, and calibration standard type.

Amount Table: In conjunction with the Peak Tracking and Peak Table tabs, contains the information required to identify peaks, perform calibrations, and convert measured area into concentration values. This table contains the peak name, peak retention time, response factor, and standard concentrations. Response Factor may be used to calculate a calibration curve and sample concentrations from a related parameter. For example, ortho-Phosphate-P can be calculated from ortho-Phosphate data by using a Response Factor of 0.326.

Peak Tracking: In conjunction with the Peak Table and Amount Table tabs, contains the information required to identify peaks, perform calibrations, and convert measured area into concentration values. This tab is used when



comparing spectral information (e.g., UV analyses) and is not relevant to this method. Information on this page should not be changed. However, should problems arise in quantitation, check that the parameters are set as follow: Check Deriv, Rel Max Dev, and Check Extr are all off. Min WL and Max WL are all Auto.

Calibration: This tab lists the calibration samples, and associated information used for calibrating the current sample. Note that the Name must be identical to the Name on the Sample List or the software will not be able to find the calibration samples. Lack of a calibration curve or skipping of a standard may be traced to this.

The Spectral Library Screening and SST tabs are not used in this method.

The method file currently in use for this method is EPA 300 Anions7.qnt. The contents of the method window are affected by how the method is accessed. If the method is opened through the folders Peaknet5 imports/methods, only the above tabs appear with the default or original information. If the qnt file is opened above the Sample List or in the Method column of the Sample List, the window will also include the results for that sample and may include the chromatogram. Note that, if the qnt window is not visible, click on the yellow menu button with green peak and black calibration line.

- 10.5.3 Sample List contains the information necessary to create a sample run, calibrate, and quantitate samples. At minimum, this list must contain a sample number (No.), sample name (Name), Sample Type (Type), Program, Method, and status. Optional but useful columns include Dilution Factor, Injection information (Inj. Date/Time), Comment, and autosampler position (Pos.). The As-40 sampler is not capable of two-way communication with the controller; therefore, the samples must be placed in the autosampler sequentially. For this reason, Pos. is analyst only information and optional. Other autosamplers may require this information in the Sample List.
- 10.6 Develop one or more Methods for analyzing samples (if necessary). Establish ion chromatographic operating parameters equivalent to those indicated in Table 2A.
- 10.7 Use the Sample List to create, store, and edit Schedules of analyses that use the Method in a logical sequence. Each line of a List specifies a sample name, sample type and program, a Method to be used for the analysis, and any optional correction factors. Automatic calibrations and shut down of the system is incorporated.

To open the Schedule Editor's main window, click on the Schedule button in the PeakNet MainMenu. The main window contains a blank spreadsheet in which each row represents one injection.

10.7.1 Sample List Parameters

- **SAMPLE:** Type in a name (no limit on number of characters) that identifies the sample.
- **SAMPLE TYPE:** Specifies whether the injection is a Sample (unknown), Calibration Standard (Standard) or Blank. If the sample Type is Calibration Standard, the program will use sample data to calculate the response factors for each sample



component and update the Method's Component Tables (peak areas and retention times).

Note: Other types of samples are available for other detectors.

- PROGRAM: DX120 for samples, shutdown for dummy sample at the end of the run
- METHOD: Click on an empty Method cell to activate the drop down box. Only the qnt in box at top are available. When you select the Method to be used to analyze the sample, the filename will be entered in the empty Method cell. If the method of interest is not available, drag a copy from the methods folder or create a new method.
- DILUTION (Optional): The dilution factor provides a mathematical correction. If there was no dilution, use the value 1. This parameter is ignored for calibration standards.

10.7.2 To SAVE the Sample List:

In the FILE Menu command, click on the **Save as** to create a new List. Type in a filename. and **SAVE AS**. To rewrite a previously saved List to the disk under the same name, click on the SAVE toolbar button or File, Save.

10.8 Collect standards/samples in the 5-mL vial. Collect them in the order they are listed in the Schedule Editor. Push the cap into the vial until the top is flush with the top of the vial. Except if a sample loop rinse is desired, fill vial with reagent water and insert cap with outer ring flush. This does not count as a sample in the List.

10.9 Start the Server Monitor by double clicking the icon in the lower right corner shaped like a chameleon head with a red X over it. If there is no X, the Server Monitor is already active. In the small box that appears, click START. Once the monitor is started, minimize or close the box.

10.9.1 In the browser, open the Folder Control Panel, Double Click on Control Panel.pan. Hit Ctrl+Tab to toggle back to the browser and click on the Sample List of interest. By using Ctrl+Tab, it is now possible to toggle between the Sample List and Control Panel.

10.9.2 The Control Panel is used to monitor the DX-120, AS-40, sample chromatogram, Sample List information, etc. It also contains the menus for running a batch [one or more Sample List(s)].

10.9.2.1 **DX120 Ion Chromatograph:** This box allows the software to control certain of the DX-120 parameters as well as reporting the status of certain parameters. A check mark in the box next to a parameter indicates it is under computer control. To run samples, Connected, Pump, SRS, and Eluent Pressure should all be checked. Column is A for this method. This box also contains information on the current position of the injection port.

10.9.2.2 **AS-40 Autosampler:** This box contains information on the status of the AS-40 autosampler. Since this autosampler is not capable of two-way communication, this is an information only box.



10.9.2.3 **DX120 Detector:** This box contains a real-time graphic of the current sample's chromatogram. It is possible to change scales and zoom in on part of the chromatogram; otherwise, it is an information only box.

10.9.2.4 **Sample:** This box contains the information associated with the batch being run as well as the sample being run. This box is information only.

10.9.2.5 **Audit Trail:** This box contains the last several commands received, actions taken by the software, and information or error messages generated by the software. It is an information only box.

10.9.3 To run a set of samples:

10.9.3.1 Choose batch from the menu at the top of the Control Panel

10.9.3.2 Choose start. This will bring up a "Start Batch on DX120?" dialog box.

10.9.3.3 Choose ADD. This activates a browser, which allows for the selection of the correct Sample List(s) to be run. Select the correct Sample List(s) and click OPEN. The Sample List(s) should now appear on the "Start Batch on DX120" box.

10.9.3.4 Select READY CHECK. This action checks the memory to determine if there is sufficient space to store the results. When manually controlling the starting of a Batch, as in this instance, it will also produce an error/information message telling you there is no start time associated with the batch. If this is the only error or information message, the system is ready to analyze the samples. Click OKAY.

10.9.3.5 Check to be sure the first sample in the autosampler is located under the sampling probe. If not, press Hold/Run and the first sample will move into position.

10.9.3.6 Click START on the "Start Batch on DX120?" box. The software will activate the autosampler and DX-120 according to the Program file instructions, and record and quantitate the samples according to the Method file.

Note: The chromatogram and results for any sample that has been analyzed may be viewed by toggling to the Sample List and double clicking on the sample name.

11.0 PROCEDURE

11.1 Calibrate and run samples as described in Section 10.9. **Note that a calibration curve must be a straight line (only linear calibration is allowed) and contain a minimum of three points to be a valid calibration. Check the calibration information to be sure that the software did not remove a calibration point from the curve, thereby invalidating the calibration curve.**

11.2 Sequence of Analysis

1. Calibration Blank



2. Standard #1
 3. Standard #2
 4. Standard #3
 5. Standard #4
 6. Standard #5
 7. Standard #6
 8. Standard #7
 9. ICV [One or more mid-range check standard(s) used as Performance Check Standard(s)]
 10. MRL [One or more standards at the Minimum Reporting Limit used as Performance Check Standard(s)]
 11. QCS [One or more standards made from a stock different from the Calibration Standards used as Performance Check Standard(s)]
 12. Continuing Calibration Blank (CCB) (same as the LRB)
 13. LFB (one for each batch, and at least quarterly or when samples are run)
 14. Samples including a sample duplicate and LFM as required (total of 9 or fewer)
 15. CCV [One or more mid-range check standard(s) used as Performance Check Standard(s)]
 16. CCB
 17. Samples including a sample duplicate and LFM as required (total of 10 or fewer)
 18. Repeat 15 through 17 as needed. If a second LFB is included with a set of samples, the total number of samples must be reduced to nine or fewer including a duplicate and LFM as needed.
 19. CCV [One or more mid-range or upper-range check standard(s) used as Performance Check Standard(s)]
 20. QCS, if requested or required [One or more standards made from a stock different from the Calibration Standards used as Performance Check Standard(s)]
 21. CCB
 22. End
- 11.3 To finish a run early and keep the data from the run, click on the Batch-Stop menu or Stop Batch toolbar button.
- 11.4 To finish a run early and discard the data, click on the Abort toolbar button.



- 11.5 A new calibration curve is done every day samples are analyzed.
- 11.6 Table 1 summarizes the recommended operating conditions for the ion chromatograph.
- 11.7 If the response of the peak exceeds the working range of the calibration curve, the sample is diluted or higher working range calibration curve is used.
- 11.8 The following extraction should be used for solids samples. Add an amount of reagent water equal to **ten times** the weight of **dry** solid sample. This slurry is mixed for **ten minutes** using a magnetic stirring device. Filter the resulting slurry using a 0.45 μ membrane type filter before collecting sample.
- 11.9 To print the calibration curve(s), open any sample chromatogram, click on the Printer Layout button in the menu, double click the analyte name above the plot of the curve, choose the correct analyte, select apply or reject for the four curves on the page, and print the page. Rename the four curves to obtain more than four analytes' plots.

12.0 DATA ANALYSIS AND CALCULATIONS

- 12.1 A calibration curve for each analyte is determined from the data acquired for each different calibration level using **external** standard calculations, by plotting instrument **response**, as **peak area**, against **standard concentration**, using a **linear** interpolation, by a least squares calculation to fit a line through the calibration data points. Direct measurement for each sample is made, by comparing sample response with corresponding calibration curve. Note that a valid curve must contain a minimum of three calibration points.

The following values, used to calculate analyte amount, are determined automatically by the software and cannot be edited.

$$\text{Amount} = KO + K1 \times \text{Area.}$$

KO indicates the Y-intercept of the calibration curve.

K1 is the slope of the calibration curve for the selected calibration level.

- 12.2 Sample data are reported in **mg/L**.
- 12.3 Report NO_2^- as NO_2^- -N
 NO_3^- as NO_3^- -N
 HPO_4^{-2} as HPO_4^{-2} -P
- 12.4 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed, or run a higher calibration curve.

13.0 METHOD PERFORMANCE

- 13.1 Participate in annual proficiency test studies.



13.2 Precision and Accuracy Quality Control Charts are reviewed monthly by the WES QA Officer.

14.0 POLLUTION PREVENTION

- 14.1 Refer to the WES Environmental Management System (EMS) policy and SOPs regarding pollution prevention.
- 14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

15.0 WASTE MANAGEMENT

- 15.1 WES laboratories fully comply with all applicable federal, state, and local environmental regulations. WES is also committed to protecting the air, water, and land by minimizing and controlling all chemical releases from fume hoods, biological safety cabinets, and bench operations. Refer to the WES EMS policy and SOPs regarding waste management.
- 15.2 All waste chemicals are collected in sealed waste containers. Once the waste containers reach capacity, they are transferred to the WES hazardous waste storage room where they are emptied into a waste drum (organic or inorganic). Within 180-days of waste accumulation, the waste drum is transported off the premises by a licensed hazardous waste management contractor. Under the WES EMS, a chemical inventory database has been developed to track purchases and use of chemicals and other hazardous materials, and the waste generated by the use of these chemicals.

16.0 REFERENCES

- 16.1 Dionex, DX-120 Ion Chromatograph Operator's Manual and on-line help.
- 16.2 U.S Environmental Protection Agency, Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.1, August 1993.



17.0 TABLES AND VALIDATION DATA

TABLE 1. Chromatographic Conditions for the Analysis of Inorganic Anions in Reagent Water by EPA Method 300.0 (02/01/2012 – 07/21/2012)

Analyte	Peak #	Retention Time (Min.)	Range (mg/L)	Linearity (r^2)
PART A				
Fluoride	1	3.8	0.00 – 6.0	>0.995
Chloride	2	6.7	0.00 – 6.0	>0.995
Nitrite-N	3	8.5	0.00 – 1.8	>0.995
Bromide	4	11.3	0.00 – 6.0	>0.995
Nitrate-N	5	13.5	0.00 – 1.4	>0.995
O-Phosphate-P	6	17.0	0.00 – 2.0	>0.995
Sulfate	7	20.4	0.00 – 6.0	>0.995
<u>Standard Conditions</u> Ion Chromatograph: Dionex DX-120 Columns: IonPac AG9-HC, 4x50 mm, AS9-HC-4x250 mm Detection: Suppressed Conductivity, ASRS-Ultra, Recycle Mode Eluent: 9.0-mM Sodium Carbonate (Na_2CO_3) Flow Rate: 1 mL/min Sample Loop: 50 μL Recommended method total analysis time: 25 minutes. System Backpressure: 2040 psi – 2070 psi Background conductivity: 22 μS – 23 μS				
PART B (2/11/2003 Data). Part B will be updated when an analytical request is received.				
Chlorite	1	4.63	0.00 - 5.00	0.9992
Chlorate	2	11.88	0.00 – 5.00	0.9997
System Backpressure: 2225 psi Background conductivity: 25.59 μS Sample Loop: 50 μL				



TABLE 2. Method Detection Limits (MDLs) and Minimum Reporting Limits (MRLs) for the Analysis of Inorganic Anions in Reagent Water by EPA Method 300.0 (Analyzed 02/01/2012 – 07/21/2012)

Analyte	No. of Samples Spiked (n)	Spiked Concentration (mg/L)	Accuracy (Mean % Recovery ^a)	Precision (SD ^b in mg/L)	MDL (mg/L)	MRL (mg/L)
PART A						
Fluoride	7	0.40	110	0.0060	0.27	0.40
Chloride	7	0.05	90	0.0077	0.02	0.05
Nitrite-N	7	0.024	88	0.0062	0.024 ^c	0.12
Bromide	7	0.40	93	0.0045	0.40 ^c	0.40
Nitrate-N	7	0.23	91	0.0035	0.23 ^c	0.23
O-Phosphate-P	7	0.13	77	0.024	0.13 ^c	0.33
Sulfate	7	0.40	90	0.057	0.40 ^c	1.0
^a Recovery of spiked concentration						
^b SD: standard deviation of mean concentration measured						
^c The analytically determined MDL was below the concentration the DX-120 can accurately detect and quantify; the lowest standard the DX-120 can accurately detect and quantify is used as the MDL.						



TABLE 3. Quality Control Elements and Acceptance Limits for EPA Method 300.0 - Determination of Inorganic Anions

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Calibration Blank	At the beginning, after calibration, after every tenth sample, and at the end of the run.	Less than or equal to the MDL. If there is no MDL, then less than or equal to ½ the MRL	Values that exceed the MDL or ½ the MRL indicate laboratory or reagent contamination or contamination of the instrument from previously analyzed samples. The problem must be identified and corrected if possible. Fresh standards prepared if problem can be identified as not instrument contamination and problem can be corrected. Recalibrate if fresh standards made.
Initial Calibration	Every sample batch	$r^2 > 0.99$ for all target analytes	Check eluent, standards, columns, and settings. Correct problem. Recalibrate.
Initial Calibration Verification (ICV)-mid-range Std	After calibration	90 - 110% recovery	ICV must be repeated or instrument recalibrated.
Continuing Calibration Verification (CCV) mid-range or upper -range Std as in Section 11.2	After every tenth sample, and at the end of the run.	90-110% recovery	All samples after the last acceptable CCV must be reanalyzed.
Quality Control Sample (QCS)	After calibration and, if required or requested at the end of the run.	90 - 110% recovery of the manufacturer's certified value	Determinative step of the method is unacceptable. The problem must be identified and corrected.
Laboratory Reagent Blank (LRB)	Every sample batch	Less than or equal to the MDL. If there is no MDL the LRB shall be less than or equal to ½ the MRL.	Check for reagent or laboratory contamination. Correct problem, if possible. Prepare fresh LRB if problem can be corrected. If problem



TABLE 3. Quality Control Elements and Acceptance Limits for EPA Method 300.0 - Determination of Inorganic Anions

QC Elements	Frequency	Acceptance Criteria	Corrective Action
			cannot be corrected, qualify samples with concentrations < 10 times the LRB. If the sample's concentration is not detected or is greater than or equal to 10 times the LRB, no qualification is required.
Laboratory Duplicates	Every ten samples or less	Relative Percent Difference (RPD) less than or equal to 20 or as specified for matrix.	Repeat using fresh sample if possible or qualify the data. If the sample is non-homogenous, qualify the sample result (add this comment to the duplicate result in the LIMS).
Laboratory Fortified Sample Matrix (LFM)	A minimum of 10% of the samples or at least one with every analysis at concentrations \geq four times the MDL, preferably the same concentration as the LFB.	Recovery Limits: 80 - 120% (Method A) 75 - 125 % (Method B)	Either matrix or solution related if the performance for that analyte is shown to be in control, not system related. Comment attached to LFM in the LIMS.
Laboratory Fortified Blank (LFB)	One per batch, ideally at the same conc. used to prepare the LFM	90 - 110% Recovery	Should be identified and resolved before continuing analyses, if possible. Otherwise, qualify the data.
Retention Time or Response	Before an analytical run a separate retention time check may be run. After every calibration using the ICV and CCV Retention Times.	$\pm 10\%$	Check eluent, standards, columns, and settings. Correct problem. Recalibrate.
MDL Determination (USEPA, 1997)	Annually	Target analyte concentration spiked into the blank matrix should not exceed 10 times (1 to 5x ideally) the experimentally determined MDL	Repeat MDL study spiking the blank matrix with lower concentration of the target analyte. If an MDL cannot be determined, an MRL can be used instead with all values below the MRL reported as < MRL.
MRL Check Standard	Every analysis batch	SDWA analytes $\pm 25\%$ All other analytes $\pm 50\%$	Remake the MRL solution(s) and reanalyze. If the remake MRL fails, this indicates that the instrumental system cannot reliably quantitate analyte(s) at the MRL and corrective action must be taken before continuing sample analysis.