Title: THE DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY EPA METHOD 300.1

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1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of the inorganic anions Bromate, Bromide, Chlorate, Chlorite and Nitrite in reagent water, surface water, ground water and finished drinking water.

1.2 This SOP has modified the method to include the analysis of anions in soil subsequent to performing a nominal ten-fold leaching procedure with deionized water.

1.3 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual.

1.4 Drinking Water Maximum Contaminant Levels (MCL) and California Detection Limits for reporting purposes (DLR) are found below (From Chemicals and Parameters in California Drinking Water Quality Database,12/29/10):

Analyte	DLR (ug/l)	MCL (ug/l)
Bromate	5	10
Bromide	--	--
Chlorate	20	--
Chlorite	20	1000
Nitrite as N	400	1000

2.0 SUMMARY OF METHOD

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

3.0 DEFINITIONS

3.1 **Analysis batch**—A group of no more than 20 field samples.

3.2 **Calibration standard**—A solution prepared from the primary stock standard and the surrogate analyte. The calibration standards are used to calibrate the instrument response with respect analyte concentration.

3.3 **Instrument Performance Check (IPC=LCV=Low-level Calibration Verification)**—A solution of target analytes, surrogate used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.4 **Laboratory Control Sample (LCS)**--An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in the control, and whether the laboratory is capable of making accurate and precise measurements. Also called the laboratory fortified blank (LFB) or blank spike (BS).

3.5 **Method Blank (MB)**—An aliquot of reagent water is treated exactly as a sample including exposure to all the glassware, solvent, reagents, and surrogate that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagent or the apparatus. Also called the Laboratory Reagent Blank (LRB) or Blank (BLK).

3.6 **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**—An aliquot of an environmental sample to which know quantities of the method analytes are added in the laboratory. Its

purpose is to determine whether the sample matrix contributes bias to the analytical results. Also called the Laboratory Fortified Matrix/Laboratory Fortified Matrix Duplicate (LFM/LFMD)

3.7 **Quality control sample (QCS/ICV)** – A solution of method analytes of known concentrations that is used to fortify an aliquot of MB. The QCS is obtained from a source separate from that used for the calibration standards.

3.8 **Surrogate**—An analyte added directly to a sample aliquot in a known amount before any sample processing procedures are conducted. The purpose of the surrogate analytes is to monitor method performance with each sample.

4.0 INTERFERENCES

4.1 Substances with retention times that are similar to and overlap those of the anions of interest can cause interferences. These substances can be divided into three categories:

- Direct chromatographic coelution: an analyte response in observed at very nearly the same retention time as the target anion.
- Concentration dependant coelution: is observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target anion.
- Ionic character displacement: retention times may significantly shift due to the influence of high ionic strength matrices overloading the exchange sites in the column and significantly shortening target analyte's retention times.

4.2 Dilute or spike a sample as necessary to solve most interference problems.

4.3 Samples that contain particles larger than 0.45 microns may require filtration to prevent damage to instrument columns and the flow systems.

4.4 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, the sample must be purged with an inert gas (Helium, Argon or Nitrogen) for approximately five minutes or until no chlorine dioxide remains. This sparging must be conducted prior to EDA preservation and at the time of sample collection.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment Required: Safety Glasses/Face Shield, Lab coat, Nitrile Gloves

5.2 Primary Materials Used

There are no materials with a health rating of 3 or 4 used in this method. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Potassium Dichloroacetate	Corrosive Irritant	Not listed	Direct skin contact may cause severe irritation, pain and possibly burns. Vapors may cause irritation of the eyes, nose and throat as well as CNS depression.
Sodium Nitrite	Poison Oxidizer	Not listed	May cause nausea, dizziness, vomiting, and spasms of abdominal pain, rapid heart beat and irregular breathing.
Chlorate Standard	Corrosive Oxidizer	Not listed	Harmful if swallowed, inhaled or absorbed through skin. Corrosive may cause severe burns. Destructive to tissue of the mucous membranes and upper respiratory tract, eyes and skin. Inhalation may be fatal as a result of inflammation, edema of the larynx and pulmonary edema.
Ethylenediamine	Poison Corrosive Irritant	10 ppm or 25 mg/m^3 TWA	Extremely hazardous in case of skin contact, of eye contact, of ingestion, of inhalation. Severe over exposure can result in death.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 Ion Chromatograph Dionex or equivalent
6.1.2 Analytical column
6.1.3 Anion Suppressor device
6.1.4 Detector – Conductivity cell
6.1.5 Autosampler

6.2 Supplies

6.2.1 Analytical balance
6.2.2 Pipets and disposable pipet tips
6.2.3 3 mL syringes with 0.22 um Acrodisc filter
6.2.4 Volumetric flasks
6.2.5 Disposable test tubes
6.2.6 Dionex vials and caps.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent grade water (Ultrapure water)
7.1.2 Ethylenediamine (EDA) 99%
7.1.3 Potassium Dichloroacetate (Cl_2CHCO_2K) (DCA)
7.1.4 Sodium carbonate, HPLC grade

All purchased and prepared reagents must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory

7.2 Standards

7.2.1 Stock standard solution 1000 mg/L -- Bromide (Br), Bromate (BrO_3), Chlorate (ClO_3), Chlorite (ClO_2). Purchased as certified solutions from two different manufacturers.
7.2.2 Alternatively, single anion stock standard solution 1000 mg/L can be prepared from

ACS reagent grade materials.

7.2.3 Sodium Nitrite, A.C.S. grade

7.2.4 1000 mg/L single anion standards from Spex or equivalent

All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable) source material.

All prepared standards must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix Waters and soil leachates	**Sample Container**	**Min. Sample Size**	**Preservation**	**Holding Time**	**Reference**
Bromate Chlorate	Plastic or glass bottle	50 mLs	50 mg/L EDA Cool >0 to 6°C	28 days	40 CFR Part 136.3
Bromide			None required Cool >0 to 6°C		
Nitrite	Plastic		Cool >0 to 6°C	**48 hours**	
Chlorite	Opaque		50 mg/L EDA Cool >0 to 6°C	14 days	

Matrix Soils	**Sample Container**	**Min. Sample Size**	**Preservation**	**Holding Time**	**Reference**
Bromate Chlorate Bromide Nitrite Chlorite	Sleeve or Jar	100 grams	Cool >0 to 6°C	28 days	N/A

*50mg/L EDA in sample this would be equivalent to adding 5.0mL of the EDA preservation solution to 1L of sample.

NOTE: Special sampling requirement and precaution for chlorite.
Sample bottles used for chlorite analysis must be opaque to protect the sample from light. When collecting a sample from a treatment plant employing chlorine dioxide, sample must be sparged with an inert gas (Helium, Argon or Nitrogen) prior to addition of the EDA preservative at time of sample collection,

EDA is used as a preservative for chlorite. Chlorite is susceptible to degradation both through catalytic reactions with dissolved iron salts and reactivity towards free chlorine, which exits as hypochlorous acid/hypochlorite ion in most drinking water as a residual disinfectant. EDA is added into sample serves as dual purpose. First, EDA helps to leach iron as well as other catalytically destructive metal cations and removes hypochlorous acid/hypochlorite ion by forming an organochloroamine. Second, EDA preservation of chlorite preserves the integrity of chlorate, which can increase, in unpreserved samples, as a result of chlorite degradation.

9.0 QUALITY CONTROL

9.1 Sample QC

The following quality control samples are prepared with each batch of samples. Each of these QC samples may be re-analyzed once if it doesn't pass, in order to verify the failure wasn't due to a physical or mechanical problem.

9.1.1 Method Blank (MB)

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. Check that there are no analytes detected above the **MDL**. If the method blank shows contamination, re-prepare and re-analyze once. If it still fails, re-prepare the entire batch and/or re-calibrate the system unless:

- The samples are ND (qualify the result accordingly).
- The sample result is > 10x the blank level (qualify the result accordingly).

9.1.2 Laboratory Control Sample (LCS)

Prepare and analyze a secondary source laboratory control sample (LCS) for every batch of 20 samples or less. The LCS recovery must be within the limits specified in **Table 1** within laboratory acceptance limits of 75-125%. If the LCS is outside of these limits, re-analyze the LCS a second time. If it passes, continue to analyze samples. If it fails, re-prepare the entire batch and/or re-calibrate the system unless:

- The LCS recovery is above the upper limit and samples are ND. Qualify sample results accordingly.

LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.

9.1.3 Matrix Spike and Matrix Spike Duplicate.

The samples used for MS/MSD are randomly selected, unless specifically requested by a client.
Prepare and analyze a matrix spike (MS) and a matrix spike duplicate (MSD) with every **10 samples or less**. The recovery and relative percent difference must be within the limits specified in **Table 1**, unless there is matrix interference. In the case of matrix interference, write an NCM.

Table 1: LCS & MS/MSD Limits

	RL (ug/L)	LCS Spike Level (ug/L)	LCS as Multiple of RL	LCS limits	LCS RPD	MS/MSD limits	MS/MSD RPD limits
Bromate	5	25	5	75-125%	20	75-125%	20
Bromide	50	250	5	75-125%	20	75-125%	20
Chlorate	20	100	5	75-125%	20	75-125%	20
Chlorite	20	100	5	75-125%	20	75-125%	20
Nitrite	10	100	10	75-125%	20	75-125%	20

9.1.4 Surrogates

DCA is added to sample prior analysis. Calculate the surrogate percent recovery, R_{surr}, from all analyses using the following formula:

$$R_{surr} = \frac{SRC}{SFC} \times 100$$

Where:

SRC= Surrogate Recovered Concentration
SFC= Surrogate Fortified Concentration

Surrogate percent recovery must fall between **90-115%** for proper instrument performance and analyst technique to be verified. 90-115% applies to all samples, QC, and calibration checks.
If the surrogate recovery is outside acceptance limits, the sample must be re-analyzed unless:

- If surrogate recovery is out high and the sample is ND the sample results may be reported with a qualifier.

9.2 Instrument QC

The following instrument QC samples are run with each analytical sequence. Each of these QC samples may be re-analyzed once if it does not pass, in order to verify the failure wasn't due to a physical or mechanical problem. Re-analysis must be performed before any batch QC or client samples are analyzed.

9.2.1 Initial Calibration Verification (ICV)

Immediately after the initial calibration, analyze the Secondary source. Verify that that its response is within ± 15% of the true value. See **Table 3**.

- If not, re-prepare the ICV standard.
- If the ICV is still out of control, re-calibrate the system

9.2.2 LCV/IPC/CCV low level

Analyze the Low-level Calibration Verification (LCV) after the ICV when a curve is run and on daily basis when the initial calibration is recalled. Its recovery must be within ± 25%.
If the CCV low level does not meet **±25%** recovery criteria, re-prepare and re-analyzed one time. If still unacceptable, recalibrate. See **Table 3**.

Proper chromatographic performance must be demonstrated by calculating the Peak Gaussian Factor (**PGF**) of the **surrogate** peak in the CCV low level. Calculate the PGF as follows:

$$PFG = \frac{1.83 \times W_{1/2}}{W_{1/10}}$$

Where:
$W_{1/2}$ is the peak width at half height
$W_{1/10}$ is the peak width at tenth height

PGF must fall between 0.80 and 1.15 in order to demonstrate proper instrument performance. If the PGF does not meet acceptance limits, perform necessary maintenance on the IC system, recalibrate if necessary, and re-analyze the CCV low level.

Inspect the retention time (**RT**) for the **surrogate** in the CCV low level and verify that its drift is no more than 2 % relative to the value in the calibration.
If the surrogate RT drift is more than 2 %, verify the preparation of eluent and instrument conditions. If the RT of the surrogate has shifted over extensive usage to any less than 80 % of the original recorded value (when the column was first used), the column may require cleaning or replacement. If no problems are found and all the target analytes are correctly identified, no further corrective action needs to be taken.

9.2.3 Continue Calibration Verification (CCV)

Analyze a CCV standard initially, after every 10 sample aliquots or less and at the end of the sequence.

- The initial CCV must be at the same level as the lowest calibration point (see LCV= low level IPC).
- Subsequent CCVs must be varied between the middle (Level 3 spike amount) and high end of the calibration curve (Level 4 spike amount).

The recovery must be within ± 25% of the true value for spike levels less than or equal to 10 times the RL and ± 15% of the true value for spike levels greater than 10 times the RL; (see **Table 3**.) If the CCV is outside recovery limits, re-analyze once at the same concentration. If it is still out the instrument must be recalibrated and samples not bracketed by acceptable CCVs be reanalyzed unless:

- If the CCV is out high, any ND samples may be reported with a qualifier.

9.2.4 Continuing Calibration Blank (CCB)
Follow every CCV with a CCB (calibration blank). The CCB must read less than the **MDL**. If the CCB is above the **MDL**, re-analyze once. If it is still out, the instrument must be recalibrated and samples not bracketed by acceptable CCBs be reanalyzed unless:

- If the CCB is out high, any ND samples may be reported with a qualifier.

9.2.5 Calibration Acceptance Summary
Refer to the “Calibration Curves” SOP and the “Selection of Calibration Points” SOP for more information on calibrating the instrument.

The calibration curve consist of a minimum of 4* calibration standards. The curve is prepared by plotting the response (peak area) of each standard and a blank against the corresponding concentration using a linear (first-order) least squares regression. The resulting correlation coefficient (r^2) must be > 0.995

*** The method specifies minimums of 3 standards to cover a single order of magnitude of concentration or 5 standards for two orders of magnitude of concentration.**

If this criterion is not met:

- Re-prepare the calibration standards and repeat the calibration.

If continuing the use of a previous calibration curve, the calibration must be verified on each day of use by analyzing a calibration blank and a low level CCV. If the following criteria are not met, a new calibration curve must be prepared:

- The calibration blank result must be less than the MDL.
- The low level CCV recovery must be within ± 25% of the true value
- PGF of the surrogate must fall between 0.80 and 1.15
- The RT drift for the surrogate is not more than 2 %

Table 3: Calibration Check Standard Criteria

	ICV Spike Level (µug/L)	ICV Limits	LCV Spike Level (ug/L)	LCV limits	CCV Spike Level (ug/L)	CCV limits
Bromate	30	85-115%	5	75-125%	25	75-125%
Bromide	300	85-115%	50	75-125%	250	75-125%
Chlorate	120	85-115%	20	75-125%	100	75-125%
Chlorite	120	85-115%	20	75-125%	100	75-125%
Nitrite	300	85-115%	20	75-125%	100	75-125%

10.0 PROCEDURE

10.1 Standard Preparation

10.1.1 Concentrated Eluent solution.
Prepare the concentrated eluent solution by adding 19.1grams Sodium carbonate to 100mL glass volumetric flask and bring up volume to 100mL with Reagent grade water. Prepare every six months; store at room temperature.

10.1.2 Working eluent solution.
Prepare the working eluent solution 9.0mM Sodium carbonate by pipetting 10mL of the concentrated eluent into a 2 liter volumetric flask and diluting to volume with Laboratory Reagent grade water; degas for approximately 10 minutes with helium. Prepare fresh daily; store at room temperature.

10.1.3 Ethylenediamine (EDA) Preservation solution.

Prepare Ethylenediamine (EDA) preservation solution 10,000 mg/L—dilute 5.6 mL of Ethylenediamine (99%) to 500 mL with Laboratory Reagent grade water. Prepare monthly and store at room temperature.

10.1.4 Dichloroacetate (DCA) surrogate solution (500 mg/L).
Prepare Dichloroacetate (DCA) surrogate solution by dissolving 0.065g dichloroacetic acid, potassium salt (Cl_2CHCO_2K) in Laboratory Reagent grade water and dilute to 100mL in a volumetric flask. Prepare every three months or if signs of degradation are present and store at room temperature.

10.1.5 Primary Stock Standards (10,000 mg/L) for Nitrite
Single anion stock standard solutions are prepared from ACS reagent grade materials dried at 105°C for 30 minutes. Prepare the 10,000 mg/L stock standard solutions by adding 1.4998g sodium nitrite to 100 ml plastic volumetric flasks and diluting to volume with Laboratory Reagent grade water.
Stock standards are stored at 0 to 6°C for up to six months from date of preparation.

10.1.6 Intermediate Calibration Standard Mix (10ppm) for Nitrite
Prepare the Nitrite primary intermediate standard by pipetting 0.1mL of the 10,000ppm primary stock solutions into a 100 ml plastic volumetric flask. Bring to volume with Reagent grade water. The standard is stored at 0 to 6°C for up to two months from date of preparation.

10.1.7 Intermediate Secondary Source Standard (10ppm) for Nitrite
Prepare the Nitrite secondary intermediate standard by pipetting 1mL of the 1000ppm purchased secondary stock solutions into a100 ml plastic volumetric flask. Bring to volume with Laboratory Reagent grade water. The standard is stored at 0 to 6°C for up to two months from date of preparation.

Prepare calibration standards for Nitrite following the **Table 4** below

Table 4: Calibration Standards for Nitrite

Calibration Std:	**Level 1**	**Level 2 LCV/IPC Low level**	**Level 3**	**Level 4 = LCS = CCV**	**Level 5**	**ICV ***
Nitrite	0µL	20µL	50µL	100µL	500µL	300µL
DCA	20µL	20µL	20µL	20µL	20µL	20µL
Final Volume	10mL	10mL	10mL	10mL	10mL	10mL
Conc.	0ppb	20ppb	50ppb	100ppb	500ppb	300ppb

* Using second source 10ppm standard

10.1.8 Anions stock standard solutions (1000 mg/L)

Prepare 1000 mg/L anions stock standard solutions by adding each of the following to **separate** 100 mL volumetric flask and bringing up to volume with Laboratory Reagent Grade water. Prepare every six months and store in refrigerator.
Bromide: 0.1288g NaBr (Sodium Bromide)

Bromate: 0.1180g $NaBrO_3$ (Sodium Bromate)
Chlorate: 0.1275g $NaClO_3$ (Sodium Chlorate)
Chlorite: 0.1676g 80%$NaClO_2$ (Sodium Chlorite)

10.1.9 Primary Calibration Standard Mix.
Prepare the primary calibration standard mix by diluting the specified amounts of 1000 ppm stock primary calibration standards (see **Table 5**) into 100 mL volumetric flask and bringing up to volume with Reagent grade water. Prepare every six months. Store in refrigerator.

10.1.10 Secondary Source Standard Mix (ICV/QCs).
Prepare the secondary calibration standard mix (ICV) by diluting the specified amounts of 1000 ppm stock secondary standards (see **Table 5**) into 100 mL volumetric flask and bringing up to volume with Reagent grade water. Prepare every six months. Store in refrigerator.

Table 5: Primary Calibration and Secondary Source Standard Mix

	Final Conc in 100 mL (mg/L)	Volume of 1000 mg/L Stock (mL)
Bromate	1.0	0.10
Bromide	10.0	1.00
Chlorate	4.0	0.40
Chorite	4.0	0.40

Prepare the calibration standards by carefully adding 50uL of EDA and volume of the primary calibration standard mix into each of separate 10mL disposable test tubes following **Table 6** below and bringing up to volume with Reagent grade water. Add 20uL of surrogate DCA on top of the 10mL standard.

Table 6: Calibration Standards

Calibration Std:	**Level 1**	**Level 2= LCV/IPC/CCV Low level**	**Level 3**	**Level 4 =LCS =CCV**	**Level 5 = CCV**	**Level 6**	**ICV/QCS**
Bromate concentration	0 µg/L	5.0 µg/L	12.5 µg/L	25 µg/L	50 µg/L	100 µg/L	30 µg/L
Bromide concentration	0 µg/L	50 µg/L	125 µg/L	250 µg/L	500 µg/L	N/A	300 µg/L
Chlorate & Chlorite concentration	0 µg/L	20/20 µg/L	50/50 µg/L	100/100 µg/L	200/200 µg/L	400/400 µg/L	120/120 µg/L
DCA (surrogate) concentration	1 mg/L	1 mg/L	1 mg/L	1 mg/L	1 mg/L	1 mg/L	1 mg/L
Primary Calibration Standard Mix (Vol)	0.0 µL	50 µL	125 µL	250 µL	500 µL	1000 µL	300 µL (secondary calibration std mix)
Surrogate Volume	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL
Final Volume	10mL	10mL	10mL	10mL	10mL	10mL	10mL

Mix thoroughly and transfer each of calibration points into separate vials to analyze.

10.1.11 Laboratory Control Sample-LCS = Level 3
Prepare by adding 50µL of EDA and 250uL of calibration standard mix into a 10mL disposable test tubes and bringing up to 10mL with Reagent grade water. Add 20uL of surrogate DCA on top of the 10mL LCS.

10.1.12 Matrix Spike/Spike duplicate-MS/MSD
Prepare by adding 50uL of EDA and 250uL of calibration standard mix into a 10mL disposable test tubes and bringing up to 10mL with sample. Add 20uL of surrogate DCA on top of the 10mL sample.
Prepare MS/MSD for Nitrite by adding 100µL of 10ppm standard and 20µL of surrogate into 10mL of sample.

10.1.13 Secondary Source ICV
Prepare the QCS/ICV standard by adding 50uL of EDA and 300 uL of the secondary calibration standard mix into 10mL disposable test tube and bring up to volume with Reagent grade water.
Add 20uL of surrogate DCA on top of the 10mL ICV.

10.1.14 Primary Source CCV: Level 2 (LCV, Low Level), Level 3, Level 4
CCVs are prepared at three different concentrations. CCVs standard are prepare by adding 50uL of EDA and the amount of the primary calibration standard mix indicated in **Table 6** into 10mL disposable test tube and bring up to volume with Reagent grade water. Add 20µL of surrogate DCA on top of the 10mL standard.

10.1.15 Instrument Performance Check Solution (IPC)= CCV low level
Prepare the IPC by adding 50µL of EDA and 50uL of primary calibration standard mix into 10mL disposable test tube and bring up to volume with Reagent grade water. Add 20µL of surrogate DCA on top of the 10mL IPC.

10.2 Sample Preparation

10.2.1 Water samples
Ensure the samples have come to room temperature prior to conducting sample analysis.

Add 5 mL of sample and 10uL of DCA directly into the vial, mix well and sample is ready for analysis (sample should already be preserved with EDA, if not, add 25 µL of EDA).

If a dilution is required, the surrogate is spiked after the dilution is made.

If filtration is required, the surrogate is spiked before the filtration. In addition, all batches QC must go through the sample filtration process.

10.2.2 Soil samples
Add an amount of Reagent grade water (40mL) equal to ten times the weight of the solid material (4 +0.04g). Add 200µL of EDA. Add 80µL DCA on top of sample. If sample size or another factor results in a ratio different from the 10X ratio, note in extraction log. Mix the sample for 30 minutes, by stirring, shaking, or tumbling. Centrifuge, and then filter the resulting slurry through a 0.2um filter. The sample is now in aqueous form. Pour 5 ml of

sample into the Dionex vial and load onto the sampler. Process a Method Blank, LCS, and MS/MSD with the samples including filtration step.

For the Soil MS/MSD: Weigh 4g of sample. Add 1000µL primary calibration standard mix and 39mL of Reagent grade water (same concentration as LCS = Level 3). Add 200µL of EDA. Add 80µL DCA on top of sample; process as a regular sample. The spike level should be 1000µg/Kg relative to the original soil sample

For the Soil MS/MSD for Nitrite: Weigh 4g of sample. Add 100µL of 10ppm of calibration standard and Laboratory Reagent Grade water to 40mL. Add 200µL of EDA. Add 80µL DCA on top of sample.

10.3 Instrument Initialization

Before starting the analysis, make enough fresh eluent to start and run the instrument for the day. Refer to instrument manual for complete operation information

10.3.1 Instrument set-up
Each instrument is configured as listed below. Any slight deviations should be documented in the maintenance logbook.

Instrument Parameters	
System Pressure	~1550-1650 psi
Flow rate	1.5 ml/min
Suppressor Current	100mA
Baseline Conductivity	~16uS
Sample Loop	10-15 uL
Run time	~12 min
Integration Parameters	
Bunch factor	7
Peak width	0.2
Noise Threshold	38
Area Threshold	~200

10.4 Calibration
For a new calibration, load the calibration standards in ascending concentration order followed by the ICV. Verify all calibration criteria are met before proceeding.

Inject each of calibration standards; calibrate the instrument, tabulate peak area responses against the concentration using a linear least squares fit. An acceptable curve has a correlation coefficient of >0.995.

To continue using a previous calibration, recall the calibration file, analyze a calibration blank and ICV. Verify acceptance criteria are met before proceeding.

10.5 Sample Analysis
A typical daily run sequence is listed below:

1	IB (requested analyte < MDL)
2	ICV[1] (± 15%) Second Source
3	Low CCV/IPC (± 25%)
4	LCS (± 15%, ± 25%)
5	Method Blank (requested analyte < MDL)
6	10 samples (including MS1 and MSD1) (± 25%)
7	Mid level CCV (± 15%)
8	CCB (requested analyte < MDL)
9	10 samples (including MS2 and MSD2) (± 25%)
10	High level CCV (± 15%)
11	CCB (requested analyte < MDL)

[1]Only analyzed when an ICAL is performed

10.6 Preventative Maintenance

Record all performed maintenance in the instrument maintenance logbook.

If an instrument is unusable or has limitation to its use, it must be tagged accordingly until such a time the problem has been corrected. Record the problem, solution and verification of proper operation into the instrument maintenance logbook.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.2 Precision (RPD)

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.3 Calibration

$$y = mx + b \qquad C = \frac{(y - b)}{m}$$

Where y is the instrument response (area)
m is the slope
x is the concentration
b is the y-intercept
C is the raw sample concentration (instrument reading

11.4 Concentration

$$C(ug/L) = Raw \times DF$$

Where C = final sample concentration
Raw = instrument raw concentration
DF = dilution factor

12.0 METHOD PERFORMANCE

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified every six months.

12.2 Retention Time Window Study

The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards measured over several days. Three times the standard deviation of retention time may be used as a suggested window size but the retention time window should not extend beyond ± 5% of the retention time any analyte in this method. A retention time window study should be performed annually and whenever a new column type is installed.

12.3 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC can be 1) 4 consecutive LCS samples at 1 to 4 times the RL (prepared from a source different than that used for the ICAL) with an average recovery and RSD within laboratory acceptance limits, or 2) passing results on a blind or PT study. An on-going DOC must be performed annually. An ODOC can be 4 consecutive LCSs at mid-level or a passing PT.

Every new analyst must perform a MDL study before performing analyses on any client samples. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL.

12.4 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

14.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

- **ICs waste** – This waste is disposed of by pouring the liquid waste into the sink, measuring the pH and neutralizing it using soda ash, and then draining the neutralized contents into the sewer system.
- **Soil waste** – Generated by analyst/technicians after samples have been prepared and analyzed in the Wetchem area. This waste is stored in 55-gallon open head metal drum in the wetchem area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid. The drum is removed from the wetchem area to the main waste storage area by sample archive technicians. Analyst/technicians let the sample archive technicians know when they need to remove this drum.

NOTE: Injuries may result when improperly placing the bolt set on the drums (includes metals ring). Therefore, only trained sample archive technicians are allowed to open the metals waste drum.

- **Foreign soil** - This soil waste is generated from samples that have been DI leached by the Wetchem procedures. The soil waste generated is stored in the Step-on waste container located in the weigh out room. Sample archive technicians remove this waste from the weight out room to the main waste storage area every two weeks or as needed. This waste is bulked as RCRA foreign soils.
- **DI Leachate** - The water waste generated from the DI leached procedures is collected in a 1 L plastic containers and label as "Quarantine/foreign soil—Drum for incineration". This waste is removed from the lab to the main waste storage area twice a week. This water waste is also bulked in the same drum of RCRA foreign soils.

Wetchem analysts/technicians or Sample archive technicians collect the carboys from the Wetchem area and transfer them to the main waste storage area twice a week.

- **Unused standards or reagents.** If the standard or reagent is hazardous and cannot be collected with one of the waste streams generated in the method, then the analysts and technicians will take this standard or reagent and place it on the shelves labeled "hazardous waste" in the main waste storage area. The waste material must be labeled with the words "Hazardous Waste", contents and the date taken to the waste storage area. The waste material will be lab packed (example: mercury standard).
- If the waste material can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4).

15.0 REFERENCES / CROSS-REFERENCES

15.1 EPA Method 300.1, PA Methods for Chemical Analysis of water and Wastes, revision 1.0, 1997.

15.2 CA-Q-S-005, Calibration Curves (General).

15.3 CA-T-P-002, Selection of Calibration Points.

15.4 IR-QA-MDL, Determination of Method Detection Limits.

16.0 METHOD MODIFICATIONS

Item	EPA Method 300.1	Modification
1	*Sec. 7.3*	*Dilute standards (Primary and Secondary Calibration mixes) are made every six months instead of every two weeks as indicated in method.*
2	*Sec 9.3.3.2*	*Historic record of RT for the surrogate is not kept as indicated by method.*
3	*Sec.9.4.3*	*The laboratory does not analyze a field or a laboratory duplicate with every analysis batch. The laboratory uses the MSD as the laboratory duplicate.*

17.0 ATTACHMENTS

17.1 **Attachment 1:** Analysis Information
17.2 **Attachment 2:** ICAL Review Checklist
17.3 **Attachment 3:** Data Review Checklist

18.0 REVISION HISTORY

18.1 **Revision 1, dated 30 May 2008**

- Integration for TestAmerica and STL operations
- This revision supersedes 300_1.SOP, revision 1 (02/20/2006)
- Method Blank must read below the MDL not the RL
- CCV must initially be at the low cal and subsequently varied between the middle and high end of the curve
- IPC = CCV low level
- New analyst must perform a MDL study before performing analyses on any client samples as part of their Demonstration of Capabilities.

18.2 **Revision 2, dated 29 January 2010**

- Addition of Safety sections 5.1, 5.2, and table
- Addition of Pollution Control wording
- Addition of Waste Management wording
- Addition of table for method modifications
- Addition of Standard ID on Calibration Checklist
- Addition of Nitrite Determination
- Addition of Soil Sample Preparation and Analysis
- Prepared by LH & KS

18.3 **Revision 3, dated 28 January 2011**

- This revision supersedes IR-WET 300.1.SOP, revision 2 (01/29/2010)

- Revision of calibration model used in order to comply with method.
- Revision of Demonstration of Capabilities
- Revision of Table of Primary Material used
- Revised by KS and LH

18.4 Revision 4, dated 21 August 2012

- This revision supersedes IR-WET 300.1.SOP, revision 3 (01/28/2011)
- Revised Matrix Spike and Matrix Spike Duplicate section.
- Revised Continuing Calibration Blank (CCB) section
- Revised Data Review Checklist
- Revised Reagents and Standards sections
- Added Level 3 Calibration Standard
- Revised by KS and LH

18.5 Revision 5, dated 30 September 2013

- Updated signatories to SOP

Attachment 1
Analysis Information

TestAmerica Irvine

8/14/2012

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Anions-Full List (300.1) in Water (EPA 300.1)								
Preservation: 4 C, Cool								
Container: 500 mL Poly			**Amount Required:** 100 ml			**Hold Time:** 2 days		
Bromate	2.0	5.0 ug/l			75 - 125	20	75 - 125	20
Bromide	10	50 ug/l			75 - 125	20	75 - 125	20
Chlorate	8.0	20 ug/l			75 - 125	20	75 - 125	20
Chlorite	8.0	20 ug/l			75 - 125	20	75 - 125	20
surr: Dichloroacetate (DCA)			90 - 115					
Anions-Full List (300.1) in Soil (EPA 300.1 MOD)								
Preservation: 4 C, Cool								
Container: 4 oz Jar/BrassSleeve			**Amount Required:** 100 grams			**Hold Time:** 28 days		
Bromate	20	50 mg/kg			75 - 125	20	75 - 125	20
Bromide	100	500 mg/kg			75 - 125	20	75 - 125	20
Chlorate	80	200 mg/kg			75 - 125	20	75 - 125	20
Chlorite	80	200 mg/kg			75 - 125	20	75 - 125	20
surr: Dichloroacetate (DCA)			90 - 115					

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Nitrite-N, 300.1 in Water (EPA 300.1)								
Preservation: 4 C, Cool								
Container: 500 mL Poly			**Amount Required:** 100 ml			**Hold Time:** 2 days		
Nitrite-N	3.0	10 ug/l			75 - 125	20	75 - 125	20
surr: Dichloroacetate (DCA)			90 - 115					

Attachment 2
ICAL Review Checklist

CALIBRATION CHECKLIST
EPA 300.1– Inorganic Anions (Part B) by IC

Analyst: _____
Analysis Date: _____
IC #: _____

2nd Level Review: _____
Date: _____
Calibration File # _____

Analyst Rev	2nd Level Rev	
_____	_____	Minimum 3-point calibration, lowest point at or below RL (for single order of magnitude), or Minimum 5-point calibration, lowest point at or below RL (for 2 orders of magnitude)
_____	_____	Linearity check : r >= 0.995
_____	_____	**Calibration Standard ID:**
_____	_____	2nd source ICV : %REC = 85-115
		ICV Standard ID:
_____	_____	All standard solutions contain 50 ppm preservative (EDA) and 1000 ppb surrogate (DCA)
		Calibration date and file checked for completeness and accuracy :
_____	_____	• Correct date, analyst's name and calibration file
_____	_____	• Correct instrument parameters, retention time and window
_____	_____	• Chromatography peak shape and baseline acceptable
_____	_____	• Calibration summary and raw data match for calibration levels and area counts
_____	_____	Date of last MDL study (required every 6 mos):
_____	_____	

Comments: _____

Standard Name:	Cal 1	Cal 2= IPC/CCV Low level	Cal 3 = LCS = CCV	Cal 4 = CCV	Cal 5	ICV
Bromate (µg/L)	0	5	25	50	100	30
Bromide (µg/L)	0	50	250	500	N/A	300
Chlorate & Chlorite (µg/L)	0	20/20	100/100	200/200	400/400	120/120
DCA surr. (mg/L)	1	1	1	1	1	1

Q:\DATA_REV\CHCKLIST\WETCHEM\IC_Anions_300_1\IC300.1_CAL1.doc
Rev 9/09/2009

Attachment 3
Data Review Checklist

DAILY DATA CHECKLIST
EPA 300.1 – Inorganic Anions (Part B) by IC

Analyst: _____ 2nd Level Review: _____
Analysis Date: _____ Date: _____
IC #: _____ **Calibration File #:** _____
QC Batches: _____

Analyst Rev	2nd Level Rev	
____	____	New sequence file created for each day of analysis
____	____	IPC/CCV low level: %REC of target analytes : 75 - 125
____	____	Peak Gaussian Factor of Surrogate : (0.8 to 1.15) _____
____	____	Surrogate Ret. Time : +/- 2% (of expected value from calibration)
____	____	ICB/CCB: After ICV/CCV: < MDL
____	____	CCV: Every 10 samples and at end of run. CCVs must be varied between the middle and the high end of the calibration curve.
____	____	%R = 85 – 115
____	____	Ret. Time of **ALL** peaks : < +/- 5% (of expected value from CCV low level)
____	____	MB: Every batch of 20 samples or less and Not Detected
____	____	< MDL unless sample conc. > 1.5 x RL and j-flagging not required
____	____	LCS: Every batch of 10 samples or less. %REC = 75 – 125; %RPD = 20
____	____	MS/MSD: Every batch of 10 samples or less. %REC= 75-125; %RPD=20
____	____	Surrogate: 1 ppm (1000 ppb) DCA in **ALL** samples
____	____	%REC = 90 – 115 (or properly qualified)
____	____	All samples checked for dilution factor, retention time drift, peak shape, integration, linear range, proper bracketing between compliant CCV/CCB and transcription errors.

Comments: _____

_____

_____

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Rev 08/21/12