# ESS Method 200.5: Determination of Inorganic Anions in Water by Ion Chromatography

**Environmental Sciences Section**
**Inorganic Chemistry Unit**
**Wisconsin State Lab of Hygiene**
**465 Henry Mall**
**Madison, WI 53706**

**Revised October 1992**

# ESS Method 200.5:
# Determination of Inorganic Anions in Water by Ion Chromatography

## 1.0 Scope and Application

1.1 This method covers the determination of the following inorganic anions: Chloride, Nitrate-N, Sulfate.

1.2 This is an ion chromatographic (IC) method applicable to the determination of the anions listed above in drinking water, surface water, and mixed domestic and industrial wastewater.

## 2.0 Summary of Method

A small volume of sample, typically 5 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor column, and conductivity detector.

## 3.0 Interferences

3.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

3.2 The water dip or negative peak that elutes near and can interfere with the chloride peak can be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (6.3 100X) to 100 mL of each standard and sample.

3.3 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.

3.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument column and flow systems.

## 4.0 Sample Collection, Preservation and Storage

4.1 Samples should be collected in scrupulously clean 60 mL polyethylene bottles.

4.2 Sample preservation and holding times for the anions that can be determined by this methods are as follows:

| *Analyte* | *Preservation* | *Holding Time* |
|---|---|---|
| Chloride | None required | 28 days |
| Nitrate-N | Cool to 4°C | 48 hours |

| | | |
|---|---|---|
| Sulfate | Cool to 4°C | 28 days |

4.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment and holding time for the total sample.

4.4 Samples should be filtered through a 0.45 m filter to remove particulate matter.

## 5.0 Apparatus and Materials

5.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

5.2 Ion chromatograph - Dionex Model 4000i complete with all required accessories including analytical columns, compressed air, detector, and integrator.

5.2.1 Anion guard column: 4 x 50 mm, Dionex P/N 37042, or equivalent.

5.2.2 Anion separator column: 4 x 250 mm, Dionex P/N 37041, or equivalent.

5.2.3 Anion suppressor column: Membrane Suppressor, Dionex P/N 43074, or equivalent.

5.2.4 Detector - Conductivity cell: approximately 6 µL volume, Dionex, CDM2, or equivalent.

5.3 Integration System

5.3.1 Dionex Model 4270 Integrator (Spectraphysics, Inc.)

5.4 Automation Accessories

5.4.1 Dionex Automated Sampler

5.4.2 Dionex Automation Interface

5.4.3 Autosampler vials with filter caps, 5 mL capacity

## 6.0 Reagents and Consumable Materials

6.1 Sample bottles: 60 mL polyethylene.

6.2 Reagent water: Milli-Q water, Millipore Corp., Bedford, Mass.

6.3 Eluent solution: Sodium bicarbonate 0.75 mm, sodium carbonate 2.00 mm. Dissolve 0.25 g sodium bicarbonate ($NaHCO_3$) and 0.933 g of sodium carbonate ($Na_2CO_3$) in reagent water and dilute to 4 L.

6.4 Regeneration solution (membrane suppressor): Sulfuric acid 0.025N. Dilute 2.8 mL conc. sulfuric acid ($H_2SO_4$) to 4 L with reagent water.

6.5 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 min.)

6.5.1 Chloride ($CL^-$) 1000 mg/L: Dissolve 1.6485 g sodium chloride in reagent water and dilute to 1 L.

6.5.2 Nitrate ($NO_3$-N) 1000 mg/L: Dissolve 6.0679 g sodium nitrate in reagent water and dilute to 1 L.

6.5.3 Sulfate ($SO_4$) 1000 mg/L: Dissolve 1.8141 g potassium sulfate in reagent water and dilute to 1 L.

6.5.4 Stability of standards: Stock standards (6.5) are stable for at least six months when stored at 4°C. Dilute working standards should be prepared weekly.

## 7.0 4000i Ion Chromatograph (IC) Operation Procedure

7.1 Check the level of the various eluant bottles on top of the 4000i. Each should contain more than enough for the planned runs.

7.2 Turn gas (Loading Dock) on. About 80 psi should be delivered to the IC. Open line toggle (up) behind instrument.

7.3 Eluent Degas Module (EDM):

7.3.1 If the IC is off, push POWER button to turn on (It is normally kept on.)

7.3.2 Turn system switch on. Mode switches should be on Pressure.

7.3.3 Turn on eluent reservoir switch (#1). EGM pressure should be about 15 psi. The black/red dial adjusts the pressure.

Eluent Reservoir Numbers:

#1 = $NaHCO_3/Na_2CO_3$ buffer. For strong acids and used with program #1/STD #1.

#2 = $Na_2B_4O_7$ buffer. For weak acids. Used with program #2/STD #2.

#3 = Various unusual buffers.

#4 = Deionized water. Use with program 6 to rinse columns.

7.4 Turn gas valve located on the left of the IC until the gauges reads 15 psi. This turns the column regenerating system on.

7.5 Conductivity Detector (CD): Be sure the proper column is in place. Then *Cell On*. Output range is usually set to 10.

7.6 Gradient Pump (GP):

7.6.1 Press *PGM*, enter program number (1 for strong acid, 2 for weak acids) Stop - Start to *Start*.

7.6.2 Let the IC run until the conductivity readout stabilizes to ±0.1 units (usually 15 to 30 minutes)

7.6.3 To list program #1 in the GP press the following:

*List PGM* 1 List (to get time), *List* (to get time 2) etc. Each push of list will give an event and the time it occurs.

7.7 Programming the Integrator (INT):

7.7.1 In using the INT, each key has three meanings: They are rotated by the *Shift* Key.

Red light on = blue command under key

(shift) - Slow red blink = number upper left

(shift) - Fast red blink = letter, upper right

(shift) - Red light on, etc.

7.7.2 Use File *1 enter* will load file #1 into active status.

*Pr file* gives a printout of the file in active status.

7.7.3 Editing a Program

Sometimes it is necessary to change a program, often a retention time changes enough that the integrator does not recognize it. In that case you must delete the entry and replace it with the new time.

*Dialog* puts integrator in editing mode

To delete an entry for a time (example 13 minutes)

*-13 enter*

To repace the entry for time 13 minutes

TT = *13 enter* etc.

Enter *Escape Escape* to exit from dialog.

7.8 To Standardize

Standard 1 - strong acids. This is run using Program 1 on the GP and Use File 8 on the integrator.

7.8.1 Pour the standard to be used into a tube and cap. Load into rack (white dot on the right).

7.8.2 On Integrator: TFN T (shift) 3 Enter TV = 1 Enter

7.8.3 On T3 Auto Sampler: Hold - Run

7.8.4 (shift) (shift) R N (shift) = 0 Enter

(shift) (shift) Z Z (shift) = Number of STDS, typically 1, *Enter*

*Calib 1 enter* (note 1 = calibration On.; = calibration Off)

Wait for status light on T3 to flash *Load*, then on integrator:

*Inject A* (After flashing *Load*, the status light changes to *Ready*)

7.9 To Run Samples (or QC's): (See Section for 10 Sample Preparations)

On Integrator:

7.9.1 Use File = 1 enter (Note: to get back to File 1from File 9)

7.9.2 TFN T (shift) *3 enter* TV = *1 Enter*

on T3 Autosampler: Hold - *Run*

*Back to integrator:

7.9.3 (shift) (shift) R N (shift) = 0 enter

(shift) (shift) Z Z (shift) = *# of injection enter*

(Note: ZZ = 2 for QC's)

Wait for status light to flash LOAD, or READY on T3

*Inject A*

## 8.0 Shut Down Procedure

8.1 Rinse the column with water, as follows:

* On EDM: Reservoir switch #4 On (i.e. UP)

* On GP: *PGM 6 Stop - Start*

This pumps $H_2O$ thru the column. Let this run for about five minutes then continue.

8.2 Complete Shutdown as follows:

* On CD: Cell *Off*

* On GP: Start - *Stop*

* Valve on side counter clockwise until dial reads 0 * Turn $N_2$ off at cylinder (loading dock)

* Loosen cap on eluent reservoir #1 to let $N_2$ escape.
(The pressure should drop on the main gauge and then on the other two). Wait until both gauges read 0.

* On EGM: turn all EDM toggle switches off (i.e. down )turn system pressure off (down).

* Tighten cap on reservoir #1.

* Turn off (down) main toggle valve (behind instrument).

* Turn main power off (blue button on CD).

## 9.0 Calibration and Standardization (High level method)

9.1 For each analyte of interest prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (6.5) to a volumetric flask and diluting to volume with reagent water. Typically, the working standard range for the high level I.C. method will be 0-2 mg/L for Chloride and Nitrate and 0-10 mg/L for Sulfate. If the working range exceeds the linear range of the system, a sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration near, but above, the method detection limit if the system is operated on an applicable attenuator range. The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, each setting must be calibrated individually.

9.2 Using injection of 0.2 mL of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. This procedure will be automatically performed by the integration system.

9.3 The working calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 10 samples. If the peak concentration response for any analyte varies from the expected values by more than ±10%, the tests must be repeated, using fresh calibration standards. If the results are still more than ±10%, an entire new calibration curve must be prepared for that analyte.

9.4 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading (all anions) should not exceed about 400 ppm.

## 10.0 Calibration and Standardization (Microlevel Method).

Calibration and operating conditions are the same for this method as the high-level method except for the following:

10.1 The working standard range is 0-0.4 mg/L for Nitrate and Chloride but 0-4 mg/L for Sulfate.

10.2 A separate anion separator column is used for the micro-level method.

10.3 The attenuation setting on the IC is changed from 10 µs to 3 µs.

## 11.0 Procedure

11.1 Operating conditions: columns as specified in Section 5.2; detector as specified in Secction 5.2; eluent as specified in Section 6.3; sample loop - 200 µL; pump volume - 2.30 mL/min; full scale - 10 mhos/cm.

**Note:** The operating conditions may need to be changed to meet specific applications.

11.2 Check system calibration daily and, if required, recalibrate as described in Section 7.0.

11.3 Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample.

11.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound.

11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, spike the sample with an appropriate amount of standard and reanalyze.

## 12.0 Automated Calculation

12.1. Both the processes of generating a calibration curve and calculating unknown sample concentrations are performed by the Dionex Model 4270 integration system.

12.2 A report including calibration coefficients is printed following the last standard run in a calibration curve.

12.3 Results for the unknown samples are printed in a report following each sample run.

12.4 Report results in mg/L.

## 13.0 Precision and Accuracy

Precision and accuracy data are available in the Inorganic Chemistry Unit Quality Assurance Manual.

## 14.0 References

14.1 Annual book of ASTM Standards, Part 31 Water, proposed test method for "Anions in Water by Ion Chromatography," p. 1485-1492 (1982).

14.2 Standard Methods for the Examination of Water and Wastewater, Method 429, 16th Ed., p. 483-488 (1985).

14.3 Dionex, System 4000i Operators Manual, Dionex Corp., Sunnyvale, California 94086.

14.4 The Determination of Inorganic Anion in Water by Ion Chromatography - Method 300.0, United States Environmental Protection Agency, EPA-600/4-84-017, March 1984.

14.5 Spectra-physics SP4270/Sp4290 Integrator User's Guide Spectra Physics, Inc., San Jose, CA 95134.