UNCONTROLLED

**WEST VALLEY NUCLEAR SERVICES, CO., INC.**

**ACM-IC-1501, Rev. 2**
**Effective Date:** 06/28/89

**ANALYTICAL CHEMISTRY METHODS**
**ANALYTICAL AND PROCESS CHEMISTRY**

# ANIONS BY CHROMATOGRAPHY

**Approved By:**

**C. W. McVay, Manager**
**Analytical and Process Chemistry**

---

## Part I

## 1.0 PURPOSE

1.1 To establish a method for the determination of anions in water, waste water, and process streams.

## 2.0 APPLICATION

2.1 This method covers the determination of the following anions: chloride, fluoride, nitrate, nitrite, phosphate, and sulfate in aqueous solutions using ion chromatography.

2.2 Detection limits are dependent on sample matrix, instrumental parameters, and the specific ion of interest. Typical detection limits are approximately 0.1 ppm in water.

## 3.0 DISCUSSION

3.1 Anion chromatography provides a convenient method for both qualitative and quantitative determination of anions in aqueous solutions. The ions present in the sample are separated on a low-capacity ion exchanger and detected with a conductivity cell. Anions are identified by their retention times and peak area gives the quantitative result. Calibration curves are prepared from known standards.

### 3.2 Sample Handling

\> 3.2.1 Samples should be filtered through 0.20 micron filter prior to injection. This is to prevent fouling or clogging of the resin columns.

3.2.2 Samples with no previous history should be diluted 1:100 for the first injection. This is to prevent overloading the column.

### 3.3 Interferences

The most common interference arises when one of the sample components is present at very high levels. This large peak may mask other peaks present. One possible solution is to further dilute the sample. If that does not work, then other steps have to be taken. If dilution does not remove the interferences, this procedure is not applicable.

## 4.0 REFERENCES

4.1 Frank C. Smith, Richard C. Change, "The Practice of Ion Chromatography," Wiley, p. 25-74.

4.2 1973 Annual Book of ASTM Standards, 11.01, p. 696-703.

4.3 EPA Test.Method 300.0, "The Determination of Inorganic Anions in Water by Ion Chromatography," March 1984. 1.

# Part II

## 5.0 EQUIPMENT

5.1 Analytical balance capable of weighing to the nearest 0.1 mg

5.2 Ion chromatograph with strip chart recorder or integrator

5.3 Anion guard column, Dionex AG-3

5.4 Anion separator column, Dionex AS-3

5.5 Anion suppressor column

5.6 Conductivity cell for detection of anion peaks

5.7 Miscellaneous glassware, pipets, and volumetric flasks

## 6.0 REAGENTS AND STANDARDS

6.1 Reagent water: Distilled water conforming to ASTM D11983, Type II.

Prepare standard per ACP 8.1.

6.2 Eluant Solution (Stock):

Dissolve 9.41g sodium bicarbonate ($NaHCO_3$) and 9.33 sodium carbonate ($Na_2CO_3$) in 500 mL of reagent water (6.1). Dilute to one litre in a volumetric flask. Store in a tightly closed container, in refrigerator. This solution should be stable for six months.

6.3 Eluant solution: Sodium bicarbonate (0.003 M)/sodium carbonate (0.0024 M). Dilute 100 mL of the eluant stock (6.2) to 4 litres in the four litre plastic eluant reservoir. This solution will have a shelf life of one week.

6.4 Regeneration solution: Sulfuric acid (0.025N). Dilute 2.8 mL $H_2SO_4$ to 4 litres with reagent water. Shelf life is six months.

6.5 Calibration stock standards: 1000 µg/mL solutions are prepared from reagent grade materials using reagent water (6.1). The following compounds may be used to prepare calibration stock standards for each anion tested; NaF, KCl, $NaNO_2$, $NaNO_3$, $KH_2$P04, and $Na_2$S04. These solutions are stable for six months except nitrate and nitrite solutions are stable for one month.

6.6 Calibration working standard: From the stock solutions (6.4) pipet aliquots necessary to obtain the following concentrations in a 100 mL volumetric flask: F-3 ppm, Cl-10 ppm, $NO_2$-20 ppm, $PO_4$-10 ppm, $NO_3$-50 ppm, and $SO_4$-50 ppm.

6.7 QC stock standards: 1000 µg/mL solutions are prepared from reagent grade materials using reagent water (6.1). The following compounds may be used to prepare QC stock standards: KF (or NaF from source and/or lot other than that used in making calibration stock standard), NaCl, $KNO_3$, and $K_2$S04. These solutions are stable for six months except the nitrate solution is stable for one month.

6.8 QC working Standard: From stock solutions (6.6) pipet aliquots necessary to obtain the following concentrations in a 100 mL volumetric flask: F-2ppm, Cl-2ppm, $No_3$-10ppm, and $SO_4$-10ppm.

## 7.0 SAFETY PRECAUTIONS

7.1 Normal safe laboratory practices should be followed when preparing reagents and operating the instrument (ACP 7.2).

7.2 Pressure on the ion exchange columns must not exceed 1,000 psi.

## 8.0 RECORDS

8.1 All measurement data and sample identification shall be recorded on the work sheet attachment A. The final result shall be recorded on the analytical request sheet (PRD 5.0).

## 9.0 CALIBRATION AND CONTROL

### 9.1 Determination of Retention Times

Retention times for each anion are determined by injecting a standard solution containing the anions of interest. The time required for each peak to appear is noted. Although times are influenced by factors such as eluant flow rates, column characteristics and ion concentrations, the order will be consistent: $F^-$, $Cl^-$, $NO_2$, $PO_4^{-3}$, $NO_3$, $SO_4^{-2}$ when using the columns and eluant specified in this procedure.

9.2 A standard containing the anions of interest shall be injected and analyzed automatically calibrating the instrument.

\> 9.3 A QC sample of known concentration is injected and recovery of anions tested. A recovery of 100 percent ±10 percent is expected for this test. If results are outside this range, the test shall be repeated. Any tests which fails the third time will be reported to the manager of Analytical Chemistry indicating the average recovery of the spike. This test is performed daily for each sample matrix being tested or every ten samples if matrix remains the same. It should also be performed after each new batch of eluant has been started. The results shall be recorded in a QC book and on a quality control chart. Per ACP 8.2.

## 10.0 PROCEDURE

10.1 Prime the pump and set all parameters to the manufacturer's specifications. Adjust the eluant flow rate to 2.5 mL/min and the suppressor regenerant to approximately 4 mL/min. Choose a detector range of suitable sensitivity for the anion concentrations in the samples. (For most work the 30 µS range is well suited.)

\> 10.2 Program the integrator (if necessary) according to the preestablished set of parameters for the specific set of analytes. See attachment C.

\> 10.3 After the baseline has stabilized, the first injection is made. Filter all samples through a 0.20 microm filter prior to injection. A minimum of 1 mL is loaded into the chromatograph using a syringe with a lock fitting. The sample is injected and the integrator or strip chart recorder is started simultaneously.

10.4 Samples are analyzed making various dilutions until suitable peak heights are obtained. Results are compared to the standards and final concentrations of each anion are calculated.

## 11.0 CALCULATIONS

Anion concentration, mg/ℓ = A x F

A = mg/ℓ obtained from calibration curve
F = dilution factor of sample

## 12.0 ATTACHMENTS

12.1 Attachment A - Anion Work Sheet

\> 12.2 Attachment B - Feed Slurry Anion Work Sheet

\> 12.3 Attachment C - Programming the Integrator

## ATTACHMENT A

PAGE ___ OF ___

## ANIONS WORKSHEET

SAMPLE NAME ______________________ LOG NUMBER ____________________

>SPECIAL INSTRUCTIONS IC SERIAL #_______________________________________

| | | | | | |
|---|---|---|---|---|---|
| SAMPLE ID | | | | | |
| ANION | | | | | |
| DILUTION | | | | | |
| ALIQUOT (PPM) | | | | | |
| SAMPLE | | | | | |
| ANION | | | | | |
| DILUTION | | | | | |
| ALIQUOT (PPM) | | | | | |
| SAMPLE | | | | | |
| ANION | | | | | |
| DILUTION | | | | | |
| ALIQUOT (PPM) | | | | | |
| SAMPLE | | | | | |
| ANION | | | | | |
| DILUTION | | | | | |
| ALIQUOT (PPM) | | | | | |
| SAMPLE | | | | | |
| ANION | | | | | |
| DILUTION | | | | | |
| ALIQUOT (PPM) | | | | | |
| SAMPLE | | | | | |

ANALYST ______________________ DATE ____________

APPROVED ______________________ DATE ____________

## ATTACHMENT B

PAGE __ of __

## FEED SLURRY ANIONS WORKSHEET

SAMPLE NAME ______________________ LOG NUMBER ____________

SPECIAL INSTRUCTIONS IC SERIAL # ______________________

| | | | | |
|---|---|---|---|---|
| SAMPLE ID | | | | |
| ANION | | | | |
| SAMPLE ALIQUOT (g) | | | | |
| SAMPLE ALIQUOT + DILUENT WT. (g) | | | | |
| DILUTION FACTOR | | | | |
| ALIQUOT (mg/L) | | | | |
| SAMPLE (µg/g) | | | | |
| ANION | | | | |
| SAMPLE ALIQUOT (g) | | | | |
| SAMPLE ALIQUOT + DILUENT WT (g) | | | | |
| DILUTION FACTOR | | | | |
| ALIQUOT (mg/L) | | | | |
| SAMPLE (µg/g) | | | | |

ANALYST ______________________ DATE ____________

APPROVED ______________________ DATE ____________

## ATTACHMENT C

## PROGRAMMING THE INTEGRATOR

1. Turn off/on the power switch at the rear of the integrator.
2. Enter the Date
3. Enter the Time
4. Press "Atten" and enter 1024

\> 5. Press "CHTSP" and enter 0.50

6. Shift to letter mode (irregular flashing light)
   Enter PW
   Shift to number mode (regular flashing light)
   Enter -6
7. Enter PT-10000 (See Step 6)
8. Press Dialog
9. Press Enter for File Name
10. TT- Enter 10 (for time of run)
11. TF- Enter ER
12. TV- Enter 1
13. TT- Press Enter
14. Method No. Enter 5
15. NV- Enter 1
16. Calibration injections- Enter 1
17. Component Table
    RT- Enter retention time for F
    CC- Enter calibration concentration for F
    CN- Enter symbol for fluoride, F
    Repeat the steps for Cl, $No_2$, $PO_4$, $NO_3$ and $SO_4$.
    Press enter to end file.
18. RP(1)- Press enter
19. AN-" Press enter
20. RA- Enter 1
21. CI- Enter 0
22. CU- PPM
23. SI- Press enter

The integrator is programmed. If power is interrupted to the integrator it will have to be reprogrammed.