METHOD 9056A

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0   SCOPE AND APPLICATION

1.1   This method addresses the sequential determination of chloride (Cl^-), fluoride (F^-), bromide (Br^-), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}) anions in aqueous samples, such as drinking water, wastewater, aqueous extracts of solids, and the collection solutions from the bomb combustion of solid waste samples (Method 5050).

1.2   The lower limit of quantitation (LLOQ), the lowest concentration level that can be measured within stated accuracy limits, varies for each individual analyte anion and as a function of sample size.

1.3   Maximum column loading should not exceed approximately 500 ppm total anions when using a 50-µL sample loop and the columns listed in Sec. 6.1. Dilution of samples may allow higher concentration samples to be analyzed.

1.4   Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5   Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1   A small volume of aqueous sample is injected into an ion chromatograph to flush and fill a constant-volume sample loop. The sample is then injected into a flowing stream of carbonate-bicarbonate eluent.

2.2   The sample is pumped through two different ion exchange columns, then a conductivity suppressor device, and into a conductivity detector. The two ion exchange columns, a precolumn or guard column and a separator column, are packed with an anion exchange resin. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The conductivity suppressor is an ion exchange-based device that reduces the background conductivity of the eluent to a low or negligible level and simultaneously converts the anions in the sample to their more conductive acid forms. The separated anions in their acid forms are measured using an electrical conductivity cell. Anion identification is based on the comparison of analyte signal peak retention times relative to those of known standards. Quantitation is accomplished by measuring the peak area and comparing it to a calibration curve generated from known standards.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1   Any species with a retention time similar to that of the desired anion will interfere. Large quantities of ions eluting close to the anion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of the method of standard additions can also be used. For example, high levels of organic acids that may interfere with inorganic anion analysis may be present in industrial wastes. Two common species, formate and acetate, elute between fluoride and chloride.

4.2   The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (100 times more concentrated than the solution described in Sec. 7.3) to 100 mL of each standard and sample.

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 baselines in ion chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks (Sec. 9.3.1). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to Chapter Three for general guidance on the cleaning of glassware.

4.4   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. The associated method blanks must also be filtered if any samples or reagents have undergone filtration.

4.5   The acetate, formate, and other monovalent organic acid anion elute early in the chromatographic run and can interfere with fluoride. The retention times of anions may differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples where acetate is used for pH adjustment.

5.0   SAFETY

5.1   This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2   The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

6.0   EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1   Ion chromatograph -- Capable of delivering 1 to 5 mL of eluent per min at a pressure of 1000 to 4000 psi (6.5 to 27.5 MPa). The chromatograph must be equipped with an injection valve, a 25- to 100-µL sample loop, and set up with the following components, as schematically illustrated in Figure 1.

6.1.1   Precolumn -- A guard column placed before the separator column to protect the separator column from being fouled by particulates or certain organic constituents. An example of a suitable column is the Dionex IonPac® AG4A-SC, or equivalent.

6.1.2   Separator (or analytical) column -- A column packed with an anion exchange resin, suitable for resolving F^-, Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}. An example of a suitable column is the Dionex IonPac® AS4A-SC, or equivalent.

6.1.3   Conductivity suppressor -- An ion exchange-based device that is capable of converting the eluent and separated anions to their respective acid forms. Examples of suitable suppressors include the Dionex AMMS-II or ASRS Ultra, or equivalent.

6.1.4   Conductivity detector -- A low-volume, flow-through, temperature-compensated, electrical conductivity cell (approximately 1.25-µL volume), equipped with a meter capable of reading from 0 to 1,000 Siemens/cm on a linear scale.   An example of a suitable conductivity detector is the Dionex CD20 or equivalent.

6.1.5   Pump -- Capable of delivering a constant flow of approximately 1 to 5 mL/min throughout the test and tolerating a pressure of 1000 to 4000 psi (6.5 to 27.5 MPa).

6.2   Syringe -- Minimum capacity of 1 mL, equipped with a male pressure fitting.

6.3   Appropriate chromatographic data and control software to acquire data. Dionex PeakNet was used to record and process the chromatogram shown in Figure 2. Alternatively, an integrator or recorder can be used to integrate the area under the chromatographic peaks. If an integrator is used, the maximum area measurement must be within the linear range of the integrator. The recorder should be compatible with the detector output with a full-scale response time of 2 seconds or less.

6.4   Analytical balance -- Capable of weighing to the nearest 0.0001 g.

6.5   Pipets, Class A volumetric flasks, beakers -- Assorted sizes.

7.0   REAGENTS AND STANDARDS

7.1   Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2   Reagent water -- All references to water in this method refer to reagent water, as defined in Chapter One.

7.3   Eluent, 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3 -- Dissolve 0.2856 g of sodium bicarbonate (1.7 mM $NaHCO_3$) and 0.3816 g of sodium carbonate (1.8 mM Na_2CO_3) in reagent water and dilute to 2 L with reagent water or follow manufacturer's guidance for the proper eluent for each specific column.

7.4   Conductivity suppressor regenerant solution (25 mM H_2SO_4), if required -- Add 2.8 mL of concentrated sulfuric acid (H_2SO_4) to 4 L of reagent water.

7.5   Stock solutions (1,000 mg/L) -- Certified standards may also be purchased and used as stock solutions. Stock solutions are stable for at least 1 month when stored at #6 EC.

7.5.1   Bromide stock solution (1.00 mL = 1.00 mg of BrG) -- Dry approximately 2 g of sodium bromide (NaBr) for 6 hr at 150 °C, and cool in a desiccator. Dissolve 1.2877 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.2   Chloride stock solution (1.00 mL = 1.00 mg of ClG) -- Dry sodium chloride (NaCl) for 1 hr at 600 °C, and cool in a desiccator. Dissolve 1.6484 g of the dry salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.3   Fluoride stock solution (1.00 mL = 1.00 mg of FG) -- Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask. Store in a chemical-resistant glass or polyethylene container.

7.5.4   Nitrate stock solution (1.00 mL = 1.00 mg of NO_3^-) -- Dry approximately 2 g of sodium nitrate ($NaNO_3$) at 105 °C for 24 hr. Dissolve exactly 1.3707 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.5   Nitrite stock solution (1.00 mL = 1.00 mg of NO_2^-) -- Place approximately 2 g of sodium nitrate ($NaNO_2$) in a 125 mL beaker and dry to constant weight (about 24 hr) in a desiccator containing concentrated H_2SO_4. Dissolve 1.4998 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

NOTE: Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

NOTE: Prepare sterile bottles for storing nitrite solutions by heating them for 1 hr at 170 °C in an air oven.

7.5.6   Phosphate stock solution (1.00 mL = 1.00 mg of PO_4^{3-}) -- Dissolve 1.4330 g of potassium dihydrogen phosphate (KH_2PO_4) in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.7   Sulfate stock solution (1.00 mL = 1.00 mg of SO_4^{2-}) -- Dissolve 1.4790 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.6   Anion calibration standards

Prepare a blank and at least three combination anion calibration standards containing the anions of interest. The combination anion solutions must be prepared in Class A volumetric flasks (see Table 2). Calibration standards should be prepared weekly, except for those that contain nitrite and phosphate, which should be prepared fresh daily. The validity of standards can be confirmed through the analysis of a freshly prepared ICV (Sec. 10.6).

7.6.1   Prepare the high-range calibration standard solution by combining the volumes of each anion stock solution specified in Sec. 7.5 in a Class A volumetric flask and diluting the mixture to 1 L with reagent water.

7.6.2   Prepare the intermediate-range calibration standard solution by diluting 10.0 mL of the high-range calibration standard solution (Sec. 7.6.1) to 100 mL with reagent water.

7.6.3   Prepare the low-range calibration standard solution by diluting 20.0 mL of the intermediate-range calibration standard solution (Sec. 7.6.2) to 100 mL with reagent water.

8.0   SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1   See the introductory material to Chapter Three, "Inorganic Analytes."

8.2   Preserve samples at #6 °C. If nitrite, nitrate and phosphate are analytes of interest, samples should be analyzed within 48 hr of collection. A longer holding time may be appropriate for chloride, fluoride, sulfate and bromide.

9.0   QUALITY CONTROL

9.1   Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2   Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with the sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for the target analyte in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish an initial demonstration of proficiency.

9.3   Sample quality control for preparation and analysis.

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, the laboratory should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch. Any method blanks, matrix spike samples, replicate samples and LCSs should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

The following should be included within each analytical batch.

9.3.1   Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable.

In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These

blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank. Refer to Chapter One for the proper protocol when analyzing blanks.

　　　　9.3.2　　　A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. Acceptance criteria should be set at a laboratory-derived limit developed through the use of historical analyses, or set by the method quality objectives (MQOs)/data quality objectives (DQOs) of the project. In the absence of historical data or well-defined MQOs/DQOs, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data must be no wider that ± 20%. Consult Method 8000 for further information on developing acceptance criteria for the LCS. When the result of a matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS result is used to verify that the laboratory can perform the analysis in a clean matrix. If the LCS result is not acceptable, then the LCS must be reanalyzed once. If the results are still unacceptable, then all samples analyzed after the last acceptable LCS must be reprepared and reanalyzed.

　　　　9.3.3　　　Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

　　　　Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

　　　　9.3.3.1　　　At least one matrix spike (MS) sample should be analyzed within each analysis batch for determining method bias and/or sample matrix effects. The MS percent recovery (%R) is calculated as follows:

$$\% R = \frac{\left(MSSR - SR \right)}{SA} \times 100$$

Where:
MSSR = MS Sample Result
SR = Sample Result
SA = Spike Added

When the sample concentration is less than the LLOQ, use SR = 0 for purposes of calculating %R.

　　　　9.3.3.2　　　The method control limits for %R are 80 - 120. Alternate limits may be used provided that they meet the data quality objectives of the specific

project. Failure to meet the MS %R criteria indicates potential problems with the analytical system and/or sample matrix effects and corrective action should be taken to investigate and resolve the problem. If %R is outside the control limits and all other QC data is within limits, a matrix effect is suspected. The associated data should be flagged according to project specifications or noted in the comments section of the report.

9.3.3.3   A duplicate or matrix spike duplicate (MSD) should be analyzed within every analytical batch in order to establish the precision of the method. Calculate the relative percent difference (RPD) between the sample and duplicate result as follows.

$$RPD = \frac{\left|S - D\right|}{\left(S - D\right)/2} \times 100$$

Where:
RPD   =   Relative Percent Difference
S   =   Sample or MS Sample Result
D   =   Duplicate or MSD Result

9.3.3.4   The method control limit for RPD is 15% for all sample concentrations that are near or above the mid-range of the calibration curve. The method control limit for RPD is 50% for sample concentrations that are near the low-range of the calibration curve. Alternate limits may be used provided that they meet the data quality objectives of the specific project. Failure to meet the duplicate RPD criteria indicates potential problems with the analytical system and/or sample matrix effects and corrective action should be taken to investigate and resolve the problem.

10.0 CALIBRATION AND STANDARDIZATION

10.1   Establish ion chromatographic operating parameters equivalent to those indicated in Table 1, or as recommended by the manufacturer.

10.2   For each analyte of interest, prepare a blank and calibration standards at a minimum of three concentrations by adding accurately measured volumes of one or more stock standards to a Class A volumetric flask and diluting to volume with reagent water. 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 at or below the laboratory's lower limit of quantitation (LLOQ). The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector.

10.3   The laboratory should establish the LLOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration levels or use of the LLOQs as the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LLOQ recoveries must be within 50% of the true values to verify the data reporting limit.

10.4   After a stable baseline is obtained (approximately 30 min), begin to inject standards starting with the lowest concentration standard and increasing in concentration to the highest standard. Use a fixed injection volume between 25 and 100 µL (determined by injection loop volume) for each calibration standard. Record the peak area responses and retention times for each analyte.

10.5   Establish the individual analyte calibration curves by plotting the peak area responses for each standard against the corresponding concentrations. Use a least squares linear regression to calculate the calibration curve formula. The linear correlation coefficient should be equal to or greater than 0.995. A weighted least squares regression may also be performed using 1/concentration or 1/(concentration)^2 as the weighting factor. The acceptance criterion for the calibration curve should be a correlation coefficient of 0.995 or higher. Refer to Method 8000 for additional guidance on calibration procedures.

10.6   Verify the accuracy of the initial calibration curve by analyzing an initial calibration verification (ICV) standard. The ICV standard must be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for the ICV standard must be no greater than ± 10% of its true value. If the calibration curve cannot be verified within the specified limits, the cause must be determined and the instrument recalibrated before samples are analyzed. The analysis data for the ICV must be kept on file with the sample analysis data.

10.7   Verify the accuracy of the working calibration curve on each working day, or whenever the anion eluent composition or strength is changed, and for every batch of 10 or less samples, through the analysis of a continuing calibration verification (CCV) standard. The CCV should be made from the same material as the initial calibration standards at or near mid-range. The acceptance criteria for the CCV standard should be ± 10% of its true value for the calibration to be considered valid. If the CCV standard result does not meet the acceptance criterion, sample analysis must be discontinued, the cause determined, and the instrument recalibrated. All samples analyzed after the last acceptable CCV should be reanalyzed. The analysis data for the CCV should be kept on file with the sample analysis data.

10.8   Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading should not exceed approximately 500 ppm total anions when using a 50-µL sample loop and the columns listed in Sec. 6.1.

11.0 PROCEDURE

11.1   Sample preparation

When aqueous samples are injected, the water passes rapidly through the columns, and a negative "water dip" is observed that may interfere with the early-eluting fluoride and/or chloride ions. In combustate samples generated by bomb combustion (Method 5050), the water dip should not be observed, since the collecting solution is a concentrated eluent solution that will be equivalent to the eluent strength when diluted to 100-mL with reagent water according to the bomb combustion procedure. Any dilutions required in analyzing other water samples should be made with the eluent solution. The water dip, if present, may be removed by adding concentrated eluent to all samples and standards such that the final sample/standard solution is equivalent to the eluent concentration. When a manual system is used, it is necessary to micropipet concentrated buffer into each sample. The recommended procedure follows:

11.1.1   Prepare a 100-mL stock of eluent 100 times a normal concentration by dissolving 1.428 g of $NaHCO_3$ and 1.908 g of Na_2CO_3 in 100 mL of reagent water or use

the manufacturer's specified eluent. Cover or seal the volumetric flask.

  11.1.2 Pipet 5 mL of each sample into a clean polystyrene micro-beaker. Micropipet 50 mL of the concentrated buffer into the beaker and stir well.

  11.1.3 Dilute the samples with eluent, if necessary, to concentrations within the linear range of the calibration.

11.2 Sample analysis

  11.2.1 Establish ion chromatographic operating parameters exactly equivalent to those used for calibration (Sec. 10.0). Establish a stable baseline. This should take approximately 30 min.

  11.2.2 Establish a valid initial calibration or otherwise verify the working calibration curve as outlined in Sec.10.0.

  11.2.3 Inject a suitable volume of sample or QC standard into the IC instrument. Use an injection volume that is optimal for the specific analytical column and instrument system. The volume of sample injected must be consistent with that used for calibration (Sec. 10.0). Record the resulting analyte peak sizes in area units as well as the peak retention times.

  11.2.4 For each sample or QC standard, identify each analyte by comparing the peak retention time to the established retention time window. The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day, and may include concentrations from both ends of the calibration range. Three times the standard deviation of a retention time may be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

  11.2.5 If the peak area response exceeds the working calibration range, then dilute the sample with an appropriate amount of reagent water or eluent and reanalyze.

  11.2.6 If the resulting chromatogram for a particular sample fails to produce adequate resolution such that the identification of the anion of interest is questionable, prepare a new sample spiked with a known amount of the anion under question and reanalyze in order to confirm the presence or absence of analyte.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Using the established calibration curve, compute the concentration of each analyte in each analysis sample or QC standard based on the peak area response. Most chromatography data analysis software systems perform such calculations automatically.

12.2 Calculate the concentration of analyte in the original sample as follows:

$$\text{Final result (mg/L)} = (C)(D)$$

Where:
C = Concentration from calibration curve (mg/L)
D = Dilution factor (if needed)

13.0 METHOD PERFORMANCE

13.1   Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods.   Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.</u>

13.2   Examples of single-operator accuracy and precision values for reagent, drinking, and surface water, and mixed domestic and industrial waste water are listed in Table 3. See EPA Method 300.0 for examples of multiple laboratory determinations of bias for the analytes using an IonPac AS4A column, bicarbonate/carbonate eluent, AMMS suppressor and conductivity detection (see Ref. 1). These data are provided for guidance purposes only.

13.3   Combustate samples

Tables 4 and 5 are based on 41 data points obtained by six laboratories, in which each laboratory analyzed four used crankcase oils and three blends of fuel oil with crankcase oil. Each analysis was performed in duplicate. The oil samples were combusted using Method 5050. Each point represents the duplicate analyses of a sample. One point was judged to be an outlier and was not included in the results. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1   Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2   The quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3   For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly

the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1.   Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, USEPA Method 300.0, "Determination of Inorganic Anions by Ion Chromatography," EPA-600/R-93-100, August 1993.

2.   Annual Book of ASTM Standards, Volume 11.01 Water, "Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography," D 4327-97, 1998.

3.   Standard Methods for the Examination of Water and Wastewater, Method 4110, "Determination of Anions by Ion Chromatography," 18th Edition of Standard Methods, 1992.

4.   Dionex, DX-500 System Operation and Maintenance Manual, Dionex Corp., Sunnyvale, CA 94086, 1996.

5.   A. Gaskill, E. D. Estes, D. L. Hardison, and L. E. Myers, "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels," prepared for U.S. Environmental Protection Agency Office of Solid Waste, EPA Contract No. 68-01-7075, WA 80, July 1988.

17.0 TABLES, DIAGRAMS, FLOW CHARTS AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

EXAMPLE CHROMATOGRAPHIC CONDITIONS AND
RETENTION TIMES IN REAGENT WATER

Chromatographic Conditions	
Columns	See Secs. 6.1.1-6.1.2
Conductivity suppressor	See Sec. 6.1.3
Conductivity detector	See Sec. 6.1.4
Eluent	See Sec. 7.3
Sample loop	50 µL
Pump flow rate	2.0 mL/min

Analyte	Concentration of Mixed Standard (mg/L)	Retention Time (min)[a]
Fluoride	2.0	1.2
Chloride	3.0	1.7
Nitrite-N	2.0	2.0
Nitrate-N	5.0	3.2
o-Phosphate-P	2.0	5.4
Sulfate	15.0	6.9

[a]The retention time given for each anion is based on the equipment and analytical conditions described in the method. Use of other analytical columns or different eluent concentrations will affect retention times accordingly.

Data are taken from Ref. 1 and are provided for guidance purposes only.

TABLE 2

EXAMPLE STANDARD SOLUTIONS
FOR INSTRUMENT CALIBRATION

Analyte	Volume of Stock Solution (in mL) used to prepare High-Range Standard[1]	Concentration in mg/L		
		High-Range Standard	Intermediate-Range Standard	Low-Range Standard
Fluoride (F⁻)	10	10	1.0	0.2
Chloride (Cl⁻)	10	10	1.0	0.2
Nitrite (NO_2^-)	20	20	2.0	0.4
Phosphate (PO_4^{3-})	50	50	5.0	1.0
Bromide (Br⁻)	10	10	1.0	0.2
Nitrate (NO_3^-)	30	30	3.0	0.6
Sulfate (SO_4^{2-})	100	100	10.0	2.0

[1]Volumes of each stock solution (1.00 mL = 1.00 mg) that are combined in a Class A volumetric flask and diluted to 1 L to prepare the high-range calibration standard (refer to Sec. 7.5). These data are provided for guidance purposes only.

TABLE 3

EXAMPLE SINGLE-OPERATOR ACCURACY AND PRECISION

Analyte	Sample Type	Spike (mg/L)	Mean Recovery (%)	Std. Dev. (mg/L)
Chloride	RW	0.050	97.7	0.0047
	DW	10.0	98.2	0.289
	SW	1.0	105.0	0.139
	WW	7.5	82.7	0.445
Fluoride	RW	0.24	103.1	0.0009
	DW	9.3	87.7	0.075
	SW	0.50	74.0	0.0038
	WW	1.0	92.0	0.011
Nitrate-N	RW	0.10	100.9	0.0041
	DW	31.0	100.7	0.356
	SW	0.50	100.0	0.0058
	WW	4.0	94.3	0.058
Nitrite-N	RW	0.10	97.7	0.0014
	DW	19.6	103.3	0.150
	SW	0.51	88.2	0.0053
	WW	0.52	100.0	0.018
o-Phosphate-P	RW	0.50	100.4	0.019
	DE	45.7	102.5	0.386
	SW	0.51	94.1	0.020
	WW	4.0	97.3	0.04
Sulfate	RW	1.02	102.1	0.066
	DW	98.5	104.3	1.475
	SW	10.0	111.6	0.709
	WW	12.5	134.9	0.466

All data are taken from Ref. 1 and are based on the analyses of seven replicates.   These data are provided for guidance purposes only.

RW = Reagent water   SW = Surface water
DW = Drinking water   WW = Waste water

TABLE 4

EXAMPLE REPEATABILITY AND REPRODUCIBILITY DATA FOR CHLORINE IN
USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY ANALYSIS

Average Value (µg/g)	Repeatability (µg/g)	Reproducibility (µg/g)
500	467	941
1,000	661	1,331
1,500	809	1,631
2,000	935	1,883
2,500	1,045	2,105
3,000	1,145	2,306

Data are taken from Ref. 5 and are provided for guidance purposes only.

TABLE 5

EXAMPLE RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY
BOMB OXIDATION AND ION CHROMATOGRAPHY ANALYSIS

Amount Expected (µg/g)	Amount Found (µg/g)	Bias (µg/g)	Bias (%)
320	567	247	+77
480	773	293	+61
920	1,050	130	+14
1,498	1,694	196	+13
1,527	1,772	245	+16
3,029	3,026	-3	0
3,045	2,745	-300	-10

Data are taken from Ref. 5 and are provided for guidance purposes only.

FIGURE 1

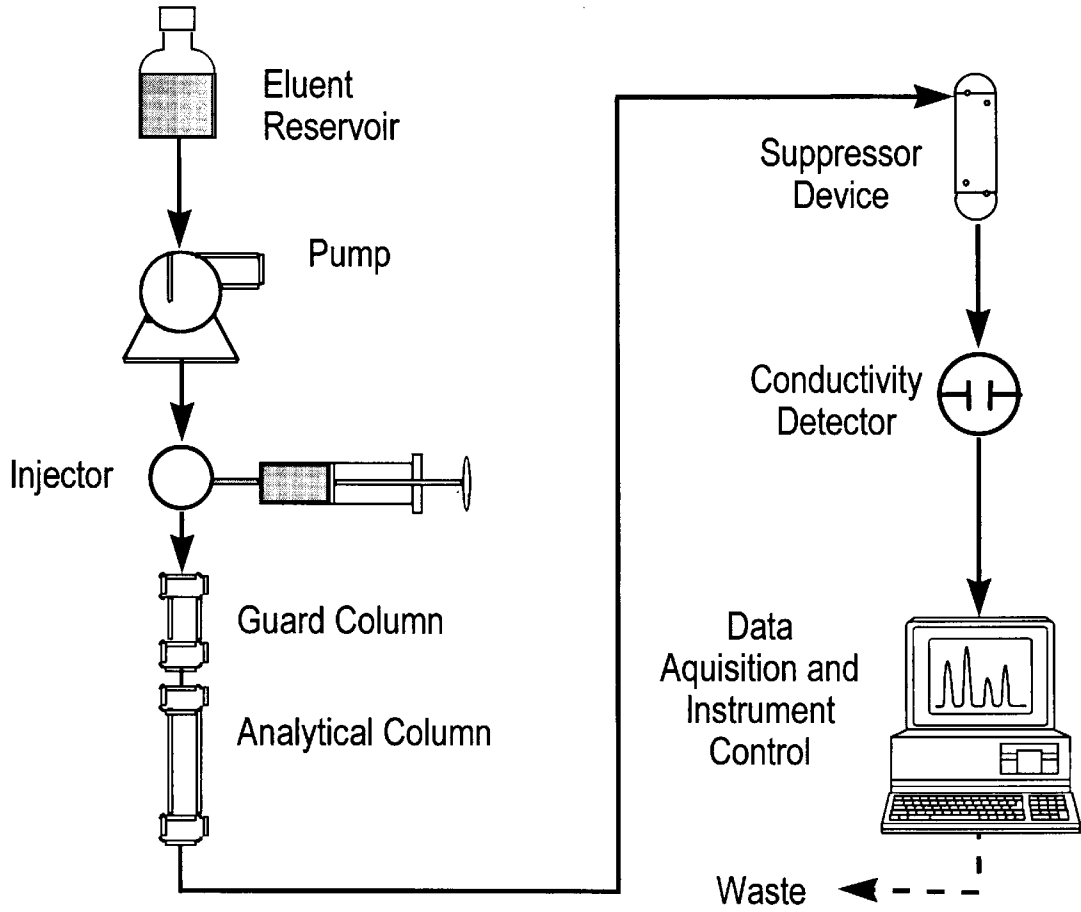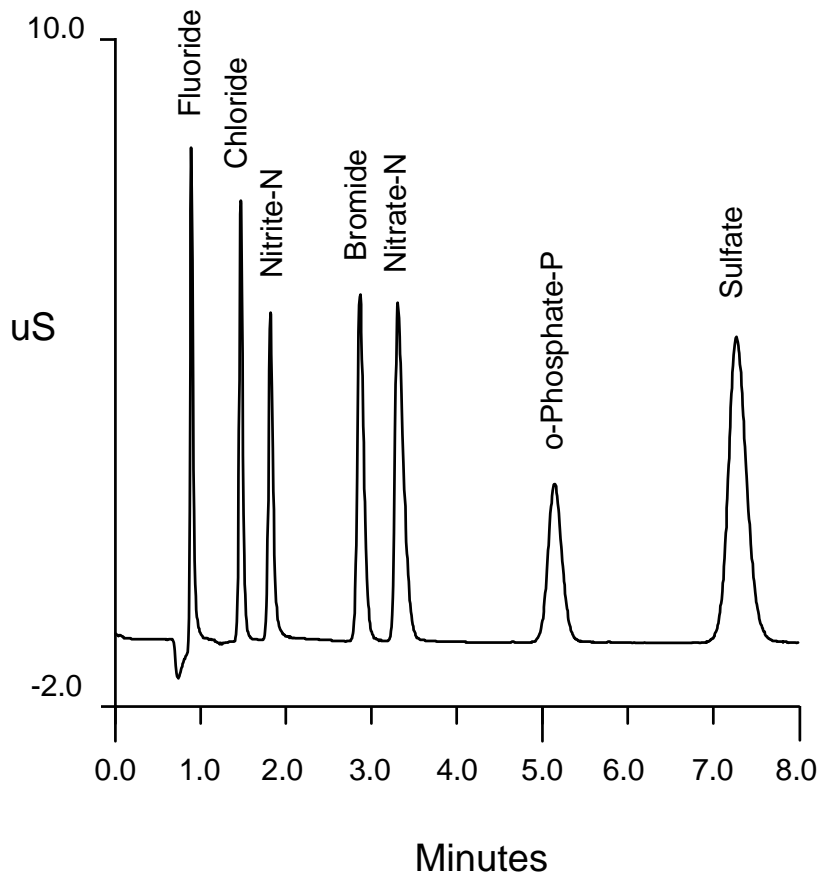SCHEMATIC OF ION CHROMATOGRAPHY INSTRUMENTATION

FIGURE 2

EXAMPLE ANION PROFILE

This figure is provided for guidance purposes only.

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

```
                    ( Start )
                        │
                        ▼
        ┌─────────────────────────────┐
        │ 10.1 Establish ion chroma-  │
        │ tography operating          │
        │ parameters.                 │
        └─────────────────────────────┘
                        │
                        ▼
        ┌─────────────────────────────┐
        │ 10.2 Prepare a minimum of   │
        │ three calibration standards │
        │ and a blank.                │
        └─────────────────────────────┘
                        │
                        ▼
        ┌─────────────────────────────┐
        │ 10.4 Analyze standards      │
        │ beginning with the lowest   │
        │ concentration. Record the   │
        │ retention times and peak    │
        │ area responses.             │
        └─────────────────────────────┘
                        │
                        ▼
        ┌─────────────────────────────┐
        │ 10.5 Prepare a calibration  │
        │ curve for each analyte of   │
        │ interest.                   │
        └─────────────────────────────┘
                        │
                        ▼
        ┌─────────────────────────────┐
        │ 10.6-10.7 Verify each       │
        │ calibration curve initially │
        │ and on each working day or  │
        │ whenever the eluent is      │
        │ changed, and for each batch │
        │ of samples.                 │
        └─────────────────────────────┘
```

11.1. Add concentrated eluent to all samples and standards to remove water dip. Dilute samples if necessary with eluent.

11.2.1 Establish ion chromatography operating parameters equivalent to those used for calibration.

11.2.3 Inject and analyze all samples and QC standards. Record the retention times and peak area responses.

11.2.4 Identify each analyte by comparing the peak retention time to the established retention time window.

11.2.5 Is the peak area response inside the working range?

No/ Peak exceeds range.

11.2.5 Dilute samples with reagent water or eluent.

No/ Peak below range.

11.2.6 Confirm analyte presence/absence by preparing and analyzing a new sample spiked with a known amount of the analyte under question.

Yes

12.1 Compute analyte concentration from calibration curve.

12.2 Calculate analyte concentration in original sample.

Stop