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ANALYSIS OF WET DEPOSITION (ACID RAIN): DETERMINATION OF THE MAJOR ANIONIC CONSTITUENTS BY ION CHROMATOGRAPHY

Prepared for publication by

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Analysis of wet deposition (acid rain): determination of the major anionic constituents by ion chromatography

Abstract - For the purposes of this document, only the major anionic constituents of wet deposition, i.e., chloride, sulfate and nitrate, will be considered. The objective of this document is to provide a set of recommended procedures for the collection, handling, and analysis of acid rain samples, and the quality assurance of the resulting data. The use of these procedures should result in greater comparability between laboratories and consequently improved reliability in data interpretation.

1. INTRODUCTION

Wet deposition, atmospheric precipitation, or, commonly, "acid rain" (which includes rainwater, snow, dew, sleet and hail) has become an environmental problem of international proportions. Extensive efforts are presently underway to determine the extent of the problem and to establish spatial and temporal trends. International networks of laboratories have been set up to monitor and record accurately the composition of rainfall. Unfortunately, discrepancies in data often occur due to differences in instrumentation and analytical methodologies. These discrepancies limit the conclusions that can be drawn from these data. This is especially true of historical data sets which do not include sufficient documentation on the methods, accuracy, precision and quality assurance procedures to evaluate the validity of the data.

The wet deposition constituents and parameters of major concern are: pH, acidity/alkalinity, conductivity, cations (e.g., sodium, potassium, calcium, magnesium, ammonium and aluminium), and anions (e.g., chloride, sulfate, nitrate, and, to a lesser extent, fluoride, bicarbonate, phosphate, and organic anions). For the purposes of this document, only the major anionic constituents, chloride, sulfate and nitrate, will be considered; the other anions are of more concern in groundwater analyses and, except in special cases, are usually too low in rainwater samples to be of general interest. The objective of this document is to provide a set of recommended procedures for the collection, handling, and analysis of acid rain samples, and the quality assurance of the resulting data. The use of these procedures should result in greater comparability between laboratories and consequently improved reliability in data interpretation. Also, depending on the monitoring objectives, different sampling periods are required. For example, weekly sampling may be appropriate for trend evaluation whereas sequential sampling within a single wet deposition event may be necessary to obtain information on scavenging processes and sources of pollution.

2. ANALYTICAL METHODOLOGY—GENERAL

While the focus of this document is the determination of the principal anionic constituents of wet deposition, certain aspects of the analytical protocol (e.g., collection, preservation and handling) are applicable to the determination of other components in the same sample.

2.1. Sample Collection

The advantages and disadvantages of the various sampling protocols have been thoroughly discussed and evaluated [ref. 1]. In addition to the technical considerations, the selection of the optimum methodology is influenced by the objectives of the study as well as economic and logistical constraints.

2.1.1. Collector design. Precipitation samples can be collected using bulk or wet-only design collectors. Bulk sampling refers to the collection of both wet and dry components of atmospheric deposition. The bulk sampling system typically consists of a bucket or funnel and bottle configuration that is open to the atmosphere during both precipitation events and dry periods. The funnel and bottle design is sometimes used with a water trap in the tubing leading from the funnel to the collection bottle to minimize sample evaporation. Open bucket collectors are susceptible to evaporation, particularly under warm weather conditions or long exposure periods. The influence of dry deposition inputs to bulk samples is dependent not only on the ion being determined, but also on the meteorological conditions and location of the sample collector. Windy and dusty conditions during a bulk sampling period will result in higher solution concentrations of terrestrial components such as calcium and magnesium compared to a wet-only collection device. Bulk sampling procedures can be used, however, for studies that focus on estimating total atmospheric inputs.

Wet-only collection devices minimize evaporation and the influence of dry deposition by utilizing an electronic sensing mechanism that exposes the collection vessel to the atmosphere only during precipitation events. The stability of samples collected with this type of device is also enhanced by the exclusion of slowly

dissolving terrestrial components [ref. 2]. In order to effectively minimize evaporation and dry deposition inputs, a wet-only sampler should be equipped with a motor-driven, reciprocating cover that fits tightly over the top of the collection vessel during dry periods. A rain gauge should be installed at the collection site to monitor continuously the volume of precipitation collected by a standard rain gauge compared to the volume collected in the sampler. An event recorder, triggered by the opening and closing of the sampler cover, is also recommended to diagnose malfunctions in the operation of the collector drive motor and sensing mechanism.

2.1.2. Siting criteria. Collection sites for regional or background precipitation chemistry studies should be located at least 100 meters from routine air, ground, or water traffic. Overhead obstructions such as power lines or trees that can interfere with sample collection should be avoided. Maintain a horizontal distance between the sampling site and any large obstruction of at least four times (Note a) the height of the obstructing object above the top of the sampler. The ground surface of the collection site should be firm and covered with grass or similar vegetative cover. For a more complete list of siting criteria refer to Topol, et al. [ref. 3]. Locate the rain gauge/event recorder near the collector with a horizontal distance of at least two meters between each instrument. Position the rain gauge parallel to both the collector and the direction of the prevailing winds to minimize any potential influence on the chemical quality of the precipitation.

2.1.3. Collection vessels. All collection buckets, liners, funnel/bottle devices, and storage bottles should be constructed from a non-contaminating material that will not adsorb the inorganic ions of interest. High density (linear) polyethylene, which has been shown to be suitable collection and storage material, is most widely used for the collection and storage of wet deposition samples (Note b). Other plastic materials such as polypropylene, conventional (low density) polyethylene, and polytetrafluoroethylene have been used successfully as well. All containers that will be used for sample collection or storage should be evaluated for adsorption/desorption properties on a continual basis since the purity of plastic products can vary among manufacturers and between different production runs from the same manufacturer. The evaluation of the collection vessel should include the cap, cap liners, and gasket materials that are used to seal the container after collection.

Thoroughly rinse all collection surfaces with reagent water (ASTM Type II [ref. 4], or equivalent) prior to use. Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyolefin matrix and be slowly leached back into the sample. Alkaline detergents may also leave residues that can affect the sample chemistry. Wear particle-free, noncontaminating gloves whenever handling clean buckets or bucket liners. Cap collection bottles after cleaning to prevent contamination from airborne contaminants. Air dry collection buckets and liners in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket or liner interior by any method other than air drying under a clean air workstation. Monitor the cleaning procedure by pouring a volume of reagent water that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the concentrations of the constituents that will be measured in the rainwater sample. If any of the analyte concentrations exceed the method detection limit, a contamination problem is indicated in the cleaning procedure. Take corrective action before the containers are used for the collection of rainwater samples.

2.1.4. Sampling frequency. The frequency of sampling is determined by the study objectives [refs. 5,6]. Event, daily, and weekly sampling schedules are the most commonly used. Sequential samples taken within a single event are also used in studies focusing on precipitation scavenging processes. Unless stringent precautions are taken, collection periods of longer than one week are generally not recommended because of the potential for sample degradation and evaporation.

2.2. Sample Handling

When servicing the collection equipment, always approach the sampler from the downwind side to prevent possible contamination from clothing, hair, or dust particles. Do not touch any of the collection surfaces when removing or installing the collection vessel. Cap or seal all samples at the time of collection to prevent contamination or loss of sample during transit to a processing facility. Collection vessels should be brought to the sampling site in clean plastic bags and installed immediately after the bag has been removed. The reciprocating cover of wet-only samplers should be inspected each time the sampler is serviced to ensure that a tight seal is maintained between the collection vessel rim and the cover. The underside of the cover should be cleaned with reagent water on at least a monthly basis to prevent the buildup of dust or dirt that could result in sample contamination. Whenever samples are collected, check the sensor mechanism on the collector for proper operation.

Field personnel responsible for the collection of samples should be instructed in the procedures that are required to operate a precipitation chemistry measurement site. In addition to operation and troubleshooting of the collection equipment, site operators should be aware of the careful handling techniques that are required to prevent sample contamination.

(Note a) This distance-height relationship is under debate; this recommendation conforms to the ISO norm.

(Note b) This strictly applies only to the anionic constituents of this report; collection and storage containers for trace elements must meet more stringent requirements.

2.3. Quality Assurance

Wet deposition samples are characterized by very low concentrations of dissolved constituents. The dilute nature of precipitation samples requires that a rigorous quality assurance (QA) program be followed to monitor and control the variables that affect sample representativeness. A quality assurance program for precipitation chemistry measurements must include all aspects of sample collection, handling, chemical analysis, and data management.

3. SAMPLE PRESERVATION AND STORAGE

Chloride is the only anion in this method that is stable in solution. Nitrate concentration is affected by biological activity within acid rain samples. Unless stabilizers are added after sample collection, the oxidation of nitrite and sulfite will result in increased concentrations of nitrate and sulfate, respectively. Sample measurements for sulfate and nitrate ions should be made immediately after collection, if possible. Refrigeration of samples at 4 °C will minimize, but not eliminate, concentration changes prior to chemical analysis.

Filtration of samples through a 0.45 micrometer membrane leached with reagent water is partially effective at stabilizing nitrate by removal of biologically active species. Refrigeration immediately after filtration is the most reliable method to ensure sample integrity for nitrate ion. Sample storage time should not exceed one week. Chloride and sulfate determinations should be made within two weeks of sample collection.

4. ION CHROMATOGRAPHY

4.1. Scope and Application

4.1.1. This method is applicable to the determination of chloride, nitrate, and sulfate in acid rain by chemically suppressed ion chromatography.

4.4.2. The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

4.1.3. The method detection limits (MDL) for the above analytes were determined from replicate analyses of calibration solutions containing 0.05 mg/L of each analyte. The measured MDL for chloride, nitrate, and sulfate are 0.03 mg/L. The analyte concentration ranges of the method are 0.03-2.00 mg/L for Cl^-, 0.03-5.00 mg/L for NO_3^-, and 0.03-8.00 mg/L for SO_4^{2-}.

4.2. Summary of Method

Ion chromatography combines conductimetric detection with the separation capabilities of ion exchange resins. A filtered aliquot of sample, ranging in size from 100 to 250 µL, is pumped through an ion exchange column where the anions of interest are separated. Each ion's affinity for the exchange sites, known as its selectivity quotient, is largely determined by its radius and charge. Because different ions have different migration rates, the sample ions elute from the column as discrete bands. Each ion is identified by its retention time within the exchange column. The sample ions are selectively eluted off the separator column and onto a suppressor column. The eluent ions are neutralized and the sample ions are converted to their corresponding strong acids which are detected in a conductance cell. The chromatograms produced are displayed on a strip chart recorder or other data acquisition device for measurement of peak height or area. The ion chromatograph is calibrated with standard solutions containing known concentrations of the anions of interest. Calibration curves are constructed from which the concentration of each analyte in the unknown sample is determined.

4.3. Interference

4.3.1. Depending on the operational conditions of the chromatographic measurements, unresolved peaks may result when the concentration of one of the sample components is much higher (e.g., 10 to 20 times) than another component that appears in the chromatogram as an adjacent peak. Decreasing the eluent concentration or the flow rate may correct this problem by increasing peak separation.

4.3.2. Interferences can be caused by ions with retention times that are similar to, and thus overlap, those of the anion of interest. Fortunately, this type of positive interference is rare in acid rain samples. If this interference occurs, as evidenced by a shoulder or asymmetry of the peak of interest, decreasing the eluent concentration or the flow rate may result in improved peak resolution.

4.3.3. Water from the sample injection will cause a negative peak or dip in the chromatogram when it elutes because its conductance is less than that of the suppressed eluent. Any ion of interest eluting near the water dip must be sufficiently resolved from the dip to be accurately quantified. This can be achieved by changing the eluent concentration or decreasing the flow rate. Alternatively, the negative peak can be eliminated by adding an equivalent of 100 µL of a prepared eluent concentrate (solution that is 100 times more concentrated than the eluent used for analysis) per 10.0 mL of sample. Proportionate eluent additions must also be included in calibration and quality control solutions.

4.3.4. Decreases in retention times and resolution are symptoms of column deterioration which may be caused by the buildup of contaminants on the exchange resin. Refer to the manufacturer's guidelines for instructions on cleaning the column resin and column filter beds.

4.3.5. The presence of air bubbles in the columns, tubing, or conductivity detector cell will cause baseline and peak variability. Avoid introducing air into the system when injecting samples and standards. A debubbler inserted in the line before the pump will help to minimize the introduction of air.

4.4. Apparatus and Equipment

4.4.1. Ion chromatograph. Select an instrument equipped with an injection valve, sample loop, a sampling system, analytical columns, compressed gas, pumps, detector, and strip chart recorder or other data acquisition device. All tubing that comes in contact with samples and standards must be manufactured from inert material such as polyethylene or polytetrafluoroethylene.

4.4.1.1. Anion Guard Column. Place before the separator column. This contains the same resin as the separator column and is used to protect the ion exchange column from being fouled by particulates or organic constituents.

4.4.1.2. Anion Separator Column. This is a column packed with a pellicular low-capacity anion exchange resin constructed of sulfonated polystyrene-divinylbenzene beads coated with quatenary ammonium active sites.

4.4.1.3. Anion Suppressor Column. Place after the separator column. This may be in the form of a packed bed, fiber or micro-membrane suppressor. The first type of suppressor is packed with a high-capacity cation exchange resin in the protonated form capable of converting the eluent to a low or negligible background conductance and converting the sample anions to their corresponding strong acids. The second two types of suppressors utilize a semipermeable membrane containing cation exchange sites to suppress eluent conductance. Both the fiber and micro-membrane suppressors are under continuous regeneration.

4.4.1.4. Compressed Gas (Nitrogen or Air). Use compressed gas that is oil-, particulate-, and water-free to actuate the valves and to pressurize the regenerant flow system as required.

4.4.1.5. Detector. Select a flow-through, temperature-compensated, electrical conductance cell with a volume of approximately 6 μL coupled with a meter capable of reading from 0 to 1000 μS/cm on an analog or digital scale.

4.4.1.6. Pump. Use a pump capable both of delivering an accurate flow rate and of tolerating the optimal pressure as suggested by the instruction manual accompanying the ion chromatograph and columns selected. A constant-pressure, constant-flow pump is recommended for enhanced baseline stability. All interior pump surfaces that will be in contact with samples and standards should be manufactured from inert materials.

4.4.1.7. Data Acquisition System

4.4.1.7.1. Recorder. This should be compatible with the maximum conductance detector output with a full-scale response time of 0.5s or less. A two-pen recorder with variable voltage input settings is recommended.

4.4.1.7.2. Integrator. If an integrating system is employed, the data acquisition unit must be compatible with the maximum detector output.

4.4.1. 8. Sample loop. Select a sample loop compatible with the column system having a capacity of 100-250 μL.

4.4.1.9. Sample introduction system. Select one of the following for sampling.

4.4.1. 9.1. Syringe. Use a syringe equipped with a male fitting with a minimum capacity of 2 mL.

4.4.1.9.2. Autosampler. Use an autosampling system capable of precise delivery, equipped with a dust cover to prevent airborne contamination.

4.4.2. Eluent and regenerant reservoirs. Select containers with a 4-20 L capacity that are designed to minimize introduction of air into the flow system. The regenerant reservoirs may be pressurized with nitrogen or air (35-70 kPa) to ensure constant delivery to the micro-membrane or fiber suppressor column.

4.4.3. Laboratory facilities. Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. Room temperature fluctuations should be controlled to within ±3 °C to prevent baseline drift and changes in detector response. Improved resolution will result from even better temperature control.

4.5. Reagents and Consumable Materials

4. 5.1. Purity of reagents. Use reagent grade chemicals for all solutions.

4.5.2. Purity of water. Use reagent water conforming to ASTM Specification D 1193, Type II [ref. 4], or equivalent. Filters (0.2 micrometer) are recommended for all faucets supplying water to prevent the

introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

4.5.3. Eluent solution. Sodium hydrogen carbonate 0.0028 mol/L, sodium carbonate 0.0022 mol/L. Dissolve 0.470 g sodium hydrogen carbonate ($NaHCO_3$) and 0.467 g of sodium carbonate (Na_2CO_3) in reagent water and dilute to 4 L. Mix the solution well.

4.5.4. Regeneration solution. Dilute concentrated sulfuric acid (H_2SO_4, density = 1.84 g/mL) to one of the following concentrations for use with packed bed, fiber, or micro-membrane suppressors.

4.5.4.1. Sulfuric Acid (0.5 mol/L). (regenerant for a packed bed column) Add 111 mL of concentrated H_2SO_4 to 2 L of water and dilute to 4 L.

4.5.4.2. Sulfuric Acid (0.0125 mol/L). (regenerant for a fiber suppressor) Add 2.8 mL of concentrated H_2SO_4 to 2 L of water and dilute to 4 L.

4.5.4.3. Sulfuric Acid (0.009 mol/L). (regenerant for a micro-membrane suppressor) Add 2.0 mL of concentrated H_2SO_4 to 2 L of water and dilute to 4 L. Other regenerant concentrations from 0.003 to 0.025 mol/L may be used.

4.5.5. Stock standard solutions. Stock standard solutions may be purchased as certified solutions or prepared from reagent grade materials that have been dried to constant weight at 105 °C as listed below. Store the solutions at room temperature in high density polyethylene or polypropylene containers.

4.5.5.1. Chloride solution, Stock (1.0 mL = 1.0 mg Cl^-) Dissolve 1.648 g of sodium chloride (NaCl) in reagent water and dilute to 1 L.

4.5.5.2. Nitrate solution, Stock (1.0 mL = 1.0 mg NO_3^-). Dissolve 1.371 g of sodium nitrate ($NaNO_3$) in reagent water and dilute to 1 L.

4.5.5.3. Sulfate solution, Stock (1.0 mL = 1.0 mg SO_4^{2-}). Dissolve 1.814 g of anhydrous potassium sulfate (K_2SO_4) in reagent water and dilute to 1 L.

4.5.6. Sample containers. Use polyolefin or glass sample cups that have been rinsed thoroughly with reagent water before use.

5. CALIBRATION AND STANDARDIZATION

5.1. Instrument Assembly Assemble the ion chromatograph according to the manufacturer's instructions.

5.2. Temperature Bring all standards, samples, eluents, and regenerants to ambient temperature before beginning any analyses. Maintain laboratory temperature conditions within ±3°C while conducting analyses.

5.3. Eluent Use the eluent strength in Sect. 4.5.3. for wet deposition analyses. If peak resolution is not adequate, it may be necessary to decrease the eluent strength. Refer to the manufacturer's recommendations for guidelines on optimizing eluent strength.

5.4. Flow Rate Adjust the instrument flow rate for optimal peak resolution. Decreasing the flow rate may provide improved peak resolution but will lengthen retention times. Increasing the flow rate decreases peak resolution and shortens retention times. Refer to the manufacturer's recommendations for guidelines on optimizing flow rate.

5.5. Equilibration Equilibrate the system by pumping eluent through all the columns and the detector until a stable baseline is obtained.

5.6. Calibration Solutions

5.6.1. Five calibration solutions and one zero standard*(Note c) are needed to generate a suitable calibration curve. The lowest calibration solution should contain the analyte(s) of interest at a concentration slightly greater than or equal to the method detection limit. The highest calibration solution should approach the expected upper limit of concentration of the analyte in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. If a second detector sensitivity scale setting is used to increase the instrument's concentration range, calibrate at the two sensitivity levels.

5.6.2. Prepare all calibration standards by diluting the stock standards (Sect. 4.5.5.). Use glass or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. Standards with a concentration greater than 0.10 mg/L of each anion are stable for one week when stored at room temperature in high density polyethylene or polypropylene containers. Prepare standards with 0.10 mg/L or less of each anion fresh every day and store at room temperature in high density polyethylene or polypropylene containers.

(Note c) Terms marked with an asterisk henceforth are discussed in the Appendix (Sect. 10).

5.6.3. Chloride, nitrate, and sulfate can be combined into a single solution at each of the five standard concentration levels.

5.7. Calibration Curve

5.7.1. Flush the sample loop with the calibration standard using at least ten times the injection loop volume. Inject the standard solution and record the peak height or area response. Repeat this step for each calibration standard. Construct calibration curves for each of the three analytes according to Sect. 8.

5.7.2. Record the retention times for each analyte. Measure retention time from an initial starting point on the chromatogram.

5.7.3. Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 6.5.

5.7.4. Whenever a new eluent or regenerant solution is made, reestablish the calibration curve.

6. QUALITY CONTROL

6.1. QC Protocols

Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control*. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency [ref. 3]. Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines should be used by all laboratories involved with wet deposition measurements. In addition, the use of cusum (cumulative sum) charts as a method for early detection of drifts or trends in the values of results can be recommended [ref. 7]. For such charts, a certified reference material (see Sects. 6.2.2 and 6.4.) can be of considerable help.

6.2. Establishment of Warning and Control Limits

Warning* and control* limits are used to monitor drift in the calibration curve, analyses of quality control check samples*, and measured recoveries from laboratory spikes*.

6.2.1. Calibration curve. After a calibration curve has been constructed, reanalyze additional aliquots of the low and high concentration standards. Determine the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\bar{x}$) for determining the control limits. A warning limit of $\bar{x} \pm 2s$ and a control limit of $\bar{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

6.2.2. Quality control check samples (QCS). Calculate warning and control limits for QCS solutions from a minimum of 10 analyses performed on 10 days. Use the calculated standard deviation at each QCS concentration level to develop the limits as described in Sect. 6.2.1. Use the concentration of a certified reference material as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 6.4. to determine when the measurement system is out of statistical control. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

6.2.3. Laboratory spike solutions. A minimum of 10 analyte spikes of acid rain samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery* data using the formula provided in the Appendix. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant bias exists, the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

6.2.4. All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability. Broadening limits may be an indication of problems with the analytical system and the cause should be investigated and corrective action taken.

6.3. Cleaning Procedure

Monitor the cleaning procedure (Sect. 2.1.3.) by pouring a volume of reagent water that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the concentrations of the anions that will be measured in wet deposition. If any of the analyte concentrations exceed the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

6.4. Check Sample Analysis

Analyze a quality control check sample (QCS) after the ion chromatograph has been calibrated. This sample may be formulated in the laboratory or obtained from the U.S. National Institute of Standards and Technology (NIST Standard Reference Material 2694, Simulated Rainwater) [ref. 8] or the Community Bureau of Reference (BCR). Verify the accuracy of internally formulated QCS solutions with a NIST or BCR traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards. If the measured value for the QCS falls outside of the $\pm 3s$ limits, or if two successive QCS checks are outside of the $\pm 2s$ limits, a problem is indicated with the ion chromatograph or calibration curve. Corrective action should be initiated to bring the results of the QCS within the established control limits. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

6.5. Calibration Curve Verification

Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 6.4., recalibrate the system. Verify the new calibration curve with the QCS according to Sect. 6.4. and reanalyze all samples measured since the last time the system was in control.

6.6. Field Blank Analysis

Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a reagent water sample or a known reference solution that approximates the concentration levels characteristic of acid rain. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the acid rain sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

7. SAMPLE INJECTION

7.1. Use the same size injection loop for both standards and samples. Samples may be injected manually with a syringe or with an autosampler.

7.2. Flush the sampling system thoroughly with each new sample using a rinse volume of at least ten times the loop size. Inject the sample, avoiding the introduction of air bubbles into the system.

7.3. Record the resulting peak heights or areas.

7.4. If the peak height or area response exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

8. CALCULATIONS

8.1. For each analyte of interest, calculate a linear least squares fit of the standard concentrations as a function of the measured peak height or area. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1 x$$

where:

y = standard concentration in mg/L
x = peak height or area measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n} (x_i - \bar{x})^2$$

where:

$\bar{x}$ = mean of peak heights or areas measure
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9990 or greater. Determine the concentration of the analyte of interest from the calibration curve.

8.2. If the relationship between standard concentration and measured peak height or area is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation ≥0.9990.

The second degree of polynomial equation is expressed as follows:

$$y = B_0 + B_1x + B_2x^2$$

A computer program is necessary for the derivation of this function. Determine the concentration of the analyte of interest from the calibration curve.

8.3. An integration system may also be used to provide a direct readout of the concentration of the analyte of interest.

8.4. Report data in mg/L as Cl^-, NO_3^- or SO_4^{2-}. Do not report data lower than the lowest calibration standard.

9. REFERENCES

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10. APPENDIX

10.1. Control Limits (CL) are statistically derived values that limit the range of acceptable random error in a measurement process. They consist of an upper and lower range of acceptable values that are defined as ±3s from the mean.

10.2. Laboratory Spike is a known volume of method analyte that is added to a sample. The concentration of analyte spiked into the sample usually approximates the expected concentration of that analyte in the unspiked sample. The difference in concentration between the spiked and the unspiked sample is used to calculate a method percent recovery.

10.3. Percent Recovery is an estimate of the bias of an analytical method determined from analyte spikes of natural samples. The percent recovery is calculated as:

$$\% \text{ Recovery} = 100\,[(a - b)/c]$$

where: a = measured concentration of spiked sample
b = measured concentration of unspiked sample
c = calculated spike concentration

10.4. Quality Control Check Sample (QCS) is a sample containing known concentrations of analytes prepared by the analyst or a laboratory other than the laboratory performing the analysis. The performing laboratory uses this sample to demonstrate that it can obtain acceptable results with procedures to be used to analyze acid rain samples. Analyte true values are known by the analyst.

10.5. Statistical Control is the description of a measurement process that is characterized solely by random errors.

10.6. Warning Limits (WL) are limits used in quality control charts to indicate that the analytical procedure is close to being out of statistical control. They consist of an upper and lower range of values that are defined as ±2s from the mean value.

10.7. Zero Standard is a calibration standard used to set the instrument response to zero. It contains all of the matrix components of the remaining calibrants except the method analyte or analyte.