



Designation: D 5085 – 9502

# Standard Test Method for Determination of Chloride, Nitrate, and Sulfate in Atmospheric Wet Deposition by Chemically Suppressed Ion Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 5085; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.06 on Atmospheric Deposition.

Current edition approved ~~Jan. 15, 1995~~; October 10, 2002. Published ~~March 1995~~; December 2002. Originally published as D 5085 – 90. Last previous edition D 5085 – 90 $\epsilon$ .

## 1. Scope

1.1 This test method is applicable to the determination of chloride, nitrate, and sulfate in atmospheric wet deposition (rain, snow, sleet, and hail) by chemically suppressed ion chromatography (1)<sup>2</sup> ~~using a two pen variable setting recorder and integrator.~~ For additional applications refer to Test Method D 4327.

1.2 The concentration ranges for this test method are listed below. The range tested was confirmed using the interlaboratory collaborative test (see Table 1 for statistical summary of the collaborative test).

	MDL (mg/L) (2)	Range of Method (mg/L)	Range Tested (mg/L)
Chloride	0.03	0.09–2.0	0.15–1.36
Nitrate	0.03	0.09–5.0	0.15–4.92
Sulfate	0.03	0.09–8.0	0.15–6.52

1.3 The method detection limit (MDL) is based on single operator precision (2) and may be higher or lower for other operators and laboratories. The precision and bias data presented are insufficient to justify use at this low level, however, many workers have found that this test method is reliable at lower levels than those that were tested.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 9.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 883 Terminology Relating to Plastics<sup>3</sup>

D 1129 Terminology Relating to Water<sup>4</sup>

D 1193 Specification for Reagent Water<sup>4</sup>

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres<sup>5</sup>

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>4</sup>

D 3670 Guide for Determination of Precision and Bias of Methods of Committee D-22<sup>5</sup>

D 4210 Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data<sup>4</sup>

D 4327 Test Method for Anions in Water by Chemically Suppressed Ion Chromatography<sup>4</sup>

D 5012 Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition<sup>5</sup>

E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)<sup>6</sup>

E 694 Specification for Laboratory Glass Volumetric Apparatus<sup>6</sup>

<sup>2</sup> The boldface numbers in parentheses refer to references at the end of this test method.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 08.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 11.03.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 14.02.

**TABLE 1 Precision and Bias for Chloride, Nitrate, and Sulfate Determined from the Synthetic Atmospheric Wet Deposition Samples Used in the Interlaboratory Comparison Study**

Analyte	Amount Added, mg/L	Mean Recovery, mg/L	$n^A$	Precision mg/L			Bias, mg/L	Significant Bias <sup>B</sup>	
				$S_t^C$	95 % Reproducibility Limit	$S_o^D$			95 % Repeatability Limit
Chloride	0.15	0.157	36	0.0535	0.150	0.0116	0.0325	0.007	no
	0.30	0.293	35	0.0554	0.155	0.0291	0.0815	-0.007	no
	0.68	0.652	36	0.0549	0.154	0.0237	0.0664	-0.028	biased low
	1.36	1.368	36	0.1	0.28	0.0431	0.121	0.008	no
Nitrate	0.15	0.138	24	0.0362	0.101	0.0289	0.0809	-0.012	no
	1.08	1.077	24	0.0495	0.139	0.0421	0.118	-0.003	no
	2.44	2.486	22	0.0197	0.0552	0.0183	0.0512	0.046	biased high
	4.92	4.999	24	0.126	0.353	0.075	0.21	0.079	biased high
Sulfate	0.15	0.172	36	0.055	0.154	0.0304	0.085	0.022	no
	1.43	1.442	35	0.0683	0.191	0.0369	0.103	0.012	no
	3.23	3.358	36	0.13	0.364	0.046	0.129	0.128	biased high
	6.52	6.775	36	0.37	1.04	0.109	0.305	0.255	biased high

<sup>A</sup> Number of samples included in final statistical analysis after removal of outlier data.

<sup>B</sup> 95 % confidence level.

<sup>C</sup> Between laboratory precision, reproducibility.

<sup>D</sup> Within laboratory precision (pooled single operator precision), repeatability.

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminologies D 883, D 1129, and D 1356 and Test Method D 4327 and Practice E 380.

~~3.1.1 *method detection limit (MDL)*—the minimum concentration of an analyte that can be reported with 99 % confidence that the value is above zero based on a standard deviation of greater than seven repetitive measurements of a solution containing the analyte at a concentration near the low standard. The solution used should not be greater than five times the estimated MDL. (3)~~

### 4. Summary of Test Method

4.1 Ion chromatography combines conductometric detection with the separation capabilities of ion exchange resins. (1) A filtered aliquot of the sample, ranging in size from 50 to 250  $\mu$ L, 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 valence. Because different ions have different selectivity quotients, 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, where the conductivity of the eluent ions is reduced and the sample ions are converted to their corresponding strong acids. The separated anions are detected by a conductance cell. The chromatograms produced are displayed on a strip chart recorder or other data acquisition device. Measurement of peak height or area is used for quantitation. The ion chromatograph is calibrated with standard solutions containing known concentrations of the anion(s) of interest. Calibration curves are constructed from which the concentration of each analyte in the unknown sample is determined. For additional information on ion chromatography refer to Test Method D 4327.

### 5. Significance and Use

5.1 This test method is useful for the determination of the anions: chloride, nitrate, and sulfate in atmospheric wet deposition.

5.2 Fig. X1.1 in the appendix represents cumulative frequency percentile concentration plots of chloride, nitrate, and sulfate obtained from analyses of over 5000 wet deposition samples. These data may be used as an aid in the selection of appropriate calibration solutions. (4)(3)

### 6. Interferences

6.1 Unresolved peaks will result when the concentration of one of the sample components is 10 to 20 times higher than another component that appears in the chromatogram as an adjacent peak. Decreasing the eluent concentration or flow rate, increasing column length, or decreasing sample size may correct this problem.

6.2 Interferences may be caused by ions with retention times that are similar to the anion of interest. The retention time of sulfite may be similar to nitrate or sulfate. Other possible interfering ions are bromide and phosphate. Before analyzing precipitation samples, measure the retention times of these possible interfering ions. Interference is common in some types of wet deposition samples. If this interference is anticipated, decreasing the eluent concentration or flow rate, increasing column length, or decreasing sample size will result in improved peak resolution.

6.3 Water from the sample injection will cause a negative peak (water dip) in the chromatogram when it elutes because its conductance is less than that of the suppressed eluent. Chloride may elute near the water dip and 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. The

potential interference of the negative peak can be eliminated by adding an equivalent of 100  $\mu\text{L}$  of a prepared eluent concentrate (solution that is 100 times more concentrated than the eluent used for analysis) per 10.0 mL of sample. Identical eluent additions must also be included in calibration and quality control solutions.

6.4 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. Excising the contaminated portion of the column and changing the filters may also improve performance. If the procedure in this section do not restore the retention times, replace the column.

6.5 Contaminated valves and sample lines may also reduce system performance causing decreased retention times and resolutions. Refer to the manufacturer's guidelines for instructions on cleaning the valves and replacing the lines.

NOTE 1—Review operational details and refer to the trouble shooting guide in the Operator's Manual to determine the cause of decreased retention times and resolution prior to extensive cleaning or changing of all valves, columns, filters, sample lines, or all of the above.

6.6 The presence of air bubbles in the columns, tubing, or conductivity detector cell may cause baseline fluctuations and peak variability. Prevent introducing air into the system when injecting samples and standards. The use of degassed water for eluents and regenerants may help to minimize the introduction of air (See 8.2).

6.7 For more information on interferences refer to Test Method D 4327.

## 7. Apparatus

7.1 *Ion Chromatograph*—Select an instrument equipped with an injection valve, a sample loop, separator column(s), suppressor column(s), pump(s), and detector meeting requirements specified. Peripheral equipment includes compressed gas, a suitable data acquisition device such as a strip chart recorder, an integrator, or computer, and may include an automatic sampler.

7.1.1 *Tubing*—Tubing that comes in contact with samples and standards must be manufactured from inert material such as polyethylene plastics or TFE-fluorocarbon.

7.1.2 *Anion Guard Column*—Also called a precolumn, it is placed before the separator column. The guard column contains the same resin as the separator column and is used to protect it from being fouled by particulates or organic constituents. Using an anion guard column will prolong the life of the separator column.<sup>7</sup> (See Table 2.)

7.1.3 *Anion Separator Column*—This is a column packed with a pellicular low-capacity anion exchange resin constructed of polystyrene-divinylbenzene beads coated with quaternary ammonium active sites.<sup>8</sup> (See Table 2.)

7.1.4 *Anion Suppressor Column*—Place following the separator column. This may be in the form of a packed bed column, fiber suppressor, or an anion micro-membrane suppressor or an anion self-regenerating suppressor. The first type of column is packed with suppressor utilizes a high-capacity cation semipermeable membrane containing anion exchange resin in the protonated form capable of converting the eluent sites to a low or negligible background conductance and converting the sample anions to their corresponding strong acids, suppress eluent conductance.<sup>9</sup> The second two types type of suppressors utilize a semipermeable membrane containing anion exchange sites to suppress eluent conductance.<sup>10</sup> (See Table 2.) suppressor uses the neutralized cell effluent as the source of water for the regenerant chamber water.

7.1.5 *Compressed Gas (Nitrogen or Air)*—Use ultra-high purity 99.999 % (v/v) compressed gas that is oil, particulate, and water free to actuate the valves and to pressurize the regenerant flow system as required needed.

7.1.6 *Detector*—Select a flow-through, temperature-compensated, electrical conductivity cell with a volume of approximately 6  $\mu\text{L}$  coupled with a meter capable of reading from 0 to 1000  $\mu\text{S}/\text{cm}$  on an analog or digital scale.

7.1.7 *Pump*—Use a pump capable both of delivering a constant flow rate of approximately 1 to 5 mL/min and of tolerating a pressure 200 1379 to 1000 psi. 13 790 kPa. 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 must be manufactured from inert, non-metallic materials.

7.1.8 *Data Acquisition System:*

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

7.1.8.2 *Integrator*—If an integrating system is employed, the data acquisition unit must be compatible with the maximum detector output to quantitate the peak height or area. If an integrator is used, the maximum peak height or area measurement must be within the linear range of the integrator.

7.1.9 *Sample Loop*—Select a sample loop with a capacity of 50 to 250  $\mu\text{L}$ .

<sup>7</sup> Dionex P/N 030986 (AG3) available from Dionex Corp., 1228 Titan Way, PO Box 3603, Sunnyvale, CA, 94088-3603, or equivalent has been found to be satisfactory.

<sup>8</sup> Dionex P/N 030985 (AS3) available from Dionex Corp., 1228 Titan Way, PO Box 3603, Sunnyvale, CA, 94088-3603, or equivalent has been found to be satisfactory.

<sup>9</sup> Dionex P/N 030829 (ASC-1) 35350 (AFS) or Dionex P/N 38019 (AMMS) available from Dionex Corp., 1228 Titan Way, PO Box 3603, Sunnyvale, CA, 94088-3603, or equivalent has been found to be satisfactory.

<sup>10</sup> Dionex P/N 35350 (AFS) or Dionex P/N 38019 (AMMS) available from Dionex Corp., 1228 Titan Way, PO Box 3603, Sunnyvale, CA, 94088-3603, or equivalent has been found to be satisfactory.

<sup>10</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

7.1.10 *Sample Introduction System*—Select one of the following:

7.1.10.1 *Syringe*—A syringe equipped with a male fitting with a minimum capacity of 2 mL.

7.1.10.2 *Autosampler*—An autosampling system capable of precise delivery, equipped with a dust cover to reduce airborne contamination.

7.2 *Eluent and Regenerant Reservoirs*—Select containers with a 4 to 20 L capacity that are designed to minimize introduction of air into the flow system for storing eluents and regenerants.

7.3 *Glassware*—Glassware, including volumetric pipettes and flasks, must be dedicated for use on atmospheric wet deposition samples only. Volumetric pipettes should be used to measure the stock solutions. The pipettes may be either fixed or variable volume and either glass or plastic. Volumetric glassware must meet the requirement for Class A items given in Specification E 694. Pipettes with disposable tips are preferred in order to reduce contamination. The pipettes must have a precision and a bias of 1 % or better. Precision and bias are determined by weighing a minimum of ten separately pipetted aliquots.

7.4 *Laboratory Facilities*—Laboratories used for the analysis of wet deposition samples must be free from sources of contamination. The use of laminar flow clean air work stations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples must always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Room temperature fluctuations must be controlled to within  $\pm^{\circ}\text{C}$  to prevent baseline drift and changes in detector response. Windows within the laboratory must be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Use reagent grade or higher grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) where such specifications are available.<sup>10</sup>

8.2 *Purity of Water*—Use water conforming to Specification D 1193, Type II. Point of use 0.2  $\mu\text{m}$  filters are recommended for all faucets supplying water to prevent the introduction of bacteria ion exchange resins, or both, into reagents, standard solutions, and internally formulated quality control check solutions. If degassing is necessary (see 6.6), de-gas the water prior to use by placing in a polyolefin or glass container, stirring vigorously, and aspirating off the liberated gasses.

8.3 *Eluent Solution*—(The eluent solution given here is for use with the AS3 or AS4 separator column. ~~For other suggested~~ ~~Other columns and eluent concentrations see Table 2.) are available.) Sodium bicarbonate 0.0028 M, sodium carbonate 0.0022 M (eluent strength recommended for wet deposition analysis). Dissolve 0.941 g sodium bicarbonate ( $\text{NaHCO}_3$ ) and 0.933 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in water and dilute to 4 L with water. Mix the solution well and de-gas before use when necessary.~~

8.4 *Regeneration Solution*—~~Dilute concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp gr 1.84) to one of the following concentrations for use with fiber, or micro-membrane suppressors.~~

8.4.1 *Sulfuric Acid (0.0125 M)*—(Regenerant for a fiber suppressor) Add 2.8 mL of concentrated  $\text{H}_2\text{SO}_4$  to 2 L of water, mix well, and dilute to 4 L.

8.4.2 *Sulfuric Acid (0.009 M)*—(Regenerate for the Anion Micro-Membrane Suppressor.) Add 2.02 mL of concentrated  $\text{H}_2\text{SO}_4$  to 2 L of water, mix well, and dilute to 4 L.

8.4.2 *Water*—Reagent water, ASTM Type I, for use with some suppressors.

8.4.3 *The self-regenerating suppressors need no regenerant solution.*

8.5 *Stock Standard Solutions*—Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials as listed in 8.5.1-8.5.3 and dried to constant weight at 105°C. Store the solutions at room temperature in high density polyethylene or polypropylene containers.

8.5.1 *Chloride Solutions, Stock* (1.000 mL = 1.000 mg Cl)—Dissolve 1.648 g of sodium chloride ( $\text{NaCl}$ ), in water and dilute to 1 L.

8.5.2 *Nitrate Solution, Stock* (1.000 mL = 1.000 mg  $\text{NO}_3$ )—Dissolve 1.371 g sodium nitrate ( $\text{NaNO}_3$ ) in water and dilute to 1 L.

8.5.3 *Sulfate Solution, Stock* (1.000 mL = 1.000 mg  $\text{SO}_4$ )—Dissolve 1.479 g anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) in water and dilute to 1 L.

8.6 *Sample Containers*—Use polyolefin or glass sample cups that have been rinsed thoroughly with water before use.

## 9. Hazards

9.1 The calibration standards, sample types, and most reagents used in this test method pose limited hazard to the analyst providing routine laboratory safety precautions are practiced (see 9.3). Use a fume hood, protective clothing, and safety glasses when handling concentrated sulfuric acid.

9.2 Keep the doors of the instrument column compartment closed at all times when pumps and columns are in use to prevent injury to the operator from column explosion if the pump pressure or column backpressure increases.

9.3 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this test method. ~~(5)~~(4)

## 10. Sampling, Test Samples and Test Units

10.1 Some chemical constituents found in atmospheric wet deposition are not stable and must be preserved before analysis.

Proper selection and cleaning of sampling containers are required to reduce the possibility of contamination. ~~(4)~~**(3)**

10.2 For additional information on sample collection and preservation of atmospheric wet deposition refer to Guide D 5012.

## 11. Calibration and Standardization

### 11.1 Determination of Retention Times:

11.1.1 The retention time for each anion is determined by injecting a standard solution containing only the anion of interest and noting the time required for the center of a peak to appear on the chromatogram. Retention times vary with operating conditions and are influenced by the concentration of ion(s) present. Prepare separate standard solutions of each anion for at least two concentrations by pipetting the appropriate amount of stock standard solutions into 1 L volumetric flasks and diluting with water. Analyze each standard of interest as defined in Section 11. Note the time in hundredths of minutes for each peak to appear on the chromatogram.

11.1.2 A locator mix must be used to determine the retention time of each standard ion in solution with the others. It is prepared by pipetting an appropriate amount of each of the stock standard solutions into a 1 L volumetric flask and diluting with water. The concentrations of each standard chosen must be proportional to the expected concentrations of the samples. The retention times are determined by injecting the locator mix and noting the time required for the center of each peak to appear on the chromatogram. See Fig. X2.1. chromatogram.

### 11.2 Calibration Solutions:

11.2.1 ~~FA minimum of~~ five uniformly distributed calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution must contain the analyte(s) of interest at a concentration approaching or equal to the MDL. The highest solution must ~~slightly exceed approximate~~ the 95 percentile of the expected ~~upper limit range of concentration of the solutions being analyzed. Samples above the highest calibration standard must be diluted for analysis.~~ If more than one detector sensitivity scale setting is used to increase the instrument's concentration range, calibrate at each sensitivity level using five calibration standards and one zero standard. Suggested calibration standard concentrations for each analyte are listed in Table 3 2.

11.2.2 Calibration solutions are prepared by diluting the stock standard solutions. Dedicated volumetric glassware meeting the requirement for Class A items given in Specification E 694 must be used to obtain the required accuracy. Calibrated volumetric pipettes with disposable tips may also be used.

NOTE 2—The precision and bias of pipettes with disposable tips should be validated. ~~(6)~~**(5)**

11.2.3 Standards may be prepared using two different methods. Serial dilutions are necessary when using glass volumetric pipettes. Disposable tipped pipettes may be used for direct dilution of stock solutions.

11.2.3.1 When using pipettes with disposable tips, select either fixed or variable volume pipettes. Rinse each new tip before use with water at least three times. Aspirate and discard a minimum of three aliquots of the stock standard. Add the amount of stock solution, calculated from Eq 1, to a volumetric flask partially filled with water. Dilute to volume and mix well.

$$\begin{aligned} & \text{amount of stock solution (mL)} && (1) \\ & = \frac{(\text{desired end volume (mL)}) (\text{desired concentration (mL)})}{(\text{stock solution concentration (mg/L)})} \end{aligned}$$

**TABLE 3 2 Suggested Calibration Standard Concentrations and Retention Times for the Determination of Anions in Wet Deposition Samples**

Analyte	Calibration Standards, <sup>A</sup> mg/L	Approximate Retention Time Range, <sup>B</sup> min
Chloride	0	1.70–3.30
	0.09	
	0.40	
	0.75	
	1.10	
	2.00	
Nitrate	0	3.67–4.00
	0.09	
	1.00	
	2.00	
	3.00	
	5.00	
Sulfate	0	5.83–9.10
	0.09	
	1.25	
	2.50	
	3.75	
	8.00	

<sup>A</sup> The calibration standards suggested are based on the range of the test samples used in the interlaboratory collaborative test.

<sup>B</sup> The retention time was measured from the time of injection.

11.2.3.2 When preparing standards by serial dilution, it is important to not use more than three dilutions in a series. Glass pipettes must be dedicated for use with one analyte and one concentration of that analyte. Pre-rinse all glass pipettes with the analyte solution prior to preparing standards.

~~11.2.4 Standards with concentrations 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. If evidence of each anion fresh every other day and store at room temperature a change in high density polyethylene or polypropylene containers. the concentration of the standards, prepare the standards more frequently.~~

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

11.2.6 For additional information on calibration refer to Test Method D 4327.

11.3 Whenever a new eluent or regenerant solution is made, re-establish the calibration curve. Retention times may change in the middle of a run. If this occurs, regeneration of the calibration curve is necessary.

## 12. Procedure

~~12.1 Bring all standards, samples, eluents, and regenerants to ambient~~

~~12.1 Laboratory temperature before beginning any analyses. Laboratory temperature must be maintained within  $\pm 3^{\circ}\text{C}$  while conducting analyses or a temperature controlled conductivity cell should be used.~~

12.2 Use the eluent strength in 8.3 for wet deposition analyses. If peak resolution is not adequate, it may be necessary to decrease the eluent strength.

12.3 Adjust the instrument flow rate for optimal peak resolution. Decreasing the flow rate may provide improved peak resolution but lengthens 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.

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

12.5 With each calibration standard, flush the sample loop with at least ten times its volume. Inject the standards and record the peak heights or area responses. Compare the peak retention times to those obtained with the locator mix (see 11.1.2). If the peak retention times are not the same, reanalyze the locator mix and the standards. Calculate the calibration function by least squares regression for each of the three analytes according to Section 13.

12.6 Verify the curve by analyzing a quality control check solution (QCS) immediately after calibration. The concentration must agree within the predetermined control limits of two times the standard deviation of the QCS. If results of the calibration check fall outside of these guidelines, analyze an additional aliquot of the standard. If problems persist, recalibrate the instrument and reanalyze all samples measured since the last time the system was in control. **(4,7)(3,6)**

~~12.7 Whenever a new eluent~~

12.7 Frequency of Calibration:

The system should be calibrated daily or regenerant solution is made, re-establish the calibration curve. on a per use basis if not used every day.

12.8 *Sample Injection:*

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

12.8.2 Flush the sample loop 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. Compare the peak retention times to those obtained with the locator mix (see 11.1.2) and the standards (see 12.5). If the peak retention times are not the same, re-analyze the locator mix, the standards, and the samples.

12.8.3 Record the resulting peak heights or areas.

12.9 If the response for a given peak exceeds the working range of the system, dilute the sample with zero standard and re-analyze. If sample concentrations exceed the working range of this test method, dilute the sample with zero standard and reanalyze.

## 13. Calculation

13.1 For each analyte of interest, calculate a least squares fit of the standard concentrations versus peak height or area measured. Determine the concentration of the analyte of interest from this equation.

13.1.1 If the peak height or area versus concentration relationship is linear, use a linear least squares equation to derive a curve. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1x \quad (2)$$

where:

$y$  = standard concentration in mg/L,

$x$  = peak height or area measured,

$B_0$  = y-intercept, and

$B_1$  = slope.

13.1.2 If the peak height or area versus concentration is nonlinear, use a second degree polynomial least squares equation to

derive the curve. The second degree polynomial equation is expressed as follows:

$$y = B_2x^2 + B_1x + B_0 \quad (3)$$

where:

- y = standard concentration in mg/L,
- x = peak height or area measured,
- B<sub>0</sub> = y-intercept, and
- B<sub>1</sub> and B<sub>2</sub> = coefficients of the first and second degree variables.

NOTE 3—Instrument response may or may not be linear for any given analyte and for all chromatographic conditions. In order to determine the correct least squares equation to use for each analyte, calculate both a linear least squares equation and a second degree polynomial least squares equation for each analyte. Determine a correlation coefficient and a standard error of estimate for each equation for each analyte. The equation with the highest correlation coefficient and the lowest standard error of estimate for a specific analyte is the correct equation to use for that analyte. Further test for goodness of fit by analyzing standards that have been prepared in replicate at each concentration or, if replicate standards are not practical, use the peak height or area measured for the standards used to generate the curve. The correct least squares equation to use will also give the best standard concentration values. Once the best fit equation is established, it can be used for subsequent measurements providing the chromatographic conditions do not change.

13.2 An integration system<sup>11</sup> or a personal computer with a chromatographic software package<sup>12</sup> may also be used to provide a direct readout of the concentration of the analyte of interest.

13.3 Report data in mg/L as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, or SO<sub>4</sub><sup>2-</sup>. Data lower than the MDL must be so indicated.

#### 14. Precision and Bias<sup>13</sup>

14.1 The collaborative test of this test method was performed using synthetic samples prepared at four different concentrations approximately representing the 10th, the 50th, the 75th, and the 95th percentile concentration values measured in atmospheric wet deposition throughout the United States. Nine laboratories participated with triplicate determinations at each level at each laboratory resulting in a total of 36 determinations for each of the three anions.

14.2 The precision and bias of this test method for chloride, nitrate, and sulfate were determined ~~according to~~ in accordance Practice D 2777 and are summarized in Table 1.

14.3 For more information on precision and bias for atmospheric samples, see Guide D 3670. For more information on reporting low-level data, see Practice D 4210.

14.4 These data may not apply to other water matrices and are for atmospheric wet deposition only.

#### 15. Keywords

15.1 atmospheric wet deposition samples; chloride; ion chromatography; nitrate; sulfate

~~Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards*~~

<sup>11</sup> ~~Spectra-Physics 4270 Integrator has been found satisfactory for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD; this use. Available from Spectra-Physics, Autolab Division, 3333 North First Street, San Jose, CA 95134.~~

<sup>12</sup> ~~Spectra-Physics 4270 Integrator~~

<sup>12</sup> ~~Nelson Analytical has been a software package found satisfactory for this use. Available from Spectra-Physics, Autolab Division, 3333 North First Street, San Jose; Nelson Analytical, 20370 Town Center Lane, Suite 130, Cupertino, CA 95014.~~

<sup>13</sup> ~~Nelson Analytical has a software package found satisfactory for this use. Available~~

<sup>13</sup> ~~Supporting data providing the results from Nelson Analytical, 20370 Town Center Lane, Suite 130, Cupertino, CA 95014; the interlaboratory test have been filed at ASTM Headquarters. Request RR: D22-1021.~~

APPENDIX

(Nonmandatory Information)

X1.

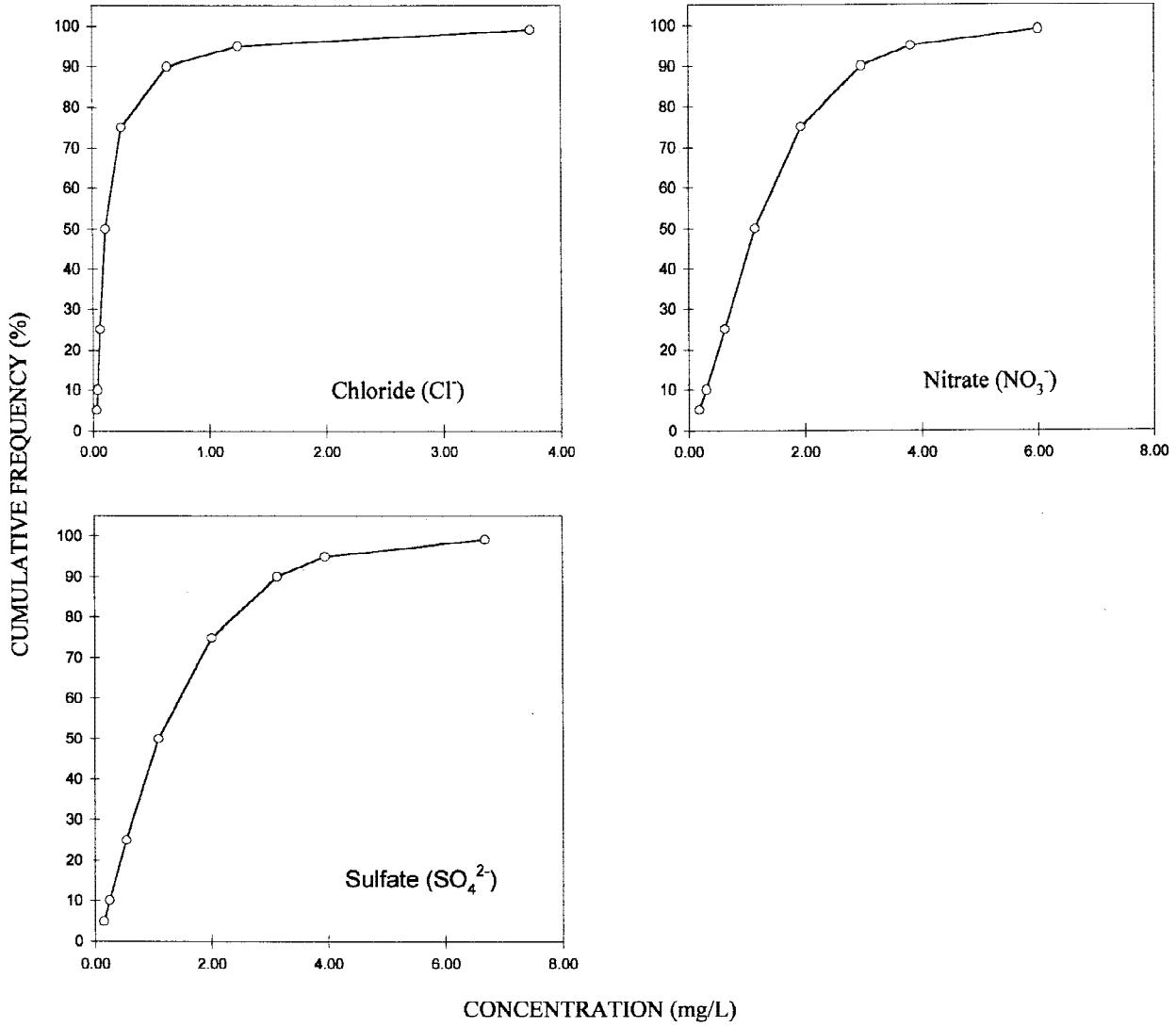
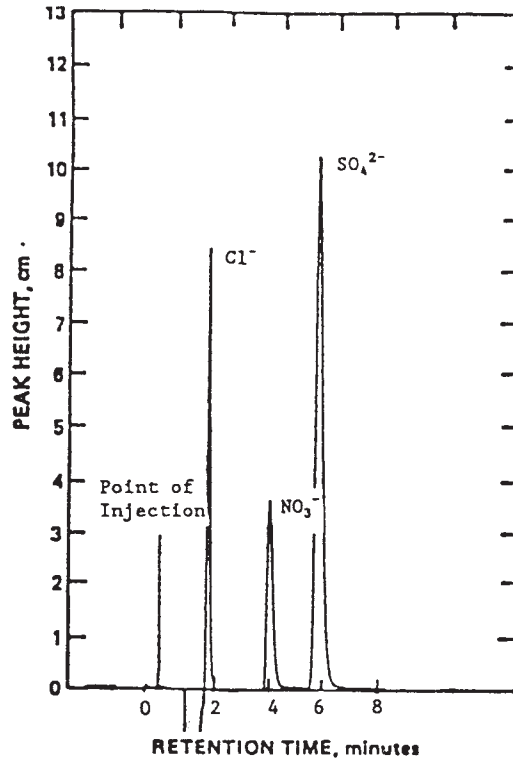


FIG. X1.1 Percentile Concentration Values Obtained from Wet Deposition Samples: Chloride, Nitrate, and Sulfate (2)





Separator Column: AS4A  
 Guard Column: AG4A  
 Eluent: 0.0020 M Na<sub>2</sub>CO<sub>3</sub>/0.00075 M NaHCO<sub>2</sub>  
 Eluent Flow Rate: 1.7 mL/min  
 Suppressor Column: AMMS  
 Regenerant: 0.0031 M H<sub>2</sub>SO<sub>4</sub>  
 Regenerant Flow Rate: 2.6 mL/min  
 Sample Loop Size: 200 μL

Concentrations:  
 Cl<sup>-</sup>: 0.387 mg/L  
 NO<sub>3</sub><sup>-</sup>: 0.619 mg/L  
 SO<sub>4</sub><sup>2-</sup>: 1.63 mg/L

FIG. X1.2 Chromatogram of a Wet Atmospheric Deposition Sample Containing Chloride, Nitrate, and Sulfate

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