



Designation: D5085 – 21

Standard Test Method for Determination of Chloride, Nitrate, and Sulfate in Atmospheric Wet Deposition by Suppressed Ion Chromatography¹

This standard is issued under the fixed designation D5085; 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 (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is applicable to the determination of chloride, nitrate, and sulfate in atmospheric wet deposition samples (rain, snow, sleet, and hail) by suppressed ion chromatography. For additional applications, see to Test Method [D4327](#).

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

	Method Detection Limit (mg/L) (1)	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 **(1)**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, it has been reported that this test method is reliable at lower levels than those that were tested. The MDLs listed above were determined following the guidance in 40 CFR Part 136 Appendix B. Other approaches to the determination of MDLs may yield different MDLs.

1.4 Method Detection Limits will vary depending on the type and length of column(s) used, the composition and strength of eluent used, the bore size of the instrumentation (that is, microbore or standard bore), eluent flow rate and other variables between instruments. The method detection limits listed above are those used in determining the Precision and Bias of this method as given in Table 1.

¹ This test method is under the jurisdiction of ASTM Committee [D22](#) on Air Quality and is the direct responsibility of Subcommittee [D22.03](#) on Ambient Atmospheres and Source Emissions.

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

1.5 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Specific precautionary statements are given in Section 9.

1.6 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:³

- [D883 Terminology Relating to Plastics](#)
- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [D1356 Terminology Relating to Sampling and Analysis of Atmospheres](#)
- [D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)
- [D3670 Guide for Determination of Precision and Bias of Methods of Committee D22](#)
- [D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data \(Withdrawn 2002\)⁴](#)
- [D4327 Test Method for Anions in Water by Suppressed Ion Chromatography](#)
- [D5012 Practice for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition](#)
- [E694 Specification for Laboratory Glass Volumetric Apparatus](#)

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ The last approved version of this historical standard is referenced on www.astm.org.

E1154 Specification for Piston or Plunger Operated Volumetric Apparatus

IEEE/ASTM SI-10 Standard for Use of the International System of Units (SI): The Modern Metric System

2.2 *Other Documents:*

40 CFR 136 Appendix B Definition and Procedure for the Determination of the Method Detection Limit⁵

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminologies **D883**, **D1129**, and **D1356** and Test Method **D4327** and Practice **IEEE/ASTM SI-10**.

4. Summary of Test Method

4.1 Ion chromatography combines conductimetric detection with the separation capabilities of ion exchange resins. A filtered aliquot of the sample, ranging in size from 5 to 250 µL, depending on instrumental system, is pumped through an ion exchange column where the anions of interest are separated. Each ion is identified by its retention time within the exchange column. The sample ions are selectively eluted off the separator column and into a suppressor, 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 conductivity detector. Data is collected using acquisition software specific to the system in use. Measurement of peak 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 **D4327**.

5. Significance and Use

5.1 This test method is 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 (2).

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, diluting the sample with reagent water, or decreasing sample injection volume may correct this problem.

6.2 Interferences may be caused by ions with retention times that are similar to the anion of interest. Before analyzing precipitation samples, determine the retention times of these possible interfering ions. Interference is common in some types of wet deposition samples. If interference is anticipated,

decreasing the eluent concentration or flow rate, or decreasing sample size will result in improved peak resolution.

6.3 Water in the sample will cause a negative peak (“water dip”) in the chromatogram when it elutes because its conductance is less than that of the suppressed eluent. Depending on the column used, 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 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. 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.

6.5 Contaminated valves and sample lines may 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. The use of degassed water for eluents and regenerants minimizes the introduction of air (See 8.2).

6.7 For more information on interferences refer to Test Method **D4327**.

7. Apparatus

7.1 *Ion Chromatograph (IC)*—Select an instrument equipped with an injection valve, a sample loop, guard column, separator column, suppressor, pump(s), conductivity detector, and suitable data acquisition software. An autosampler is recommended. Compressed gas, typically high purity helium or nitrogen, may be required for some IC systems.

7.1.1 *Tubing*—Tubing that comes in contact with samples and standards must be manufactured from inert material such as polyethylethylketone (PEEK) or tetrafluoroethylene (TFE).

7.1.2 *Anion Guard Column*—Located upstream from the separator column. The guard column is used to protect the separator column from being fouled by particulates or organic constituents.

7.1.3 *Anion Separator Column*—This column is generally packed with a pellicular low-capacity anion exchange resin.

7.1.4 *Anion Suppressor Column*—Place between the separator column and the detector.

7.1.5 *Compressed Helium*—High purity grade.

7.1.6 *Detector*—A flow-through, temperature-compensated, electrical conductivity cell.

7.1.7 *Pump*—Capable of delivering a constant flow rate. Flow rates and back pressures are dependent on the specific manufacturer’s IC system. All interior pump surfaces that will

⁵ Available from U.S. Government Publishing Office (GPO), 732 N. Capitol St., NW, Washington, DC 20401, <http://www.gpo.gov>.

be in contact with samples and standards must be manufactured from inert, non-metallic materials.

7.1.8 *Data Acquisition System*—A computer operating system-specific acquisition software to collect and process data.

7.1.9 *Sample Loop*—Select a sample loop with a capacity of 5 to 250 μL .

7.1.10 *Autosampler*—An autosampling system capable of precise delivery.

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. Reservoirs may be blanketed with helium or nitrogen per manufacturer's guidelines.

7.3 *Labware*—Glassware or plasticware, including volumetric pipettes and flasks, must be dedicated only for use with atmospheric wet deposition samples. Volumetric glassware or plasticware must meet the requirement for Class A items given in Specification E694.

NOTE 2—More sensitive instruments may have issues with contamination from borosilicate glassware. High density polyethylene (HDPE), low density polyethylene (LDPE), or polystyrene is a suitable alternative to glass volumetrics.

7.4 *Pipettes*—Fully adjustable, air-displacement pipets, for small-volume dispensing of aqueous fluids of moderate viscosity and density. Pipets must comply with Specification E1154 for piston operated volumetric devices.

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.⁶

8.2 *Purity of Water*—Use water conforming to Specification D1193, Type II. Point of use 0.2 μm 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 performed (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*—Eluent solutions are specific to the column being used. Refer to column manufacturer's instructions for eluent preparation. Automated eluent generators may be used.

8.4 *Regenerant*—Regenerant solutions are specific to the suppressor being used. Refer to manufacturer's instructions for regenerant preparation and use. Self-regenerating suppressors do not require a separate regenerant solution.

8.5 *Stock Standard Solutions*—NIST-traceable commercially-prepared 1000 mg/L solutions of chloride, nitrate and sulfate.

8.6 *Sample Containers*—Use analyte-free glass, high density polyethylene (HDPE) or low density polyethylene (LDPE) containers. Containers include both autosampler vials and any bottles that may be used in the transportation of the sample.

9. Hazards

9.1 The calibration standards, sample types, and most reagents used in this test method pose limited hazard to the analyst when following typical laboratory safety practices (see 9.2).

9.2 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this test method (3).

10. Sampling, Sample Preservation 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 (2).

10.2 For additional information on sample collection and preservation of atmospheric wet deposition refer to Guide D5012.

10.3 Data are reported in mg/L as CL^- , NO_3^- , or SO_4^{2-} .

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 anions 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, the columns used, the flow rate of eluent, and the eluent composition. Prepare separate standard solutions of each anion for at least two concentrations as described in 11.2.2. Analyze each standard of interest as defined in 12.8. Note the time in hundredths of minutes for each peak to appear on the chromatogram.

11.1.2 A multi-anion mixed standard must be used to determine the retention time of each standard ion in solution with the others. Prepare as described in 11.2.2. The retention times are determined by injecting the mixed standard and noting the time required for the center of each peak to appear on the chromatogram.

11.2 Calibration Solutions:

11.2.1 A minimum of five uniformly distributed calibration solutions and one zero standard (blank) are needed to generate a suitable calibration curve. The lowest calibration solution concentration must contain the analyte(s) of interest at a concentration approaching or equal to the detection limit. The highest calibration solution concentration is per the column manufacturer's guidelines. Samples above the highest calibration standard must be diluted with reagent water for analysis.

11.2.2 Calibration solutions are prepared by diluting the stock standard solutions. Use dedicated volumetric labware (7.3) and calibrated volumetric pipettes with disposable tips (7.4).

⁶ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

11.2.2.1 Add the amount of stock solution, calculated from Eq 1, to a volumetric flask partially filled with water. Dilute to volume and mix well.

$$\text{mL stock solution} = \quad (1)$$

$$\frac{(\text{desired concentration in mg/L}) \times (\text{final dilution volume in mL})}{(\text{concentration stock solution in mg/L})}$$

11.2.3 Calibration standards are stable for one week when stored at room temperature in high density polyethylene or polypropylene containers. If there is evidence of a change in the concentration, prepare the standards more frequently. Refrigeration at or below 4 °C can prolong the shelf life of the standards.

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

11.2.5 For additional information on calibration refer to Test Method D4327.

12. Procedure

12.1 Laboratory temperature must be maintained within ± 3 °C while conducting analyses or a temperature controlled conductivity cell should be used.

12.2 Use the eluent concentration recommended by the column manufacturer. If peak resolution is not adequate, it may be necessary to decrease or increase the ionic strength of the eluent.

12.3 Adjust the instrument flow rate for optimal peak separation. Decreasing the flow rate may provide improved peak separation but lengthens retention times. Increasing the flow rate decreases peak separation and shortens retention times. Refer to the manufacturer's recommendations for guidelines on optimizing flow rate.

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

12.5 Inject the standards and record the peak area responses. Compare the peak retention times to those obtained with the mixed standard (11.1.2). If the peak retention times are not the same, reanalyze the mixed standard and the calibration 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 (2).

12.7 *Frequency of Calibration*—The system should be calibrated at a frequency recommended by the manufacturer, or when repeated failures of the QCS occur.

12.8 Sample Injection:

12.8.1 Use the same size injection loop for both standards and samples.

12.8.2 Inject the sample 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 similar, re-analyze the locator mix, the standards, and the samples.

12.8.3 Record the resulting peak areas.

12.9 If the response or concentration for a given peak exceeds the calibration range, dilute the sample with reagent water and re-analyze.

13. Calculation

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

NOTE 3—Instrument response may or may not be linear for any given analyte and for all chromatographic conditions. One means of determining the correct least squares equation to use for each analyte is to 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. Most data acquisition software programs have the ability to perform these steps within their calibration functions.

13.2 Report data in mg/L as Cl^- , NO_3^- , or SO_4^{2-} . Data lower than the detection limit must be so indicated.

14. Precision and Bias⁷

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 in accordance Practice D2777 and are summarized in Table 1.

14.3 For more information on precision and bias for atmospheric samples, see Guide D3670. For more information on reporting low-level data, see Practice D4210.

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

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D22-1021. Contact ASTM Customer Service at service@astm.org.

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 ^B	
				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

^A Number of samples included in final statistical analysis after removal of outlier data.

^B 95 % confidence level.

^C Between laboratory precision, reproducibility.

^D Within laboratory precision (pooled single operator precision), repeatability.

APPENDIX

(Nonmandatory Information)

X1.

X1.1 See Fig. X1.1 and Fig. X1.2.

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