Designation: D5085 – 21

Standard Test Method for Determination of Chloride, Nitrate, and Sulfate in Atmospheric Wet Deposition by Suppressed Ion Chromatography[1]

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 L (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.

1.5 *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

[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.

[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 Limit[5]

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.