Designation: D 5085 – 02

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

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 (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 (rain, snow, sleet, and hail) by chemically suppressed ion chromatography (**1**)[2]. 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:* [3]

D 883 Terminology Relating to Plastics
D 1129 Terminology Relating to Water
D 1193 Specification for Reagent Water
D 1356 Terminology Relating to Sampling and Analysis of Atmospheres
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water
D 3670 Guide for Determination of Precision and Bias of Methods of Committee D-22
D 4210 Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data
D 4327 Test Method for Anions in Water by Chemically Suppressed Ion Chromatography
D 5012 Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition
E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)
E 694 Specification for Laboratory Glass Volumetric Apparatus

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.

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 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 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.

[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.

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.

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. **(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 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 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.[4]

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 quartenary ammonium active sites.[5]

7.1.4 *Anion Suppressor Column*—Place following the separator column. This may be in the form of an anion micromembrane suppressor or an anion self-regenerating suppressor. The first type of suppressor utilizes a semipermeable membrane containing anion exchange sites to suppress eluent conductance.[6] The second type of 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 needed.

7.1.6 *Detector*—Select a flow-through, temperature-compensated, electrical conductivity 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.

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 1379 to 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 µL.

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 ±°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.[7]

8.2 *Purity of Water*—Use water conforming to Specification D 1193, 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

[4] 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.

[5] 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.

[6] 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.

[7] *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.