Designation: D 6328 – 98

Standard Guide for
Quality Assurance Protocols for Chemical Analysis of Atmospheric Wet Deposition[1]

This standard is issued under the fixed designation D 6328; 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 guide describes quality assurance (QA) protocols for the determination of the anions and cations in Atmospheric Wet Deposition (AWD) shown in Table 1.

1.2 Included in this guide are minimum recommended requirements for the preparation of calibration standards and suggested procedures for validating laboratory measurement results.

1.3 This guide describes minimum requirements for the frequency of analysis of quality assurance samples and recommends procedures for the evaluation of quality assurance data.

1.4 The guide's recommendations are based upon expected anion and cation concentrations in AWD **(1)**[2] and Appendix X2.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

TABLE 1 Common Techniques of Analysis for Atmospheric Wet Deposition Samples

Automated Colorimetry	Ion Chromatography
NH_4^+	Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+
Flame Atomic Absorption Spectrophotometry	Electrometric
Na^+, K^+, Ca^{2+}, Mg^{2+}	pH, specific conductance

2. Referenced Documents

2.1 *ASTM Standards:*

D 596 Practice of Reporting Results of Analysis of Water[3]

D 1193 Specification for Reagent Water[3]

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[4]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[3]

D 5012 Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition[4]

D 5015 Test Method for pH of Atmospheric Wet Deposition Samples by Electrometric Determination[4]

D 5085 Test Method for Determination of Chloride, Nitrate, and Sulfate in Atmospheric Wet Deposition by Chemically Suppressed Ion Chromatography[4]

D 5086 Test Method for the Determination of Calcium, Magnesium, Potassium, and Sodium in Atmospheric Wet Deposition by Flame Atomic Absorption Spectrophotometry[4]

D 5111 Guide for Choosing Locations and Sampling Methods to Monitor Atmospheric Deposition at Non-Urban Locations[4]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[5]

E 178 Practice for Dealing with Outlying Observations[5]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[6]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide refer to Terminology D 1356 or the Compilation of ASTM Standard Definitions.[7]

4. Summary of Guide

4.1 This guide describes QA procedures to be used in conjunction with standard test methods.

4.2 This guide does not include all components of a complete QA program for AWD measurement systems but provides minimum protocols to assist in the development of such a program. The procedures for the preparation of materials used for the collection and preservation of AWD are included in Guide D 5012. The procedures for choosing locations and sampling atmospheric deposition are included in Guide D 5111.

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[1] This guide is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.06 on Atmospheric Deposition.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this guide.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 11.03.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

[6] *Annual Book of ASTM Standards*, Vol 15.05.

[7] Compilation of ASTM Standard Definitions, 7th ed ASTM, 1990.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.[8] Other reagents may be used provided it can be demonstrated that they are of sufficiently high purity to permit their use without decreasing the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D 1193, Type II.

5.3 *Standard Solutions*—Unless otherwise indicated, reference to standard solutions shall be understood to mean solutions conforming to Practice E 200. Standard Solutions are prepared from primary standards or ACS reagent grade salts or may be purchased as secondary standards from commercial laboratory suppliers.

6. Storage of Standard Solutions

6.1 TFE-fluorocarbon, polyethylene, and polypropylene containers are recommended for the storage of standard solutions. Glass containers are not suitable for storage of most standard solutions needed to analyze AWD.

7. Verification of Standard Solutions

7.1 Use two or more of the following procedures to ensure that the standard solutions are correctly formulated.

7.1.1 Confirmation of standard solution analyte concentration by an independent laboratory determination;

7.1.2 Confirmation of standard solution analyte concentration by an independent analytical procedure within the laboratory.

7.1.3 Comparison of the standard solution analyte concentrations of the same standard solution prepared by different analysts from the same laboratory or comparison of the analyte concentration of the new standard solution with the analyte concentration of a prior standard solution; or

7.1.4 Comparison of the analyte concentration from the standard solution with the concentration of a standard reference material (SRM) or certified reference material (CRM) **(2)**.

7.2 The results of the confirmation analyses must be within the confidence limits of each measurement. New standard solution(s) must be prepared if the results are not in statistical agreement.

8. Reference Materials (RM)

8.1 The RM should be a SRM or a commercially available CRM.

8.2 Immediately following calibration (Test Methods D 5015, D 5085, D 5086), at least one RM is to be analyzed to ensure that the system is functioning properly and that standards were correctly prepared and that no degradation or contamination of the standards has occurred. The frequency of RM analysis is specified in the test method but must be at least one per analytical run.

8.3 *Evaluation of RM Data*—Compare the measured RM concentration to the certified value immediately after measurement. The analyst must ensure that the concentration value falls within the limits previously established from the repeated analysis of solutions at that concentration level. The measurement of samples must be suspended whenever the RM measurement system is out of control.

NOTE 1—If the confidence interval of the measurement intersects the confidence or tolerance interval of the RM, there is agreement. If not, then a discrepancy exists that needs to be investigated **(2)**.

8.3.1 When the concentration of the RM differs from the certified value by greater than the established acceptance limits, reanalyze the RM immediately to determine if the current measurement is reproducible. If this second measurement also differs from the acceptance limits about the certified value, cease analyzing samples.

8.3.2 Whenever RM values indicate that the system is out of control, determine the reason and correct the condition. Reanalyze all samples measured after the last RM value that was in control.

9. Blanks

9.1 *Preparation and Frequency of Analysis*:

9.1.1 Prepare reagent blanks according to the procedures recommended in the appropriate test method. Use water conforming to Specification D 1193, Type I.

9.1.2 Measure reagent blanks each day determinations are performed or whenever new reagents are used to check for contamination in sample preparation or analysis.

9.1.3 Use field blanks for analytes whose expected concentrations are less than 1 mg/L. Field blanks are Type I water samples subjected to all aspects of sample collection, field processing, preservation, transportation, and laboratory handling as an environmental sample.

9.1.4 Other types of blanks may be necessary to determine the cleanliness of collection vessels, sample storage bottles, and membrane filters. Refer to Guide D 5012 for specific procedures.

9.2 *Evaluation of Blank Data*:

9.2.1 Reagent blank contamination can be highly variable depending on the source of contamination. When variable concentrations of analytes are found in reagent blanks, the source(s) of contamination should be determined and minimized.

9.2.2 Subtract the concentration of the analyte in the reagent blank from the concentration of the analyte in the sample only when the analyte concentration in the blank is low, for example <1 %, in relation to the samples being measured and its value is constant. When the analyte concentration in the blank is highly variable, reanalyze samples suspected of contamination.

9.2.3 Field blank contamination is often more variable than reagent blanks. The field blank concentrations should be used to determine if the AWD sample analyte concentrations are real

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[8] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

or artifacts. Field blank concentrations of analytes are not to be routinely subtracted from AWD sample analyte concentrations.

10. Method Detection Limit Definition

10.1 To improve the comparability of AWD data, it is strongly recommended that the following definition of method detection limit be adopted and implemented.

10.1.1 *Method Detection Limit (MDL)*—The minimum concentration of an analyte that can be reported with 99 % confidence to have a value that is above zero. The MDL is operationally defined as:

$$MDL = St_{(n-1,\, 1-a\, =\, 0.99)} \tag{1}$$

where:

S = the standard deviation of a minimum of seven measurements of a solution containing the analyte at a concentration near the lowest calibration standard recommended in the test method, and

$t_{(n\text{-}1,\, 1-a\, =\, 0.99)}$ = the student's t value for a one-tailed test at the 99 % confidence level and n-1 degrees of freedom.

Obtain the data used to calculate the standard deviation (S) during seven separate analyses by measuring a freshly prepared standard solution in a matrix that matches the calibration solutions; that is, a new solution is prepared and measured on each of seven different days. Use a solution concentration not greater than five times the estimated MDL **(3)**.

10.2 Every laboratory must determine its own MDL values for each analyte.

10.3 Flag data reported for samples that contain analyte concentrations lower than the MDL to indicate that concentrations lower than the detection limit have been measured.

10.4 MDL values must be recalculated at least yearly or whenever instrumental operating conditions are modified.

11. Precision and Bias

NOTE 2—Blind samples are samples submitted for analysis whose composition is known to the submitter but unknown to the analyst. A double blind sample is one of known composition that is submitted to the analyst in such a manner that neither its composition nor its identification are known to the analyst.

11.1 Blind samples are a recommended subset of the normal sample flow to determine the precision and bias of the analytical methods. Prepare control charts or a statistical tabulation of the blind sample data as soon as analysis results are available. The submission of blind samples must be performed by someone other than the analyst, typically the laboratory manager, director, or QA officer.

11.1.1 Samples used to assess intra-day repeatability (precision) may include duplicate, split, blind and double blind samples, and calibration check standards. Samples used to assess inter-day repeatability may include delayed reanalysis, split, blind and double blind samples, and calibration check standards. The precision characteristics of the intra-day and inter-day samples are expected to differ. Data from the two sample sets, therefore, should not be presented on a single control chart or in a combined statistical summary.

11.1.2 Samples used to determine bias include SRM, CRM, blind and double blind, and laboratory spike samples.

NOTE 3—Use percent recoveries (calculated from spike samples) cautiously when assessing bias **(4)**. They should be used only when matrix interferences are present or suspected in the sample or when a RM is not available for either the sample matrix being analyzed or the concentration level of interest.

11.2 Perform analytical precision and bias determinations on a scheduled basis following the procedure listed in the test method. Evaluate each precision and bias determination by plotting the data in a control-chart format.[9]

11.2.1 Compare the current precision and bias results with the previous two sets of results. If a downward or upward concentration trend appears to exist, evaluation of RM data should be considered to look for assignable causes.

12. External Quality Assessment

12.1 *Laboratory Intercomparisons*:

12.1.1 Chemistry laboratories involved in the analysis of AWD samples are encouraged to participate in intercomparisons conducted by external agencies at least twice per year. Refer to Appendix X1 for a list of these agencies and their addresses.

12.1.2 Use data from these intercomparisons to assess analytical measurement bias, reproducibility, and laboratory comparability.

13. Criteria for Reanalysis of Samples

13.1 Use data obtained from the evaluation of control charts and the calculation of ion and conductivity percent differences when selecting samples for reanalysis. When data indicate the analyses are out of control, samples analyzed during the out of control period must be reanalyzed.

13.2 *Evaluation of Control Charts*:

13.2.1 Examine control charts each day determinations are performed for out of control or bias conditions by the person responsible for QA activities and the analyst. For additional information on the application of control charts refer to Guide D 3856.

13.2.1.1 There is less than a 1 % chance for two successive measurements to exceed the upper or lower two standard deviation warning limits due to chance alone. Whenever two successive measurements exceed the warning limits, the measurement system is out of control.

13.2.1.2 The measurement system is out of control whenever quality assessment data exceed the upper or lower three standard deviation control limits.

13.2.1.3 Data points should be randomly distributed about the central line. There is a 99 % chance that bias in the data exists if seven successive data points fall on one side of the central line. If the magnitude of the bias exceeds specified data quality objectives, corrective action is necessary.

13.2.2 Suspend sample analyses whenever quality assessment data indicate that the system is out of control or that an intolerable bias condition exists. The reason(s) causing the out

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[9] *Manual on Presentation of Data and Control Chart Analysis*, ASTM Manual Series: MNLT, Special Technical Publication, *ASTM STP 15D*, 1989.

of control or bias condition(s) must be determined, corrected, and documented before analyses are resumed. Reanalyze all samples analyzed after the last quality assessment value that was in control.

13.3 *Ion Percent Difference*:

13.3.1 Use ion-percent difference calculations to detect analytical errors or to identify analytes that have not been measured. If all the major ions in AWD samples have been measured, the equivalent concentration of the anions will equal the equivalent concentration of the cations.

13.3.2 The ion-percent difference calculations for each sample is calculated using the equation specified in Practice D 596.

$$\text{Ion \% Difference} = \frac{\Sigma\text{Cations}-\Sigma\text{Anions}}{\Sigma\text{Cations}+\Sigma\text{Anions}} \times 100 \qquad (2)$$

13.3.2.1 Measured values, in microequivalents L^{-1} (µequiv L^{-1}), for the following ions should be included in Eq 2: Cl^-, NO_3^-, SO_4^{2-}, H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+. Appendix X3 contains conversion factors for the calculation of µequiv L^{-1} for these ions. The concentration of HCO_3^- should also be included in Eq 2 and is calculated using Eq 3 **(5)**:

$$[HCO_3^-] = \frac{K_H K_1 P_{CO2}}{[H^+]} \times 10^{12} \qquad (3)$$

where:

the concentrations of HCO_3^- and H^+ are in µequiv L^{-1}, K_H is derived from Henry's Law, K_1 is the first dissociation constant for CO_2 and $P_{CO2} = 335 \times 10^{-6}$ *atm*. Table 2 lists values for the K_H and K_1 equilibrium constants at various solution temperatures.

NOTE 4—The concentration of H^+ is determined from the pH measurement for the sample. The measurement of pH in AWD samples is covered in Test Method D 5015.

13.3.2.2 Determine allowable ion-percent differences on the total microequivalent sum of the cations and anions. An ion-percent difference data base should be developed for individual sites or networks, and specific sample reanalysis criteria should be developed for individual sites or networks. The recommended allowable ion-percent differences are:

(a) Sixty percent for ion sums less than 50 microequivalents per litre,

(b) Thirty percent for ion sums from 50 to 100 microequivalents per liter, and

(c) Fifteen percent for ion sums greater than 100 microequivalents per liter **(6)**.

13.3.2.3 In those cases where site or network specific criteria are unavailable, examine samples that have ion-percent differences greater than ± 15 % for mathematical, transcription, and analytical errors. If no errors are found, reanalyze the samples. If a large ion imbalance remains after sample reanalysis, it is probable that the sample contains ions that have not been measured and thus have not been included in the equation.

TABLE 2 Equilibrium Constants for the Calculation of Bicarbonate Concentrations (5)

	5°C	20°C	25°
K_H mol L^{-1} atm^{-2}	0.064	0.039	0.034
K_1 mol L^{-1}	3.0×10^{-7}	4.2×10^{-7}	4.5×10^{-7}

13.4 *Comparison of Calculated and Measured Conductivity*:

13.4.1 If Ca^{2+}, Cl^-, K^+, Mg^{2+}, Na^+, NO_3^-, pH, and SO_4^{2-} have been determined for a sample, the measured conductivity will nearly equal the calculated conductivity.

13.4.2 The conductivity-percent difference for each sample is calculated using Eq 4 **(6)**.

$$\text{conductivity \% difference} = \frac{\text{calculated conductivity} - \text{measured conductivity}}{\text{measured conductivity}} \times 100 \qquad (4)$$

13.4.2.1 The calculated conductivity (specific conductance) is calculated by summing the equivalent conductivity of each ion at infinite dilution **(6)**. Specific conductance values for precipitation samples are calculated using Eq 5.

$$\begin{aligned} k = [&10^{-pH}(349.65) + (SO_4)^2(80.0) + (NO_3)(71.42) + (Cl)(76.31) \\ &+ (NH_4)^+(73.5) + (Na^+)(50.08) + (K^+)(73.48) + (Ca^{2+})(59.47) \\ &+ (Mg^{2+})(53.0) + (HCO_3^-)(44.5)] \times .001 \end{aligned} \qquad (5)$$

where:

k = the specific conductance in microSiemens cm^{-1} (µS cm^{-1}), the ions in parentheses represent the measured ion concentrations in equiv L^{-1}, and the numbers in parentheses are equivalent ionic conductivity factors at 25°C in 10^{-4} m^2 S equiv^{-1} units.

13.4.3 Develop conductivity-percent difference data bases for individual sites and network specific reanalysis criteria. Until the data base is developed, the recommended allowable conductivity-percent differences are presented in Table 3.

13.4.3.1 Examine samples for mathematical, transcription, and analytical errors if site or network specific criteria or if the reanalysis criteria in Table 3 are violated. If no errors are found, reanalyze the samples.

13.4.3.2 If neither a transcription, mathematical, or analytical error is responsible for a large negative conductivity difference value, it is probable that the sample contains ions that have not been measured and thus have not been included in the equation. A large positive conductivity difference value indicates that at least one of the concentration values in the calculation is incorrect.

14. Keywords

14.1 atmospheric deposition; atomic absorption spectrophotometry; ion chromatography; quality assurance; quality control; wet deposition

TABLE 3 Reanalysis Criteria for Atmospheric Wet Deposition Samples Using Conductivity Percent-Difference Data (1)

Conductivity Percent Difference	Reanalysis Required
less than (<) –40	Yes
greater than (>) +10	Yes

$$\text{conductivity \% difference} = \frac{\text{calculated conductivity} - \text{measured conductivity}}{\text{measured conductivity}} \times 100$$

APPENDIXES

(Nonmandatory Information)

X1. AGENCIES THAT PROVIDE REFERENCE SAMPLES FOR ATMOSPHERIC WET DEPOSITION STUDIES OR CONDUCT ATMOSPHERIC WET DEPOSITION LABORATORY INTERCOMPARISONS

X1.1 The agencies listed in X1.1.1-X1.1.4 provide reference samples for AWD studies or conduct AWD laboratory intercomparisons.

X1.1.1 National Institute of Standards and Technology
Standard Reference Materials Program
Room 202, Building 204
Gaithersburg, Maryland 20899-0001

X1.1.2 Environmental Protection Agency- Research Triangle Park
NERL/QATSD (MD-77B)
Research Triangle Park, NC 27711

X1.1.3 National Water Research Institute
867 Lakeshore Road
P.O. Box 5050
Burlington, Ontario L7R4A6
Canada

X1.1.4 High Purity Standards
P.O. Box 30188
Charleston, SC 29417

X2. PERCENTILE CONCENTRATION VALUES OF CHEMICAL AND PHYSICAL PARAMETERS MEASURED IN WEEKLY ATMOSPHERIC WET DEPOSITION SAMPLES

TABLE X2.1 Percentile Concentration Values of Chemical and Physical Parameters Measured in Weekly Atmospheric Wet Deposition Samples[A]

Parameter	Percentile Concentration Value (mg/L)				
	5th	25th	50th	75th	95th
Ca^{2+}	0.016	0.046	0.102	0.221	0.686
Mg^{2+}	0.004	0.011	0.022	0.042	0.128
K^+	<0.003	0.009	0.017	0.035	0.107
Na^+	0.019	0.040	0.075	0.159	0.639
NH_4^+	<0.02	0.09	0.20	0.38	0.87
NO_3^-	0.21	0.61	1.10	1.83	3.73
Cl^-	0.04	0.07	0.12	0.24	0.98
SO_4^{2-}	0.20	0.61	1.17	2.17	4.52
PO_4^{3-}	<0.02	<0.02	<0.02	<0.02	<0.02
pH (units)	4.08	4.44	4.88	5.52	6.46
Cond. (µS/cm)	3.2	7.0	12.6	22.7	45.5

[A] National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) 1993 (**1**) wet side samples.

X2.1 Table X2.1 gives the percentile concentration values of chemical and physical parameters measured in weekly AWD samples.

X3. CONVERSION FACTORS

TABLE X3.1 Conversion Factors

Concentration Unit Given	Operation Performed for Conversion	Desired Concentration Unit
	Multiply By	
mg $\mathrm{L^{-1}}$	A	µequiv $\mathrm{L^{-1}}$
µmol $\mathrm{L^{-1}}$	B	mg $\mathrm{L^{-1}}$
µmol $\mathrm{L^{-1}}$	C	µequiv $\mathrm{L^{-1}}$
	Divide By	
µequiv $\mathrm{L^{-1}}$	A	mg $\mathrm{L^{-1}}$
mg L-1	B	µmol $\mathrm{L^{-1}}$
µequiv $\mathrm{L^{-1}}$	C	µmol $\mathrm{L^{-1}}$
	Table of Constants	

	A	B	C
Ca^{2+}	49.9	0.04008	2
Mg^{2+}	82.288	0.024305	2
Na^{+}	43.4975	0.02299	1
K^{+}	25.574	0.039098	1
NH_4^{+}	55.436	0.018039	1
NO_3^{-}	16.128	0.062007	1
SO_4^{2-}	20.821	0.09606	2
Cl^{-}	28.206	0.035453	1

X3.1 Table X3.1 gives the conversion factors for the percentile concentrations of chemical and physical parameters measured in weekly AWD samples (see Table X2.1).

REFERENCES

(**1**) James, Kenni O.W., 1993 Quality Assurance Report NADP/NTN Deposition Monitoring, National Atmospheric Deposition Program, Illinois State Water Survey, Champaign, IL, 61820-7495, 1995, p. 101.

(**2**) Taylor, John K., Quality Assurance of Chemical Measurements, Lewis Publishers, Inc., Chelsea, MI, 48118, 1987, p. 328.

(**3**) Rules and Regulations, 1984, Federal Register, Vol 49, No. 209, p. 198.

(**4**) Kirchner, C.J., Quality Control in Water Analysis, *Environ. Sci. & Technol*., 17, 1983, p. 174A-181A.

(**5**) Semonin, R.G., et al., Study of Air Pollution Scavenging, Pub. No. COO-1199-58, Illinois State Water Survey, 1977, p. 63.

(**6**) Peden, M.E., et al., Standard Methods for the Collection and Analysis of Wet Deposition, Vol. 1, Illinois State Water Survey, EPA Contract No. CR 810780-01, 1986, p. 14.