



# Standard Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition<sup>1</sup>

This standard is issued under the fixed designation D 5012; 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>ε1</sup> NOTE—Section 9 was editorially added in April 1994.

## 1. Scope

1.1 This guide presents recommendations for the cleaning of plastic or glass materials used for collection of atmospheric wet deposition (AWD). This guide also presents recommendations for the preservation of samples collected for chemical analysis.

1.2 The materials used to collect AWD for the analysis of its inorganic constituents and trace elements should be plastic. High density polyethylene (HDPE) is most widely used and is acceptable for all samples including samples for the determination of the anions of acetic, citric, and formic acids. Borosilicate glass is a collection alternative for the determination of the anions from acetic, citric, and formic acid; it is recommended for samples for the determination of other organic compounds.

1.3 *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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

- D 883 Terminology Relating to Plastics<sup>2</sup>
- D 1125 Test Methods for Electrical Conductivity and Resistivity of Water<sup>3</sup>
- D 1129 Terminology Relating to Water<sup>3</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- D 1356 Terminology Relating to Sampling and Analysis of Atmospheres<sup>4</sup>

<sup>1</sup> This guide 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 Nov. 24, 1989. Published March 1990.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 08.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.03.

- D 1695 Terminology of Cellulose and Cellulose Derivatives<sup>5</sup>
- D 2914 Test Methods for Sulfur Dioxide Content of the Atmosphere (West-Gaeke Method)<sup>4</sup>
- D 4453 Practice for Handling of Ultra-Pure Water Samples<sup>3</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definitions of terms used in this guide, refer to Terminology D 1129.

3.1.2 For definition of **plastic** refer to Terminology D 1695 and Terminology D 883.

3.1.3 For definition of AWD (**precipitation, meteorological**) refer to Terminology D 1356.

## 4. Significance and Use

4.1 Some chemical constituents of AWD are not stable and must be preserved before chemical analysis. Without sample preservation, it is possible that analytes can be lost through decomposition or sorption to the storage bottles.

4.2 Contamination of AWD samples can occur during both sample preservation and sample storage. Proper selection and cleaning of sampling containers are required to reduce the possibility of contamination of AWD samples.

4.3 The natural sponge and talc-free plastic gloves used in the following procedures should be recognized as potential sources of contamination. Individual experience should be used to select products that minimize contamination.

## 5. Apparatus

5.1 Instruments shall be selected in accordance with an applicable test method given in Test Methods D 1125.

5.2 The conductivity cell shall be pipet or dip type with a cell constant ( $K$ ) of 0.1 .

## 6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade acids and other

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 06.03.

**TABLE 1 Preservation of AWD Samples Collected for Inorganic Cation and Anion Determinations**

Preservation Technique	Species Determined	Remarks	Reference
No preservation	All inorganic cations and anions	Rapid analysis is required after collection because ion concentrations may change in samples. Ammonium, nitrate, and ortho-phosphate concentrations may be reduced in samples that are biologically active. Cation and trace metal concentrations may be reduced by sorption onto container surfaces.	<b>(10-14)</b>
Refrigerate 4°C	All inorganic cations and anions	Chilling may reduce the loss of ammonium, nitrate, and ortho-phosphate in samples that are biologically active. Samples must be allowed to come to ambient temperature (23–27°C) before performing pH and specific conductance determinations. Specific conductance and pH determinations should be performed on-site as soon as possible after sample collection.	<b>(15-17)</b>
HNO <sub>3</sub> pH ≤ 2	Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup>	Samples must first be filtered, or acid addition may dissolve particles in the AWD samples (see 7.4.1). Acid addition will interfere with anion determination, so a separate aliquot will be needed for other ion determinations.	<b>(11,12)</b>
HgCl <sub>2</sub> or tetrachloromercurate (Na <sub>2</sub> HgCl <sub>4</sub> ) <sup>A</sup>	Ammonium, nitrate, nitrite, phosphate	Mercury (II) is a known biocide and will preserve samples for 9 to 16 days and possibly longer periods of time. Dissolved mercury may interfere with other ion determinations, and this will require an additional aliquot. Final dissolved mercury (II) concentration in the AWD sample must be at least 30 mg/L.	<b>(1,17)</b>
Filtration	All inorganic cations and anions	pH and specific conductance determinations may be affected by filtration. Care must be taken to minimize the possibility of sample contamination during filtration.	<b>(18)</b>

<sup>A</sup> Several of the suggested preservatives, such as tetrachloromercurate and mercuric chloride, are environmental and human health hazards and the use and disposal of these preservatives should be carefully controlled (Test Method D 2914, Section A4).

chemicals shall be used to reduce the risk of contaminating the AWD samples. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>6</sup>

6.2 Nitric acid, ultra pure.

6.3 Nitric acid (1+9)—Dilute 1 volume concentrated nitric acid with 9 volumes of water.

6.4 Chloroform, high performance liquid chromatography reagent.

6.5 Sodium tetrachloromercurate (II), 40 g/L Hg—Dissolve 54.4 g of mercuric chloride (HgCl<sub>2</sub>) and 23.4 g sodium chloride (NaCl) in distilled water and adjust volume to 1000 mL.

6.6 Mercuric chloride.

6.7 Sodium chloride.

6.8 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D 1193. AWD samples collected for organic analysis may require Type II (distilled) reagent water.

## 7. Sample Preservation

7.1 Interaction between the sample and the atmosphere must be minimized. The sample container should be sealed as soon as possible after collection or sub-sampling. AWD samples can be easily contaminated because of the low concentration levels of their analytes. Trace metals, and possibly other ions in AWD samples, can be lost through sorption with the bottle or container in which they are stored. AWD samples may contain biologically active microorganisms which could affect the concentration of many analytes. Immediate analysis of AWD samples is best and chemical preservation should be used only

when the preservation is shown not to interfere with the analysis being performed.

### 7.2 Samples Collected for Inorganic Cation and Anion Determinations:

7.2.1 Samples collected for pH, specific conductance, calcium, magnesium, potassium, sodium, chloride, fluoride, and sulfate analysis are often only placed in pre-cleaned plastic containers (see Section 8) before analysis. If there is a delay between time of collection and time of analysis, a preservation technique may eliminate or moderate chemical and biological changes in the AWD samples. Table 1 summarizes the recommended sample preservation techniques for AWD samples.

### 7.3 Samples Collected for Organic Acids:

7.3.1 Samples collected for the analysis of acetate, citrate, formate and other low molecular weight organic acid anions (C<sub>1</sub>-C<sub>12</sub>) should be preserved within minutes after collection. Organic acids have been determined in AWD samples collected from locations around the world **(1-7)**.<sup>7</sup> These compounds (in particular formic and acetic acids) can constitute from a small fraction to mostly all of the free acidity in AWD samples. Because these acids are unstable in AWD samples, samples must be analyzed within hours after collection or else a preservation technique is required. Table 2 summarizes the recommended sample preservation techniques for AWD samples.

### 7.4 Samples Collected for Trace Dissolved Metals:

7.4.1 Samples collected for trace metals should be filtered to remove insoluble particulate matter often found in AWD samples unless an AWD particulate trace element analysis is desired. Filter pore size should be ≤0.45 μm. Filter materials may contain trace elements, and the filters should be preconditioned before use by filtering 300 mL of water in order to leach soluble impurities on the filter and from the filtration apparatus itself **(8)**. Any filters used for AWD samples should be tested to determine if the filter causes losses or gains of trace elements to the AWD sample. Test the preconditioned filters by

<sup>6</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.

<sup>7</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

**TABLE 2 Preservation of AWD Samples Collected for Organic Acid Determinations**

Preservation Technique	Species Determined	Remarks	Reference
HgCl <sub>2</sub> or tetrachloromercurate (Na <sub>2</sub> HgCl <sub>4</sub> ) +4°C storage <sup>A</sup>	Low molecular weight acids	AWD samples preserved with Hg (II) can be analyzed by capillary GC-MS or for low molecular weight organic anions by ion-exclusion chromatography. Sample disposal may be a problem because mercury and its compounds are a toxic waste. The preservative is usually coupled with sample storage at 4°C. See Table 1 for dissolved mercury (II) concentration in AWD samples.	(1,2)
Chloroform	Acetate, citrate formate, C <sub>1</sub> –C <sub>5</sub>	Analysis is usually by ion-exclusion chromatography because chloroform may interfere with capillary GC-MS analysis. This preservative is often coupled with sample storage at 4°C. When chloroform treatment is combined with storage in the dark at 4°C, samples are reportedly stable for 60 days. Final chloroform concentration in the AWD sample must be 0.2 % by weight.	(3,4)
Freeze at – 20°C	Short-chain dicarboxylic acids C <sub>2</sub> –C <sub>12</sub>	Analysis is by capillary gas chromatography or GC-MS. Sample must be completely in the liquid state before sample is prepared for analysis. Maximum storage time has not been reported.	(6)
Chill at 4°C	Low molecular weight acids	This is a minimum procedure for organic acid preservation. This preservation technique will not preserve acetate and formate longer than 3 days. Degradation may occur in less than 3 days.	(7)

<sup>A</sup> Several of the suggested preservatives, such as tetrachloromercurate and mercuric chloride, are environmental and human health hazards and the use and disposal of these preservatives should be carefully controlled (Test Method D 2914, Section A4).

filtering 50 mL of water and determine the analyte concentrations of interest in the filtrate.

7.4.2 Acidify the AWD sample with nitric acid to pH ≤2 to minimize container adsorption of trace metals. The highest purity acid available should be used. Most AWD samples are poorly buffered and only small quantities of acid (about 1 mL/L) are required to reduce the AWD sample to a pH ≤2. Samples acidified with an acid may not be used for the determination of pH and certain other analytes.

## 8. Sample Containers

8.1 Many AWD sampling networks use samplers that utilize either a bucket or bottle that is an integral component of the AWD samplers. These collection techniques allow “wet-only” samples to be obtained, meaning the bucket or bottle is only exposed to the atmosphere during the precipitation event. The preparation or cleaning procedures described in Section 8 apply to the automated AWD samplers that use buckets, and the sample storage bottles to which the AWD sample is transferred from the collection bucket. The procedure described in 8.3 could also be used as a cleaning procedure for AWD sampling that uses a bottle as the principal collection container.

NOTE 1—Any materials used for the collection and preservation of AWD should be dedicated to the use intended.

### 8.2 Inorganic Ions—Buckets and Lids:

8.2.1 Sample containers shall be made of materials that will not contaminate the sample and shall be cleaned thoroughly before use. Plastic containers of polyethylene and polypropylene are recommended for AWD samples collected for inorganic ions. HDPE is most commonly used.

8.2.2 Wipe the exterior of the bucket with damp cloth or brush.

8.2.3 Clean collector buckets and lids only with water. The inside of the bucket and inner side of the lid should not come into contact with any object other than a natural sponge that has been preconditioned with water by soaking the sponge for at least 24 h.

NOTE 2—The initial preparation procedure for newly obtained natural sponges requires that the sponge is washed with copious amounts of water at least four times. Soaking a new natural sponge in 4 L of water for two or three days, after washing, is suggested.

8.2.4 Rinse the interior of the bucket two or more times with water using 100 mL for each rinse.

8.2.5 Place at least 1000 mL of water in the bucket.

8.2.6 Scrub all the inner surfaces of the bucket with the sponge and then swirl the water in the bucket to rinse the inner surfaces. Discard all remaining water.

8.2.7 Rinse the interior of the bucket two or more times with water using 100 mL for each rinse.

8.2.8 Fill the bucket to about 7.5 cm depth with water, cover with a clean lid (see 8.2.11 and 8.2.12) and store overnight.

8.2.9 Measure the specific conductance of the water in the bucket. Transfer a portion of the rinse water to a clean measuring vessel and determine the specific conductance. If the specific conductance is greater than 2 μS/cm (Test Method D 1125), repeat 8.2.4-8.2.8.

8.2.10 Shake the inverted bucket to remove any excess water and place the bucket in a clean plastic bag, making sure that only the interior of the bag contacts the interior of the bucket. Seal the bag with rubber bands or twist ties.

8.2.11 Scrub the inner surface of the lid with the sponge. Rinse the lid with water.

8.2.12 Soak the lids for at least 24 h in water.

8.2.13 Rinse lids with water, shake free the excess water, and place lid in a plastic bag. Seal the bag with a rubber band or twist tie.

NOTE 3—All cleaning and packaging steps should be performed while wearing talc-free plastic gloves. Both hands should be gloved. Gloves should be worn for all procedures that are used to prepare materials for the collection and preservation of AWD.

### 8.3 Inorganic Ions—Plastic Bottles:

8.3.1 Sample containers shall be made of materials that will not contaminate the sample and shall be cleaned thoroughly before use. HDPE is most commonly used.

8.3.2 Soak the bottle closures (caps) in water while the bottles are being prepared.

8.3.3 Rinse each bottle a minimum of three times with water. The amount of water used for each rinse is dependent on the bottle volume. For 250-mL or smaller bottles, use about one-half the bottle volume. For bottles larger than 250 mL, use at least 200 mL of water.

8.3.4 Fill each bottle as full as possible with water and seal

with the cap. Store the full bottles at least overnight (see Note 3).

8.3.5 Randomly select bottles and determine the conductivity of the bottle contents. If there is more than one bottle with a conductivity greater than 2  $\mu\text{S}/\text{cm}$ , the bottles should be rewashed.

8.3.6 Slowly drain the water from the bottles, shake free any excess water, and recap the bottles immediately.

8.3.7 The bottle soak solution should be analyzed for the ions of interest on a regular basis and each time a new supply of plastic bottles is obtained.

#### 8.4 Trace Elements—Plastic Bottles:

8.4.1 Sample containers must be made of a material that will not contaminate the sample and must be acid cleaned before use. HDPE and fluorohydrocarbon bottles are most frequently used.

8.4.2 Rinse each bottle two times with water. Volume of water used for each rinse should be at least 50 mL.

8.4.3 Prepare a 1.6 N  $\text{HNO}_3$  (1+9) (higher normality is acceptable) solution of sufficient volume to soak the bottles and caps.

NOTE 4—The appropriate concentration needed for leaching the bottles and caps has been discussed extensively in the literature, and 1.6 N  $\text{HNO}_3$  (1 + 9) is the minimum concentration used.

8.4.4 Soak the caps in 1.6 N  $\text{HNO}_3$  while rinsing the bottles.

8.4.5 Fill each bottle as full as possible with 1.6 N  $\text{HNO}_3$  and seal with the cap. Store the full bottles for at least 24 h.

8.4.6 Slowly drain the acid from the bottles, shake free any

excess acid, and rinse each bottle three times with water. See 8.3.3 for rinse volumes.

8.4.7 Soak the bottle caps in water while preparing the bottles in 8.4.5.

8.4.8 Refill the bottles as full as possible with water and seal with the cap. Store the full bottles at least 24 h.

NOTE 5—A literature reference recommends soaking the bottles with water until the bottles are used for sampling (9).

8.4.9 Rinse the bottles with water before using.

8.4.10 The bottle soak solution should be analyzed for the ions of interest on a regular basis and each time a new supply of plastic bottles is obtained.

#### 8.5 Organic Acids:

8.5.1 Organic materials can be leached from HDPE materials. However, the leached compound concentrations can be reduced by the cleaning and soaking procedures described for inorganic ions. Many investigators (2-7) are using HDPE containers to collect and store organic acid AWD samples; however, borosilicate glass is recommended for dicarboxylic acids.

8.5.2 Prepare the collection vessels as described in 8.2, and prepare the storage bottles as described in 8.3.

## 9. Keywords

9.1 atmospheric wet deposition samples; collection materials; sample containers; sample contamination; sample preservation

## REFERENCES

- (1) Chapman, E. G., Sklarew, D. S., and Flickinger, J. S., "Organic Acids in Springtime Wisconsin Precipitation Samples," *Atmospheric Environment*, 20, 1986, pp. 1717-1725.
- (2) Kawamura, K., and Kaplan, I. R., "Organic Compounds in the Rainwater of Los Angeles," *Environmental Science & Technology*, 17, 1983, pp. 497-501.
- (3) Keene, W. C., and Galloway, J. N., "Considerations Regarding Sources for Formic and Acetic Acids in the Troposphere," *Journal of Geophysical Research*, 91, 1986, pp. 14,466-14,474.
- (4) Bachman, S. R., and Peden, M. E., "Determination of Organic Acid Anions in Precipitation by Ion Chromatography Exclusion," *Water, Air, and Soil Pollution*, 33, 1987, pp. 191-198.
- (5) Krupa, S. V., Lodge, J. P., Jr., Nosal, M., and McVehil, G. E., "Characteristics of Aerosol and Rain Chemistry in North Central USA," *Acid Rain: Scientific and Technical Advances*, ed. by Perry R. et al, Selper Ltd., London, 1987, pp. 121-128.
- (6) Kawamura, K., Steinberg, S., and Kaplan, I. R., "Capillary GC Determination of Short-Chain Dicarboxylic Acids in Rain, Fog, and Mist," *International Journal of Environmental Analysis and Chemistry*, 19, 1985, pp. 175-188.
- (7) Keene, W. C., Galloway, J. N., and Holden, J. D., Jr. "Organic Acidity in Precipitation from Remote Areas of the World," *Proceedings of the Third Annual National Symposium on Recent Advances in Measurement of Pollutants in Ambient Air and Stationary Sources*, U.S. Environmental Protection Agency, Research Triangle Park, NC., Report No.: EPA-600/9-84-006, 1984.
- (8) Keller, B. J., Peden, M. E., and Skowron, L. M., "Methods for Collection and Analysis of Precipitation: Trace Metals," *Illinois State Water Survey*, Champaign, IL, ISWS report 438, 1988, p. 71.
- (9) Ross, H. B., "The Importance of Reducing Sample Contamination in Routine Monitoring of Trace Metals in Atmospheric Precipitation," *Atmospheric Environment*, Vol 20, No. 2, 1986, pp. 401-405.
- (10) Peden, M. E., et al, "Development of Standard Methods for the Collection and Analysis of Precipitation," *Illinois State Water Survey*, Champaign, Illinois, ISWS Report 381, 1986, p. 375.
- (11) Chan, W. H., Tomassini, F., and Loescher, B., "An Evaluation of Sorption Properties of Precipitation Constituents on Polyethylene Surfaces," *Atmospheric Environment*, Vol 17, No. 9, 1983, pp. 1779-1785.
- (12) Good, A. B., and Schroder, L. J., "Evaluation of Metal Ion Absorptive Characteristics of Three Types of Plastic Sample Bags Used for Precipitation Sampling," *Journal of Environmental Science and Health*, Vol A19, No. 5, 1984, pp. 631-640.
- (13) Eicholz, G. G., Nogel, A. E., and Hughes, R. B., "Adsorption of Ions in Dilute Aqueous Solutions on Glass and Plastic Surface," *Analytical Chemistry*, Vol 37, No. 7, 1965, pp. 863-868.
- (14) U.S. Environmental Protection Agency, "Handbook of Methods for Acid Deposition Samples, Laboratory Analysis for Surface Water Chemistry," U.S. EPA, Office of Acid Deposition, Environmental Monitoring, and Quality Assurance, Washington, DC, USEPA REPORT EPA 600/4-87/026.
- (15) Jenkins, D., "The Differentiation, Analysis, and Preservation of Nitrogen and Phosphorus Forms in Natural Waters," *Trace Inorganics in Water, Advances in Chemistry Series 73*, 1968, pp. 265-280.
- (16) Klingamen, E. D., and Nelson, D. W., "Evaluation of Methods for Preserving the Levels of Soluble Inorganic Phosphorus and Nitrogen in Unfiltered Water Samples," *Journal of Environmental Quality* 5, 1976, pp. 42-46.

(17) Fishman, M. J., Schroder, L. J., and Shockey, M. W., "Evaluation of Methods for Preservation of Water Samples for Nutrient Analysis," *International Journal of Environmental Studies*, Vol. 26, 1986, pp. 231–238.

(18) Graham, R. C., oral presentation, NADP/NTN Subcommittee 1 meeting, April 11–12, 1988, St. Louis, MO. Science Research Laboratory, U.S. Military Academy, West Point, NY 10996.

*The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.*

*This standard is copyrighted by ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or [service@astm.org](mailto:service@astm.org) (e-mail); or through the ASTM website (<http://www.astm.org>).*