



Designation: ~~D5012–01 (Reapproved 2013)~~ D5012 – 20

## Standard GuidePractice 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 D5012; 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.

### 1. Scope

1.1 This guidepractice presents recommendations for the cleaning of plastic or glass materials used for collection of atmospheric wet deposition (AWD). This guidepractice 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 most 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

1.5 *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:<sup>2</sup>

D883 Terminology Relating to Plastics

D1125 Test Methods for Electrical Conductivity and Resistivity of Water

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1695 Terminology of Cellulose and Cellulose Derivatives

~~D2914 Test Methods for Sulfur Dioxide Content of the Atmosphere (West-Gaeke Method)~~

D4453 Practice for Handling of High Purity Water Samples

<sup>1</sup> This guidepractice 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.

Current edition approved Oct. 1, 2013; Sept. 1, 2020. Published October 2013; September 2020. Originally approved in 1989. Last previous edition approved in 2008; 2013 as D5012 – 01 (2008); (2013). DOI: 10.1520/D5012-01R13; 10.1520/D5012-20.

<sup>2</sup> 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.

### 3. Terminology

#### 3.1 Definitions:

3.1.1 For definitions of terms used in this ~~guide, practice,~~ refer to Terminology **D1129**.

3.1.2 For definition of *plastic*, refer to Terminology **D1695** and Terminology **D883**.

3.1.3 For definition of AWD (~~(precipitation, meteorological)~~precipitation, meteorological), refer to Terminology **D1356**.

### 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 **D1125**.

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

**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>(3-7)</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>(8-10)</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>(4,5)</b>  |
| HCl, 5 mL/L             | All dissolved Hg and total Hg  | Samples for dissolved Hg are filtered through 0.45 μm capsule filter. Samples collected directly into specially cleaned, pretested, fluoropolymer bottle.  | <b>(1,2)</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>(11)</b>   |

### 6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade acids and other 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>3</sup>

6.2 Nitric acid, ultra pure.

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

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications, 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. Pharmaceutical Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

| Preservation Technique | Species Determined  | Remarks  | Reference |
|------------------------|---|--|-----------|
| Chloroform             | Acetate, citrate, formate,<br>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. | (14,15)   |
| Freeze at – 20°C       | Short-chain dicarboxylic acids<br>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.  | (17)      |
| 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.  | (18)      |

6.4 Chloroform, high performance liquid chromatography reagent.

6.5 Hydrochloric acid, pretested for total and methyl mercury.

6.6 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification **D1193**. 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. Samples collected for total and methyl mercury determinations are to be collected directly into specially cleaned, pretested, fluoropolymer bottle(s) **(1 and 2)**.<sup>4</sup>

### 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 **(12-18)**. 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 **(19)**. 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 filtering 50 mL of water and determine the analyte concentrations of interest in the filtrate.

<sup>4</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

7.4.2 Acidify the AWD sample with nitric acid to  $\text{pH} \leq 2$  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  $\text{pH} \leq 2$ . Samples acidified with an acid may not be used for the determination of pH and certain other analytes.

7.4.3 Acidify the AWD sample with 5 mL/L of pretested HCl for dissolved mercury and total mercury.

## 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  $2 \mu\text{S}/\text{cm}$  (Test Method Methods D1125), 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.