



Designation: D8404 – 21

# Standard Practice for Preparation of Soil Samples by Ammonium Bifluoride-Nitric Acid Digestion for Subsequent Analysis for Metals and Metalloids<sup>1</sup>

This standard is issued under the fixed designation D8404; 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 practice covers drying, homogenization, and ammonium bifluoride-nitric acid digestion of soil samples and associated quality control (QC) samples for the determination of metals and metalloids using laboratory atomic spectrometry analysis techniques such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry (FAAS), and graphite furnace atomic absorption spectrometry (GFAAS). For ammonium bifluoride-nitric acid digestion of airborne dust and dust-wipe samples for the determination of metals and metalloids, see Practice D8344.

1.2 This practice is based on U.S. EPA SW 846, Test Method 3050, Test Method D7202, and Practice D8344.

1.3 This practice contains notes that are explanatory and are not part of the mandatory requirements of this standard.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

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.*

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.*

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality. Current edition approved Sept. 1, 2021. Published October 2021. DOI: 10.1520/E8404-21.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D653 Terminology Relating to Soil, Rock, and Contained Fluids
- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D1356 Terminology Relating to Sampling and Analysis of Atmospheres
- D3974 Practices for Extraction of Trace Elements from Sediments
- D4840 Guide for Sample Chain-of-Custody Procedures
- D7202 Test Method for Determination of Beryllium in the Workplace by Extraction and Optical Fluorescence Detection
- D8344 Practice for Ammonium Bifluoride and Nitric Acid Digestion of Airborne Dust and Dust-Wipe Samples for the Determination of Metals and Metalloids
- E288 Specification for Laboratory Glass Volumetric Flasks
- E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
- E1154 Specification for Piston or Plunger Operated Volumetric Apparatus
- E1605 Terminology Relating to Lead in Buildings
- E1727 Practice for Field Collection of Soil Samples for Subsequent Lead Determination

### 2.2 U.S. Government Analytical Method:<sup>3</sup>

- U.S. EPA SW 846 Test Methods for Evaluating Solid Waste Physical/Chemical Methods

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

### 2.3 ISO Standards:<sup>4</sup>

**ISO Guide 30 Terms and Definitions Used in Connection with Reference Materials**

**ISO 1042 Laboratory glassware — One-mark volumetric flasks**

**ISO/IEC 17011 Conformity assessment—Requirements for accreditation bodies accrediting conformity assessment**

**ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories**

## 3. Terminology

3.1 *Definitions*—For definitions of terms relating to the preparation of soil samples that are not given here, refer to Terminologies **D653**, **D1129**, **D1356**, or **E1605**.

3.1.1 *batch, n*—a group of field or quality control samples that are processed together using the same reagents and equipment.

3.1.2 *digestate, n*—the acidified aqueous solution that results from digestion of the sample.

3.1.3 *digestion, n*—high temperature sample preparation process that involves chemical breakdown to solubilize targeted analytes present in a sample.

3.1.4 *method blank, n*—a sample, devoid of analyte, that is analyzed to determine its contribution to the total blank (background) reading.

3.1.5 *non-spiked sample, n*—a sample, devoid of analyte, that is targeted for addition of analyte but is not fortified with all target analytes prior to sample preparation.

3.1.5.1 *Discussion*—Analysis results for this sample are used to correct for background levels in the blank medium that is used for spiked and spiked duplicate samples.

3.1.6 *reagent blank, n*—a digestate that reflects the maximum treatment given any one sample within a batch of samples, except that it has no sample placed initially into the digestion vessel. (The same reagents and processing conditions that are applied to field samples within a batch are also applied to the reagent blank.)

3.1.6.1 *Discussion*—Analysis results from this sample provide information on the level of potential contamination resulting from only laboratory sources that are experienced by samples processed within the batch.

3.1.7 *reference material (certified reference material) (CRM), n*—reference material accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed; each certified value is accomplished by an uncertainty at a stated level of confidence. **ISO Guide 30**

3.1.8 *spiked sample or spiked duplicate sample, n*—a sample portion (split from an original sample) that is spiked with a known amount of analyte.

3.1.8.1 *Discussion*—Analysis results for these samples are used to provide information on the precision and accuracy of the overall process.

## 4. Summary of Practice

4.1 A representative soil sample is dried and homogenized, and then digested (in a batch mode with other samples) in a hot block using ammonium bifluoride and nitric acid. The digestate is diluted for final volume prior to measurement for metals and metalloids.

## 5. Significance and Use

5.1 There is a need to monitor the content of metals and metalloids in order to determine the presence of potential hazards. Hence, effective and efficient methods are required for the preparation of soil samples for determination of metals and metalloids present therein.

5.2 This practice may be used for the digestion of soil samples that are collected during various construction and renovation and hazard survey activities in and around buildings and related structures. The practice is also suitable for the digestion of soil samples for metal and metalloid analyses collected from other locations, such as near roads and steel structures. For some other extraction procedures, see Practices **D3974**.

5.3 This practice is intended to be used to prepare samples that have been collected for hazard assessment purposes but may be used for other applications such as, for example, monitoring the effectiveness of remediation activities.

5.4 This practice may be capable of determining metals and metalloids bound within matrices, such as silica, that are not soluble in nitric acid alone.

5.5 This practice includes drying and homogenization steps to help assure that reported results are representative of the sample and are independent of potential differences in soil moisture levels among different sampling locations or changing weather conditions.

## 6. Reagents and Materials

### 6.1 Equipment:

6.1.1 *Analytical Balance*, capable of accurately determining the mass to the nearest 0.001 g.

6.1.2 *Drying Oven*, preferably a gravity convection type capable of maintaining a temperature of 100 °C to 120 °C.

6.1.3 *Grinding Apparatus*—Mortar and pestle (porcelain or agate), shatter box, or mixer mill.

6.1.4 *Micropipettors with Disposable Plastic Tips* conforming to Specification **E1154**, sizes needed to make reagent additions, and spiking standards.

NOTE 1—In general, the following sizes should be readily available: 1 mL to 5 mL adjustable, 1000 mL, 500 mL, 250 mL, and 100 mL.

6.1.5 *Sieves*, 4.75 mm (U.S. Standard No. 4), 2 mm (No. 10), and 500 µm (No. 35), plastic or stainless steel. When sieves containing soldered joints are used, then all solder joints shall be coated with epoxy resin prior to use to protect samples from potential lead contamination originating in the solder. Visually inspect prior to use for the presence of bare metal.

<sup>4</sup> Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandinnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <https://www.iso.org>.

NOTE 2—Plastic or stainless steel sieves are better for use instead of brass sieves to alleviate possible lead contamination of the soil samples from contact with lead solder common to brass sieves.

6.1.6 *Thermometers*, that cover a range from 0 °C to 110 °C.

6.1.7 *Plastic Gloves*, powderless.

6.1.8 *Air-Tight Sample Containers*, 1 L (1 qt) or 4 L (1 gal) re-sealable plastic bags, or plastic 50 mL centrifuge tubes.

6.1.9 *Tongs*, metal.

6.1.10 *Spoon*, stainless steel or plastic, or both.

6.1.11 *Heat Block*, controllable to maintain the specified digestion temperature in wells sized to accept the screw top plastic centrifuge tubes used for the digestion.

6.1.12 *Centrifuge Tubes*, plastic, 50-mL, with screw top caps.

6.1.13 *Labware*, plastic (for example, beakers, flasks, graduated cylinders, etc.), of assorted sizes as needed.

6.1.14 *Forceps*, plastic or plastic-coated.

6.1.15 *Syringes*.

NOTE 3—The filtration process can be carried out by attaching a 25-mm diameter syringe filter to Luer lock syringes and pouring the liquid contents into the syringe. The liquid is forced out through the filter into a separate 50-mL centrifuge tube.

6.1.16 *Microfilters*.

NOTE 4—Filters with 0.2 to 0.45- $\mu\text{m}$  pore size are acceptable. Preferred filters are made out of nylon, polyethersulfone, or hydrophilic polypropylene. Polytetrafluoroethylene (PTFE) filters are unsuitable because they may partially dissolve in ammonium bifluoride solution during filtration.

6.1.17 *Borosilicate Glassware*—Volumetric flasks with stoppers meeting Specification E288 or conforming to ISO 1042, 100 mL; Griffin beakers, 100 mL, 150 mL or 250 mL; watch glasses sized to cover Griffin beakers.

6.1.18 *Air-Tight Sample Containers*—1 L (1 qt) or 4 L (1 gal) re-sealable plastic bags, or plastic 50 mL centrifuge tubes.

6.1.19 *Volumetric Flasks*, meeting Specification E288 or conforming to ISO 1042, 100 mL and other sizes as needed to make dilutions of sample digests or standards.

6.1.20 *Spoon*, stainless steel.

6.1.21 Other general laboratory apparatus, as needed.

## 6.2 Reagents:

6.2.1 *Purity of Reagents*—Reagent grade chemicals shall be used in this practice. 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>5</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening accuracy of the determination.

6.2.2 *Water*—Unless otherwise indicated, references to water shall be understood to mean reagent defined as Type I in Specification D1193 (ASTM Type I Water: minimum resistivity of 18 M $\Omega$ -cm or equivalent).

6.2.3 *Calibration Stock Solutions*—1000 mg/mL of the metal, metals, or metalloids of interest in dilute nitric acid obtained from a commercial supplier accredited to ISO/IEC 17025 by an accreditation body complying with ISO/IEC 17011.

6.2.4 *Extraction (or Dissolution) Solution*—Mass fraction 1 % ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>) solution (aqueous) for dissolution of metals and metalloids in collected particulate matter. (**Warning**—Ammonium bifluoride will etch glass, so it is essential that all NH<sub>4</sub>HF<sub>2</sub> solutions be contained in plastic labware.)

6.2.5 *Nitric Acid*—Redistilled, concentrated nitric acid, 16 N, specific gravity 1.42.

6.2.6 *Acetone*—Reagent grade.

## 7. Equipment Preparation

7.1 Wash glassware and plastic equipment with laboratory detergent, rinsed with tap water, soak for at least 4 hours in volume fraction 35 % nitric acid and water, rinse three times with ASTM Type I Water, and allow to dry preferably in a fume hood. Commercial, automatic systems are available that perform a similar process.

7.2 Alternatively, soak glassware and plastic equipment in volume/volume 1+1 nitric acid and water in a plastic tub preferably in a working hood with the hood sash down, rinse three times with ASTM Type I Water, and allow to dry preferably in a fume hood.

## 8. Procedure

### 8.1 Sample Pre-treatment:

8.1.1 Treat each sample in a processing batch equally.

8.1.2 If possible before removal, break up the soil sample within the original containers containing the samples as received from the sampler.

NOTE 5—This will not be possible for wet soil samples.

8.1.3 Label a 100 mL, 150 mL, or 250 mL Griffin beaker (or other vessel suitable for oven drying of soils that will not contaminate the sample with metals or metalloids of interest) with a high temperature wax pen or any other marker that will be visible after exposure to the drying oven.

8.1.4 Transfer the entire soil sample to the labeled Griffin beaker. Cover with a watch glass (tip to one side to permit moisture removal), and place in a drying oven for a minimum of 6 h at a temperature of 110 °C  $\pm$  10 °C. Samples that cake or plug the sieve require additional drying.

NOTE 6—Soil samples should not cake or exhibit packing characteristic of moisture, but should flow freely through the sieve when broken apart.

8.1.5 If the received soil sample is excessively large, then any attempts to sub-sample prior to drying and sieving are likely to cause bias. If possible, use a larger beaker to contain the entire sample. If not, then use multiple beakers followed by re-combining after drying. Samples that cake or plug the sieve require additional drying.

8.1.6 Using tongs, remove the beakers containing the samples and allow them to cool to room temperature.

8.1.7 Don a pair of plastic gloves and push the soil sample through a clean 4.75 mm sieve (U.S. Standard No. 4) to remove

<sup>5</sup> 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.



any large objects or root material, or both. Discard material retained on the sieve. Clean the sieve between samples by tapping or using forced air or other dry method to prevent cross-contamination. Perform this step in a location well removed from other samples in process and in an area where soil dust will not contaminate the laboratory operations such as in front of a fume hood.

NOTE 7—If the samples do not appear to contain any large objects or root material, it is not necessary to perform this step with the 4.75 mm sieve.

NOTE 8—In order to minimize small particle size soil losses, this step should not be performed inside a fume hood.

8.1.8 Don a pair of plastic gloves and push the soil sample through a clean 2 mm sieve (U.S. Standard No. 10) to remove coarse material. Discard material retained on the sieve. Clean the sieve between samples by tapping or using forced air or other dry method to prevent cross-contamination. Perform this step in a location well removed from other samples in process, and in an area where soil dust will not contaminate the laboratory operations, such as in front of a fume hood.

8.1.9 Grind the sample using an agate (preferred) or porcelain mortar and pestle or other appropriate homogenization apparatus such as a shatter-box or mixer mill while guarding for possible sample contamination from metal components. Clean the grinding apparatus between samples to prevent cross-contamination between samples by rinsing with water and drying. When any material is retained from 9.1.10, delay cleaning until this retained material for the sample is re-ground as described in 9.1.11. An acetone rinse will facilitate drying.

NOTE 9—Acetone should not be used on sieves since it can damage epoxy coatings which may be present to seal lead solder joints.

8.1.10 Place the ground up sample on a clean 500 mm sieve (U.S. Standard No. 35). Use a stainless steel spoon to help move material around until no more sample will pass through the sieve. Do not discard the retained material. Return any retained material for one more grinding as described in 9.1.9.

NOTE 10—A second re-grinding step is included for retained material to avoid inadvertent loss of larger pieces of material that can remain as a result of inadequate grinding.

8.1.11 Place the ground-up retained sample material back on the clean U.S. Standard No. 35 (500 mm sieve). Using a stainless steel spoon, move material around until no more sample will pass through the sieve, adding the passed material to the previous sample material that passed through the sieve. Discard any retained material. Clean the sieve between samples by tapping or using forced air or other dry method to prevent cross-contamination. Perform this step in a location well removed from the samples in process.

8.1.12 Label acid-cleaned 100 mL, 150 mL, or 250 mL Griffin beakers and watch glasses for each soil sample and associated QC samples.

8.1.13 Transfer sieved portion to a labeled Griffin beaker and place in a drying oven overnight or for a minimum of 12 h, or to constant mass at a temperature of  $110\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$ . Constant mass for this procedure is defined as a less than 0.1 % change in mass for repeated measurements (a minimum of two) taken over a minimum of a 1 h interval. Remove from oven and allow to cool to room temperature.

8.1.14 Store the dried, homogenized, and sieved soil samples inside new labeled air-tight sample containers.

## 8.2 Sample Digestion:

8.2.1 Turn or roll the sample container repeatedly for about 1 min. Determine the mass of each dried homogenized sample to the nearest 0.001 g and transfer a  $0.50\text{ g} \pm 0.10\text{ g}$  portion of the sample to a labeled 50 mL centrifuge tube. Record the mass of each sample.

NOTE 11—Pipet 5 mL of the 1 % ammonium bifluoride extraction solution into each of the tubes containing the samples.

8.2.2 Carefully pipet 5 mL of concentrated nitric acid into each of the tubes containing the samples.

8.2.3 Digest using hot block type heating or heated sonication.

## 8.3 Hot Block Heated Digestion:

8.3.1 Preheat the hot block to  $95\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ .

8.3.2 Reflux for 30 min allowing the reflux wetting band to reach no closer than 2 cm from the mouth of the tube.

8.3.3 Remove from the hot block and allow to cool to room temperature.

8.3.4 Pipet 5 mL of concentrated nitric acid into each of the plastic tubes containing the samples.

8.3.5 Reflux for 30 min allowing the reflux wetting band to reach no closer than 2 cm from the mouth of the tube.

8.3.6 Remove from the hot block and allow to cool to room temperature.

8.3.7 Make to 50 mL volume in the tube with water.

## 8.4 Heated Sonication Digestion:

8.4.1 Preheat the sonication bath to  $85\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ .

8.4.2 Sonicate for 30 min.

8.4.3 Remove from the bath and allow to cool to room temperature.

8.4.4 Pipet 5 mL of concentrated nitric acid into each of the plastic tubes containing the samples.

8.4.5 Sonicate for 30 min.

8.4.6 Remove from the bath and allow to cool to room temperature.

8.4.7 Make to 50 mL volume in the tube with water.

## 8.5 Filtration:

8.5.1 Filter aliquots (for example, 5 mL) of extract solution through inert microfilters as needed.

## 8.6 Calibration:

8.6.1 *Preparation of Calibration Standards*—Using calibration stock solution, concentrated nitric acid, and the 1 % aqueous ammonium bifluoride solution, prepare at least four standards covering the concentration range of interest.

8.6.2 *Calibration Blank and Calibration Stock Standard Solutions Preparation*—Calibration blanks are prepared by adding in a proportion of 1:19 (by volume) a 0 mg/mL standard and water in a centrifuge tube. Ensure that these are mixed properly. Calibration standard solutions are also made in a similar fashion where the calibration standard are mixed in a volumetric ratio of 1:19 (a 20× dilution). At least four standard measurement solutions that when possible cover the expected concentration range of the samples, plus a blank, must be made for calibration for each metal and metalloid of interest.