



Standard Test Method for Determination of Volatile Inorganic Acids (HCl, HBr, and HNO₃) Using Filter Sampling and Suppressed Ion Chromatography¹

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1. Scope

1.1 This test method is intended for use in the determination of the time-weighted average mass concentration of hydrogen chloride gas and hydrochloric acid mist, hydrogen bromide vapor and hydrobromic acid mist, and nitric acid vapor and mist in workplace air. The samples are collected on an alkali-impregnated quartz fiber filter and analyzed by ion chromatography. The method is also appropriate for measuring short term exposures.

1.2 This test method assumes that air samples are collected using appropriate and applicable ASTM International standards for sampling of workplace air.

1.3 The procedure is targeted for occupational and environmental hygiene monitoring purposes.

1.4 No detailed operating instructions are provided because of differences among various makes and models of suitable instruments. Instead, the analyst shall follow the instructions provided by the manufacturer of the particular instrument. This standard does not address comparative accuracy of different devices or the precision between instruments of the same make and model.

1.5 The values stated in SI units are to be regarded as the standard.

1.6 The practice contains notes, which are explanatory and not part of mandatory requirements of the standard.

1.7 *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.*

¹ This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

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2. Referenced Documents

2.1 ASTM Standards:²

D882 Test Method for Tensile Properties of Thin Plastic Sheet

D1193 Specification for Reagent Water

D4840 Guide for Sample Chain-of-Custody Procedures

D5337 Practice for Flow Rate Adjustment of Personal Sampling Pumps

D7035 Test Method for Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

E1370 Guide for Air Sampling Strategies for Worker and Workplace Protection

2.2 ISO and European Standards:

ISO 648 Laboratory glassware—One mark pipettes³

ISO 7708 Air quality—Particle size fraction definitions for health-related sampling³

ISO 1042 Laboratory glassware—One-mark volumetric flasks³

EN 482 Workplace atmospheres—General requirements for the performance of procedures for the measurement of chemical agents⁴

EN 1076 Workplace atmosphere—Procedures for measuring gases and vapours using pumped samplers—Requirements and test methods⁴

3. Summary of Test Method

3.1 A known volume of air is drawn through a pre-filter and an alkali-impregnated quartz fiber filter, mounted in an inhalable sampler, to collect HCl, HBr and HNO₃. The acids are collected on the impregnated quartz fiber filter, while particulate salts of the acids are trapped on the pre-filter.

² 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 Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

⁴ Available from European Committee for Standardization (CEN), Avenue Marnix 17, B-1000, Brussels, Belgium, <http://www.cen.eu>.

3.2 The acids collected on the sampling filter are extracted with water or eluent to solubilize the analytes of interest.

3.3 Aliquots of the sample solution are subjected to ion chromatography in order to separate the extracted chloride, nitrate or bromide from other anions. Following this separation, the anions are measured using a conductivity or UV-vis detector and analytical results are obtained by plotting the measured conductivity or absorbance as a function of concentration.

3.4 The results can be used for assessment of occupational exposure to HCl, HBr and HNO₃ in air.

4. Significance and Use

4.1 Exposure to inorganic acids in workplace air can cause irritations of the skin, eyes and respiratory tract, and exposure limits for hydrochloric acid, hydrobromic acid and nitric acid in air have been established to reduce exposure risks to potentially affected workers (1).⁵ Sampling and analytical methods for volatile inorganic acids are needed for exposure assessment and risk reduction purposes.

5. Apparatus

5.1 Chlorides and nitrates are found ubiquitously in the environment and the presence of chloride and nitrate in reagents can lead to high blank values. It is therefore necessary to check the blank values of all chemicals and labware before use.

5.2 Sampling Equipment:

5.2.1 *Air samplers*, designed to collect the inhalable fraction of airborne particles, as defined in ISO 7708. Suitable for mounting a pre-filter (5.2.2) and sampling filter (5.2.3) separated by a spacer (5.2.4), manufactured from a material that does not react with acids, for collecting personal air samples as described in Test Method D7035.

NOTE 1—The sampling method has only been tested at flow rates up to 2 L/min so the inhalable samplers used should have a design flow rate of 2 L/min or less.

NOTE 2—If samplers have an internal filter cassette, this too has to be manufactured from a material that does not react with acids.

NOTE 3—Materials which do not react with acids, from which samplers and internal filter cassettes can be manufactured, include polytetrafluoroethylene (PTFE) and other fluorinated polymers, polyvinyl chloride (PVC), polyethylene, polypropylene and polycarbonate.

5.2.2 *Filters*, of a diameter suitable for use with the samplers:

5.2.2.1 *Quartz Fiber Filters*,

5.2.2.2 *Membrane Filters*, PVC, 5-μm pore size or below, and

5.2.2.3 *Membrane Filters*, PTFE, 5-μm pore size or below.

5.2.3 *Impregnated Filters*, suitable for sampling of acid gases, for example, 25-mm diameter quartz fiber filters impregnated with 200 μL of 265 g/L sodium carbonate solution (see 6.7.1) or 37-mm diameter quartz fiber filters impregnated with 500 μL of 106 g/L sodium carbonate solution (see 6.7.2).

5.2.4 *Spacer*, of a diameter suitable for use with the samplers, for separating the prefilters and impregnated quartz fiber filters, for example, polypropylene sleeves or PTFE-coated screens.

5.3 *Sampling Pumps*, with an adjustable flow rate and capable of maintaining the selected flow rate (between 1 L/min and 2 L/min for personal sampling pumps) to within ±5 % of the nominal value throughout the sampling period.

5.4 *Flow Meter*, portable, capable of measuring the selected volumetric flow rate within ±2 %, and calibrated against a primary standard.

5.5 Ancillary Equipment:

5.5.1 *Flexible Tubing*, of a diameter suitable for making a leak-proof connection from the sampler to the sampling pump.

5.5.2 *Belts or Harnesses*, to which the sampling pump can be conveniently fixed for personal sampling.

5.6 Laboratory Equipment:

5.6.1 Ion chromatograph having the following components:

5.6.1.1 *Pump*—Capable of delivering a constant flow within the range 0.1 mL/min to 5 mL/min at a pressure of 15 MPa to 150 MPa.

5.6.1.2 *Injection Valve*—A low dead volume, non-metallic valve fitted with a sample loop having a volume of up to 500 μL, for injecting the sample solution into the eluent stream.

5.6.1.3 *Guard Column*—A column, placed before the separator column, to protect the latter from fouling by particles or strongly adsorbed organic constituents of the sample solution.

5.6.1.4 *Separator Column*:

1. *Separator Column for Suppressed Ion Chromatography*: A column packed with high capacity pellicular anion exchange resin, suitable for resolving nitrates chlorides or bromides from other inorganic anions.

2. *Separator Column for Non-suppressed Ion Chromatography*: A column packed with silica or organic polymers, suitable for resolving chloride, bromide and nitrate from other inorganic anions.

5.6.1.5 *Suppressor Module*—A module to reduce the total conductivity of the eluent suitable for use with the separator column.

5.6.1.6 *Detector*:

1. *Conductivity Detector*: A low volume flow through with a non-metallic flow path conductivity detector.

NOTE 4—A conductivity detector can be used with both suppressed and non-suppressed ion chromatography

2. *Ultraviolet-visible (UV-vis) Detector*: A low volume flow through UV-vis detector with a non-metallic flow path detector.

NOTE 5—A UV-vis detector can be used with non-suppressed ion chromatography for inverse UV detection.

5.6.1.7 *Recorder, Integrator, or Computer*—A device compatible with detector output, capable of recording detector response as a function of time for the purpose of measuring peak height or area.

5.6.1.8 *Eluent Reservoir*—A container suitable for storing a manually prepared eluent solution.

⁵ The boldface numbers in parentheses refer to a list of references at the end of this standard.

5.6.1.9 *Eluent generation system*, for producing an eluent suitable for use with the selected separator column, as an alternative to use of a manually prepared eluent (5).

5.6.2 *Ultrasonic bath*, preferably with a timer, suitable for use in the ultrasonic extraction method for hydrogen chloride, nitric acid or hydrogen bromide.

5.6.3 *pH Meter*

5.7 *Laboratory Supplies:*

NOTE 6—It is normally preferable to use plastic labware rather than glassware.

5.7.1 *One-mark Volumetric Flasks*, of capacities between 20 mL, 100 mL and 2 L.

5.7.2 *One-mark Pipets*, complying with the requirements of ISO 648.

5.7.3 *Disposable Screw-cap Polyethylene Vessels*, of 15 mL capacity.

5.7.4 *Disposable Filters*, PTFE, pore size 0.45 µm, for use in ion chromatography.

5.7.5 *Disposable 2-mL or 5-mL Syringes*, with luer lock connector, for use with disposable filters.

5.7.6 *Cation Exchange Resin Cartridges*, suitable for removal of carbonate from test solutions to be analyzed by electronically-suppressed ion chromatography.

5.7.7 *Autosampler Vials*, of 1.5 mL-2 mL capacity.

5.7.8 *Pipet Tips*, plastic, disposable, of assorted sizes, as needed.

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

5.7.10 *Tweezers*, manufactured from plastic or tipped with PTFE, for loading and unloading filters into samplers.

5.7.11 *Personal Protective Wear*, for example, respirators, masks, gloves, lab coats, safety eyewear, etc., as needed.

5.7.12 *Other General Laboratory Supplies*, as needed.

6. Reagents and Materials

6.1 *Water*—Unless otherwise indicated, references to water shall be understood to mean reagent-grade, as defined by Type 1 of Specification D1193 (ASTM Type 1 water: minimum resistance of 18 MΩ-cm or equivalent)

6.2 *Stock Standard Solution*, 1000 mg/L anions (Cl^- , Br^- , NO_3^-) in water: Use a commercial standard solution with a certified concentration, for example, 1000 mg/L of chloride, bromide and nitrate traceable to national standards. Observe the manufacturer's expiration date or recommended shelf life.

6.3 *Working Standard Solution*, 100 mg/L anions (Cl^- , Br^- , NO_3^-) in water: Accurately pipet appropriate volumes, for example, 10 mL, of the Calibration stock solution I (6.7.2) into a 100 mL one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly. Prepare this solution fresh monthly.

6.4 *Sodium Carbonate* (Na_2CO_3), anhydrous, purity >99.9 % (m/m).

6.5 *Sodium Hydrogen Carbonate* (NaHCO_3), purity >99.5 % (m/m).

6.6 *Sodium Carbonate Impregnation Solution:*

6.6.1 *Sodium Carbonate Impregnation Solution for 25 mm Filters*, 2.5 mol/L (265 g/L). Dissolve 26.5 g Na_2CO_3 in water, quantitatively transfer the solution into a 100 mL one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

6.6.2 *Sodium Carbonate Impregnation Solution for 37 mm Filters*, 1 mol/L (106 g/L). Dissolve 10.6 g Na_2CO_3 in water. Quantitatively transfer the solution into a 100 mL one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

6.7 *Reagents for Chemically Suppressed Ion Chromatography:*

NOTE 7—The sodium carbonate/sodium hydrogen carbonate eluent prescribed below is an example that can be used with separator columns for the determination of chloride, bromide and nitrate by chemically suppressed ion chromatography. The column manufacturer's literature will give information on the composition of the eluent to be used with a specific column type.

6.7.1 *Sodium Carbonate/Sodium Hydrogen Carbonate Extraction and Eluent Stock Solution*, 0.62 mol/L Na_2CO_3 and 0.069 mol/L NaHCO_3 . Dissolve 6.6 g of sodium carbonate and 0.58 g sodium hydrogen carbonate in 25 mL of water and swirl to mix. Quantitatively transfer the solution to a 100 mL one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

6.7.2 *Sodium Carbonate/Sodium Hydrogen Carbonate Extraction and Eluent Solution*, 0.0031 mol/L Na_2CO_3 and 0.00035 mol/L NaHCO_3 . Transfer 10 mL of sodium carbonate/sodium hydrogen carbonate stock solution to a 2 L one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

6.7.3 *Potassium Hydroxide Cartridge*, suitable for use with the eluent generation system, if appropriate.

6.8 *Reagents for Non-Suppressed Ion Chromatography:*

NOTE 8—The phthalic acid and borate/gluconate solutions prescribed below are two examples of eluents used for the determination of HCl, HBr and HNO_3 using electronically suppressed ion chromatography. The column manufacturer's literature will give information on the composition of the eluent to be used with a specific column type.

6.8.1 *Phthalic Acid* ($\text{C}_8\text{H}_6\text{O}_4$), mass fraction >99.5 %.

6.8.2 *Acetonitrile* ($\text{C}_2\text{H}_3\text{N}$), HPLC grade.

6.8.3 *Methanol* (CH_3OH), HPLC grade.

6.8.4 *Lithium Hydroxide Monohydrate* ($\text{LiOH}\cdot\text{H}_2\text{O}$), mass fraction >99.5 %.

6.8.5 *Boric acid* (H_3BO_3), mass fraction >99.8 %.

6.8.6 *Gluconic Acid Solution*, mass fraction approximately 50 % of D-gluconic acid ($\text{C}_6\text{H}_{12}\text{O}_7$) in water.

6.8.7 *Glycerol* ($\text{C}_3\text{H}_8\text{O}_3$), mass fraction >99 %.

6.8.8 *Phthalic Acid Extraction and Eluent Stock Solution*, 0.1 mol/L phthalic acid in 9:1 acetonitrile:methanol. Dissolve 1.66 g of phthalic acid in 900 mL of acetonitrile and 100 mL of methanol in a suitable 1-L vessel and mix thoroughly.

6.8.9 *Lithium Hydroxide Solution*, 1 mol/L lithium hydroxide. Dissolve 4.2 g of lithium hydroxide monohydrate in water. Quantitatively, transfer the solution into a 100 mL one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly.