Designation: D7773 – 12

Standard Test Method for Determination of Volatile Inorganic Acids (HCl, HBr, and HNO_3) Using Filter Sampling and Suppressed Ion Chromatography[1]

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D882 Test Method for Tensile Properties of Thin Plastic Sheeting
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 pipettes [3]
ISO 7708 Air quality—Particle size fraction definitions for health-related sampling[3]
ISO 1042 Laboratory glassware—One-mark volumetric flasks[3]
EN 482 Workplace atmospheres—General requirements for the performance of procedures for the measurement of chemical agents[4]
EN 1076 Workplace atmosphere—Procedures for measuring gases and vapours using pumped samplers—Requirements and test methods[4]

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 HNO_3. The acids are collected on the impregnated quartz fiber filter, while particulate salts of the acids are trapped on the pre-filter.

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[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] 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 HNO_3 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 form 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.

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[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 ($C_8H_6O_4$), mass fraction >99.5 %.*

6.8.2 *Acetonitrile (C_2H_3N), HPLC grade.*

6.8.3 *Methanol (CH_3OH), HPLC grade.*

6.8.4 *Lithium Hydroxide Monohydrate ($LiOH \times H_2O$), mass fraction >99.5 %.*

6.8.5 *Boric acid (H_3BO_4), mass fraction >99.8 %.*

6.8.6 *Gluconic Acid Solution,* mass fraction approximately 50 % of D-gluconic acid ($C_6\ H_{12}O_7$) in water.

6.8.7 *Glycerol ($C_3H_8O_3$),* 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.

6.8.10 *Phthalic Acid Extraction and Eluent Solution, for example, 0.005 mol/L phthalic acid, pH 4.2.* Transfer an appropriate volume, for example, 50 mL, of phthalic acid solution to a 1 L one-mark volumetric flask, add approximately 900 mL of water, adjust to pH 4.2 with lithium hydroxide solution and dilute to the mark with water.

6.8.11 *Borate/Gluconate Extraction And Eluent Stock Solution.* Dissolve 17 g of boric acid, 4.8 g of lithium hydroxide monohydrate, 8.8 mL of gluconic acid and 62.5 mL of glycerol in water. Quantitatively, transfer the solution into a 500 mL one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

6.8.12 *Borate/Gluconate Extraction And Eluent Solution.* Transfer 15 mL of borate/gluconate stock solution and 120 mL of acetonitrile to a 1 L one-mark volumetric flask and dilute to the mark with water, stopper and mix thoroughly.

7. Sampling

7.1 *Filter Impregnation*—Impregnate the quartz fiber filters with sodium carbonate impregnation solution (6.6) by distributing the solution evenly on the filter. Ensure that the filter is completely moistened. Before use, dry the filter in a desiccator at room temperature overnight.

7.2 *Preparation of Samplers*—Load each clean sampler with one impregnated filter (5.2.3) and one pre-filter (5.2.2), and place a spacer between the two filters to prevent contamination. Label each sampler so that it can be uniquely identified, and seal with its protective cover or plug.

7.3 *Air Sampling*—Collect workplace air samples for volatile inorganic acids in accordance with Test Method D7035. Use samplers at their design flow rate and in accordance with the instructions provided by the manufacturer. Use personal sampling pumps calibrated in accordance with Practice D5337.

7.4 *Sample Transport:*

7.4.1 *Samplers with an Internal Cassette*—For samplers with an internal filter cassette, remove the filter cassette from each sampler and fasten with its lid or transport clip.

7.4.2 *Samplers of Disposable Cassette Type*—For samplers of the disposable cassette type, transport the samples to the laboratory in the samplers in which they were collected.

7.5 *Chain of Custody*—If applicable, follow sampling chain-of-custody procedures to document sample traceability. Ensure that the documentation that accompanies the samples is suitable for a chain of custody to be established in accordance with Guide D4840.

8. Analysis

8.1 Wear appropriate personal protection during sample preparation and analysis activities. To minimize the risk of damage or contamination, only handle filters in a clean area where the concentration of HCl and HNO_3 in air is as low as possible and only handle filters using plastic or plastic-coated tweezers (5.7.10).

8.2 *Sample Preparation:*

8.2.1 *Selection of the Extraction Solution*—Decide whether to use water (6.1) or the eluent (6.7.2 or 6.8.10 or 6.8.12), depending on the analytical technique and separator column used to prepare test solutions for the determination of HCl, HBr or HNO_3.

8.2.2 *Extraction of Air Filter Samples:*

8.2.2.1 For equilibration prior to analysis, the filters shall be stored in the closed sampling cassette at room temperature for a minimum of four days.

8.2.2.2 Open the samplers and, using clean plastic or plastic-coated tweezers (5.7.10), remove the pre-filters and sampling filter from the cassette and place them separately into 15 mL screw-cap polyethylene vessels (5.7.3).

8.2.2.3 Pipet 10 mL of extraction solution (8.2.1) into the screw cap vessels containing the air filter samples.

8.2.2.4 Cap the vessels and place them in an ultrasonic bath (5.6.2).

8.2.2.5 Swirl gently to mix the contents, ensuring that the filter remains completely immersed. A final treatment for 15 min in an ultrasonic bath is recommended.

8.2.2.6 If the samples become hot during the extraction step, allow them to cool to ambient temperature before aliquots are removed.

8.2.2.7 For preparation of test solutions for analysis by chemically-suppressed ion chromatography, filter a portion of each sample solution through a PTFE filter (5.7.4), for example, by using a disposable syringe (5.7.5), dispensing each filtrate into an individual, labelled, autosampler vial (5.7.7).

8.2.2.8 For preparation of test solutions for analysis by electronically-suppressed ion chromatography, pass a portion of each sample solution, for example, 2 mL, through a cation exchange resin cartridge (5.7.6) to remove carbonate.

8.2.3 *Analysis:*

8.2.3.1 Inject the calibration solutions into the ion chromatography system in order of increasing concentration and measure the chloride, bromide and nitrate peaks for each calibration solution, in peak area mode.

8.2.3.2 Use the instrument's computer to generate a calibration function using a linear regression. Repeat the calibration if the coefficient of determination, r^2, is not >0.999.

NOTE 9—If r^2 <0.999, it might be possible to remove an erroneous calibration point and reprocess the data to obtain an acceptable calibration.

8.2.3.3 Inject the blank and sample test solutions into the ion chromatography system and make measurements for each solution. Use the stored calibration function to determine the chloride, bromide and nitrate concentrations in mg/L.

8.2.3.4 Analyze the calibration blank solution and a mid-range calibration solution after the initial calibration and then after every ten test solutions. If the measured concentration of chloride, bromide or nitrate in the continuing calibration blank (CCB) is above the method detection limit or, if the measured concentration of chloride, bromide or nitrate in the continuing calibration verification (CCV) has changed by more than ±5 %, take one of the following corrective measures. Either use the instrument software to correct for the sensitivity change (reslope facility), or suspend analysis and recalibrate the instrument. In either case, reanalyze the test solutions that were analyzed during the period in which the sensitivity change occurred, or if this is not possible, reprocess the data to take account of the sensitivity change.

8.2.3.5 Analyze reagent blank solutions, laboratory blank solutions and quality control solutions and use the results to monitor the performance of the method.

8.2.3.6 If concentrations of chloride, bromide or nitrate are found to be above the upper limit of linear calibration range, dilute the test solutions in order to bring them within the linear range and repeat the analysis. Add an appropriate volume of extraction solution (see 8.2.1) when making dilutions, so that the diluted test solutions and the calibration solutions are matrix-matched, and record the dilution factor (DF).

8.2.4 *Estimation of the Method Detection Limit (MDL) and the Method Quantitation Limit (MQL):*

8.2.4.1 Estimate the MDL and the MQL for each of the acids of interest under the working analytical conditions and repeat this exercise whenever experimental conditions (for example, retention time) are changed.

8.2.4.2 Prepare at least ten blank test solutions from unused filters of the same type used for sample collection. Follow sample extraction and filtration procedures used to prepare sample test solutions (8.2.2).

8.2.4.3 Make measurements on the test solutions, and calculate the MDL and MQL for each of the acids of interest as three times and ten times the sample standard deviation of the mean concentration values, respectively.

9. Calculations

9.1 *Calculation of Anion Concentration in Samples*—From the calibration curve, obtain the solution concentration for each sample, C_s (mg/L), and the average blank, C_b (mg/L).

9.2 *Calculation of Concentration of Acid in Air:*—Using the volumes of the sample solution, V_s (mL), and the media blank solution, V_b (mL), calculate the concentration, C_{acid} of HCl, HBr and HNO_3 in the air volume sampled, *V(L)*, while accounting for the dilution factor *DF* and the conversion factor for anion to acid, F_{acid}:

$$C_{acid} = \frac{(C_s \times V_s \times DF) - (C_b \times V_b)}{V} \times F_{acid} \quad (1)$$

where:

C_{acid} = Concentration of acid in air (mg/m^3),
C_s = Concentration of anion in the sample solution (mg/L),
V_s = Volume of the sample solution (mL),
C_b = Mean concentration of anion in the blank solution (mg/L),
V_b = Volume of the blank solution (mL),
V = Sampled air volume (L),
DF = Dilution factor, and
F_{acid} = Conversion factor for anion to acid (1.0284 for Cl^-, 1.0126 for Br^- and 1.0163 for NO_3^-)

NOTE 10—Alternatively, $C = (W_s - W_b) \times F_{acid}/V_m$, mg/m^3 , where W_s and W_b are the amounts of anions in milligrams on the sample and the blank filter, respectively, and V_m is the volume of the air sampled in m^3 (1000 L).

10. Quality Control

10.1 *Laboratory and Field Blanks*—Carry reagent blanks (water and reagents) and media blanks (filters, flasks, syringes) throughout the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory activities. Field blanks shall also be obtained. Process laboratory blanks at a minimum frequency of one per batch.

10.2 *Quality Control Samples:*

10.2.1 Carry spiked media and spiked duplicate media throughout the entire sample preparation and analytical process in order to estimate the method accuracy on the sample batch, expressed as a percent recovery relative to the true spiked value. Spiked samples and spiked duplicate samples consist of filters, to which known amounts of chloride or nitrate have been added. Process these quality control samples according to a frequency of at least 1 per 20 samples, minimum of one per batch.

10.2.2 Monitor the performance of the method by plotting control charts of the relative percent recoveries and of the relative percent differences between the spiked samples and spiked duplicate samples. If quality control results indicate that the method is out of control, investigate the reasons for this, take corrective action, and repeat the analyses. See ASTM Guide D882 for general guidance on the use of control charts.

10.3 *Certified reference materials (CRMs)*—If available, certified reference materials (CRMs) for hydrochloric acid, hydrobromic acid or nitric acid should be analyzed prior to or during routine use of the sample preparation and analytical method to establish whether the percent recovery relative to the certified value is satisfactory.

10.4 *External Quality Assessment*—If the laboratory carries out analysis of volatile inorganic acids in workplace air, on a regular basis, it is recommended to participate in relevant external quality assessment and proficiency testing schemes.

11. Records

11.1 *Sampling Records*—Maintain sampling records in accordance with Test Method D7035.

11.2 *Laboratory Records*—Record all reagent sources (lot numbers and vendors) used for sample preparation and analysis in a laboratory notebook. Record any inadvertent deviations, unusual happenings and notable observations on a real time basis as the samples are processed. Use these records to add supplemental information when reporting the results.

12. Report

12.1 Data to report shall include, at a minimum, the following:

12.2 All sample receipt and chain-of-custody information, if applicable;

12.3 All sample analysis results;

12.4 Applicable quality assurance and quality control data;

12.5 Information on instrumentation and equipment used;

12.6 Instrument parameters used;

12.7 Identity of laboratory and analyst(s);

12.8 Any other information deemed appropriate.

13. Precision and Bias

13.1 *Interlaboratory Evaluation*—An interlaboratory evaluation of the method was carried out by three laboratories at a test gas facility using different sampler and filter types. At different concentrations between 1.0 mg/m^3 and 12 mg/m^3 for HCl and 1.0 mg/m^3 and 12 mg/m^3 for HNO_3 and environmental conditions (humidity ~25 %-75 %) samples were taken (**2**). The three samplers (**7**) showed a slightly different recovery:

TABLE 1 Mean Recovery of Hcl and Hno_3 on Three Different Personal Air Samplers

NOTE 1—The lower recoveries obtained with the IOM sampler were due to practical difficulties mounting multiple filters in the filter cassette.

Sampler Type	Mean Recovery of HCl	Mean Recovery of HNO_3
GSP^A	99.0 ± 2.3 %	94.0 ± 4.9 %
CFC^B	97.8 ± 4.8 %	93.3 ± 4.5 %
IOM^C	88.9 ± 11.9 %	88.1 ± 10.0 %

^{A}*GSP*: GSP sampler with plastic cone designed to operate at an air flow of 2 L/min; 37-mm quartz fiber pre-filter and quartz fiber filter impregnated with 500 µL 1 M Na_2CO_3, separated by a polypropylene spacer.

^{B}*CFC*: Closed face cassette, 3-piece design, air flow 2 L/min, 37-mm PVC-A pre-filter and 2 quartz fiber filters impregnated with 500 µL 5 % Na_2CO_3 in series. Results reported are the sum of those obtained from both impregnated filters.

^{C}*IOM*: Air flow 2 L/min, 25-mm quartz fiber pre-filter and quartz fiber filter impregnated with 200 µL 2.5 M Na_2CO_3 separated by a polypropylene spacer.

Data for precision (in terms of repeatability and reproducibility) were processed in accordance with EN 482. Repeatability was calculated by using the data from method development for each acid level. Precision data are summarized in Table 2.

TABLE 2 Repeatability, Recovery, and Reproducibility for Volatile Acids Measurements from Performance Evaluation

Acid Level	Number of Samples	Concentration (mg/m^3)	Recovery	S_r	RSD_r
HCl					
Low	6	0.136	0.984	0.0028	0.021
Medium low	6	0.345	1.003	0.0046	0.013
Medium high	6	2.69	1.020	0.0151	0.006
High	6	6.53	0.984	0.0757	0.012
Mean recovery			0.994		
HNO_3					
Low	6	0.77	1.026	0.0042	0.029
Medium low	6	0.332	1.031	0.0058	0.019
Medium high	6	2.58	1.009	0.0499	0.019
High	6	6.28	0.972	0.0991	0.016
Mean recovery			1.006		
HBr					
Low	6	0.129	1.024	0.0011	0.008
Medium low	6	0.652	1.003	0.0062	0.009
Medium high	6	3.07	1.005	0.0266	0.009
High	6	9.73	0.992	0.1384	0.014
Mean recovery			1.006		

13.2 *Sampler Capacity*—At very high acid concentrations the sampler capacity can result in a reduced recovery. At acid concentrations of 10 mg/m^3 for HCl and HNO_3, a 4 h sampling time with an air flow rate of 2 L/min is possible using a 12 filter impregnated as given in 5.2.3. For a longer sampling time of up to 8 h, the flow rate is reduced to 1 L/min.

NOTE 11—Acid concentrations of ≥9 mg/m^3 for HCl and HNO_3 at the same time are not to be expected in normal workplaces.

13.3 Estimates of method recovery were computed by simply dividing the difference between the measurand and the reference value by the reference value, $B = (\mu_i - R_i)/R_I$, where μ_i and R_i are the mean and reference acid contents, respectively, for the ith acid loading level in each performance evaluation sample. Bias data from the method development study are summarized in Table 3.

TABLE 3 Interference Measurements from Performance Evaluation

Interference	Number of samples	Recovery^A	
		HCl	HNO_3
Without interference	6	0.97	0.93
Fe_2O_3	6	0.95	0.91
ZnO	6	<0.05	<0.05
Welding fume MIG/MAG	6	0.66	0.62
Welding fume FCAW	6	0.51	0.33

^{A}Calculated for the sampling filters.

14. Interferences

14.1 The ubiquitous presence of chlorides and nitrates leads to blank values being produced by the reagents and equipment used in the method (chemicals, glassware). Therefore the blank values of all chemicals and equipment have to be carefully checked.

14.2 *Alkaline Substances*—An interlaboratory evaluation of the method was carried out at a test gas facility using different sampler and filter types. Samples were collected at a concentration of 2 mg/m^3 for HCl and HNO_3 under typical environmental conditions (temperature ~20°C, humidity ~50 %). For estimation of possible interferences the pre-filter was preloaded with a number of potential interferents. It was found that iron, zinc oxide and welding fume can react with the acid gases and lead to significant decreases in measured acid concentrations. Iron oxide was found not to interfere with the determination (**2**). Interference data are summarized in Table 3.

14.3 *Other Acids*—If particulate salts of the volatile acids are collected on the pre-filter together with another strong acid this leads to displacement of chloride, bromide and nitrate and results in a positive interference on acid results (**2**).

14.4 *Filter Materials*—A detailed study on the suitability of filter materials has shown that not all filter materials can be used effectively for sampling volatile acids in workplace air (**2**). Hydrophobic filter materials like PTFE are difficult to impregnate with aqueous solutions and are suitable for use only as pre-filters, while other filter materials such as PVC or cellulose nitrate cause a significant blank value for some anions (notably Cl^- and NO_3^-, respectively). Quartz fiber filters are the most suitable filter types for sampling of inorganic acids. Several manufacturers offer quartz fiber filters commercially; nevertheless it is essential to check the quality of each filter batch used for sampling inorganic acids.

15. Keywords

15.1 filter; hydrobromic acid; hydrochloric acid; ion chromatography; nitric acid; workplace air

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