Designation: D6735 – 01 (Reapproved 2009)

Standard Test Method for
Measurement of Gaseous Chlorides and Fluorides from Mineral Calcining Exhaust Sources—Impinger Method[1]

This standard is issued under the fixed designation D6735; 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 (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

The bias and precision statements included in Section 14 of this test method are based on field test measurements at limestone calcining sources. Procedures for assessing the test-specific bias and the precision at each source are included in the body of the method.

Additional optional procedures are included in Appendix X1 that can be used to demonstrate the bias and precision of the method for specific source categories. These procedures were used to develop the bias and precision statements included in Section 14 and may be applied when using the method at sources where no previous test data have been acquired.

1. Scope

1.1 This method will measure the concentration of gaseous hydrochloric and hydrofluoric acids, and other gaseous chlorides and fluorides that pass through a particulate matter filter maintained at 177°C (350°F). This method is specific for sampling combustion effluent from mineral calcining industries and other stationary sources where the reactive/adsorptive nature of the particulate matter may affect measurements.

1.2 This method utilizes ion chromatography to quantify the aqueous samples, and thus measures only the $C1^-$ and F^- ions.

1.3 Based on a one-hour sampling run, the method will provide results of known accuracy and precision for chloride and fluoride in-stack concentrations of 0.5 ppm (v) dry or greater. Extending the run duration and sampling a greater volume of effluent will extend the range to lower concentrations.

1.4 This method includes optional post-test quality assurance procedures to assess the bias of the test results, and optional paired sample train runs to assess the precision of test results.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D2986 Practice for Evaluation of Air Assay Media by the Monodisperse DOP (Dioctyl Phthalate) Smoke Test (Withdrawn 2004)[3]

D3195 Practice for Rotameter Calibration

D6348 Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared (FTIR) Spectroscopy

2.2 *EPA Standards:*[4]

Method 1—Sample and Velocity Traverses for Stationary Sources

Method 2—Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)

Method 3—Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight

Method 4—Determination of Moisture Content in Stack Gases

---

[1] This test method 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, 2009. Published December 2009. Originally approved in 2001. Last previous edition approved in 2001 as D6735 - 01. DOI: 10.1520/D6735-01R09.

[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] The last approved version of this historical standard is referenced on www.astm.org.

[4] United States Environmental Protection Agency Code of Federal Regulations, 40 CFR Parts 60 and 63, available from the Government Printing Office, Washington, DC.

Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media

3. Terminology

3.1 See Terminology D1356 for definition of terms used in this test method.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *analyte spike, n*—the optional procedure contained in this method to assess bias attributed to the measurement system. The analyte spike procedure consists of adding a known amount of the certified compressed gas into the impinger train upstream of the particulate filter after the end of a run.

3.2.2 *blank train, n*—an impinger train that is assembled and recovered but does not collect effluent gas. The blank train provides an estimate of the amount of contamination that can occur during a field test.

3.2.3 *certified compressed gas, n*—an HCl or HF gas standard that is certified by the manufacturer to a known degree of accuracy. For HCl and HF compressed gas standards the accuracy is often certified to 5–10 % of the certified value.

3.2.4 *conditioning run, n*—a sampling run conducted before the first run of the test series. The impinger contents from the conditioning run are not analyzed nor included in the test results.

3.2.5 *cylinder gas analysis, n*—a procedure to verify the concentration of the certified compressed gas and to provide the direct cylinder value. See 11.2.7.4.

3.2.6 *direct cylinder value, n*—the value of the certified cylinder gas, or the value obtained from conducting the cylinder gas analysis. See 11.2.7.4.

3.2.7 *hazardous air pollutants (HAPs), n*—approximately 188 compounds or groups of compounds identified in Title III of the Clean Air Act Amendments.

3.2.8 *impinger train, n*—a series of midget impingers connected together by glass or TFE-fluorocarbon u-tubes.

3.2.9 *midget impinger, n*—cylindrical glass (or other appropriate material) containers that hold approximately 50 mL.

3.2.10 *mineral calcining industry, n*—industries that use thermal devices to remove CO_2 and other compounds from non-ferrous mineral material.

3.2.11 *paired runs, n*—two impinger trains operated simultaneously at the same sampling location.

3.2.12 *partition ratio, n*—the amount of a substance at equilibrium with its gas and particulate phases.

3.2.13 *proportional controllers, n*—a temperature control device that uses a sensor to make small adjustments to the power output. These types of controllers prevent wide fluctuations in the temperature of the heated measurement system components.

3.2.14 *reagent blank, n*—a 20–30 mL sample of the 0.1 N H_2SO_4 impinger solution that is diluted to 100 mL.

3.2.15 *sampling system leak check, n*—a procedure that tests the sampling system for negative pressure leaks.

3.2.16 *spiked train, n*—a train in which HCl(g) or HF(g) has been added after the test run to determine measurement system bias.

3.2.17 *"u" tubes, n*—connecting tubes constructed of either glass or TFE-fluorocarbon to assemble the impinger train.

3.2.18 *volatile compounds, n*—compounds that are gases at the effluent temperature.

4. Summary of Test Method

4.1 *Sampling:*

4.1.1 This method involves collecting an integrated sample of stack gas in a series of five midget impingers. Two of the five impingers contain 0.1 N H_2SO_4, two are empty and one contains silica gel.

4.1.2 Sampling is conducted from a single point within the stack or duct at a constant sampling rate of 2 L/min (±5 %) for a period of at least one h per sample run.

4.1.3 The sampling system heated components must be maintained at a temperature of 350 ± 15°F (177 ± 8°C). The sampling system is conditioned before conducting the first run by sampling 120 L of stack gas at 2 L/min, and then discarding the impinger solutions.

4.1.4 A test is comprised of three or more sample runs.

NOTE 1—The conditioning run is to minimize HCl and/or HF adsorption during the ensuing sampling runs by passivating active sites in the probe and filter box components.

NOTE 2—The impingers from the conditioning run are rinsed thoroughly with deionized water before recharging to start the first run. Rinsing the probe and filter assembly must not be performed.

NOTE 3—The particulate matter from mineral calcining facilities adsorbs HCl and HF to varying degrees. The amount of adsorption depends on process parameters and the physical/chemical properties of the dust. Measures such as turning the probe nozzle opening away from the stack or duct flow minimize collection of particulate matter on the filter material and thus reduce the adsorption of HCl and HF. Other measures that reduce collection of particulate matter are acceptable. Such measures include installing a shrouded large pore sintered filter (> 20 microns) on the end of the probe. This apparatus will reduce collecting particulate matter while allowing gases and small particles to enter.

4.2 *Analysis:*

4.2.1 Quantification of chloride and fluoride ions is accomplished by analyzing an aliquot of the impinger solution using ion chromatography.

4.2.2 The total mass of chloride or fluoride ions collected in the impinger solution sample is a product of the ion chromatographic (IC) output in either mg or µg and the total volume of the sample. For example, if the IC analysis for chloride is 0.02 mg, and the total sample volume is 100 mL, then the total mass of chloride collected for the run is equivalent to 2 mg (assuming a 1-mL injection into the IC).

4.2.3 Use the following equation to determine the total mass of chloride or fluoride ions in the sample.

$$(IC/IV)*(SV) = \text{mg of ion in total sample} \qquad (1)$$

where:

IC = ion chromatographic results in mg,
IV = volume of sample injected into ion chromatograph in mL, and
SV = sample volume in mL.

4.2.4 The equivalent in-stack concentration of the sample is equivalent to the mg catch of anion in the impinger solution sample divided by the gas sample volume at standard conditions.

5. Significance and Use

5.1 This field-test method provides chloride and fluoride concentration results on a dry basis. Concentration data for gaseous chlorides and fluorides are assumed to be hydrochloric acid gas, and hydrofluoric acid gas when calculating mass emission rates.

5.2 Mass emission rates of HCl and HF can be calculated if the effluent volumetric flow rate is known. Volumetric flow rates can be calculated by conducting EPA Methods 1–4 or their equivalents.

5.3 This field test method provides data having bias and precision for HCl consistent with the values in Section 14. In addition, the test-specific bias can be assessed for each test by conducting the post-test quality assurance check. The procedure is identified as optional, and the performance of this procedure depends on the test specific data quality objectives, and end use of the data.

5.4 The test-specific precision may be determined by conducting paired-runs. Paired runs aid in identifying possible suspect data and provide backup in the event one train is invalidated. Performing paired runs depends on the test-specific data quality objectives.

5.5 The reaction of gaseous HCl with ammonia (NH_3) to form solid ammonium chloride (NH_4Cl) is well known. At stack temperatures common to the exits of baghouses and ESPs at mineral calcining facilities (that is, 250 to 450°F or 121 to 232°C), an equilibration between the gaseous HCl/NH_3, the condensed $NH_4Cl(s)$, and the effluent particulate matter can exist. It is impossible to know the exact partition ratio between the gas and particulate phases of these compounds in the sampling system. Furthermore, it is very difficult to control the effects of these partitioning reactions within the various sampling system components.

NOTE 4—Use of this method is cautioned when trying to quantify HCl (g) in the presence of ammonium chloride and ammonia.

6. Interferences

6.1 *Sampling Interferences:*

6.1.1 The particulate matter (dust) from mineral calcining industries adsorbs HCl and HF to a varying degree, which will reduce the amount of gaseous chloride and fluoride ions that reach the impinger solutions.

6.1.2 Condensed water vapor in the probe and filter area due to heater failure or poor heating will reduce the amount of gaseous chloride and fluoride ions reaching the impinger solutions.

6.1.3 Improper filter seating in the filter holder will allow leakage of particulate matter into the impinger solutions. This may result in more chloride and fluoride ions reaching the impinger solutions.

6.2 *Analytical Interferences*—Ensuring that the chromatographic conditions are optimized for separating chloride and fluoride from other ions minimizes analytical interferences.

7. Apparatus

7.1 *Sampling*—See Fig. 1.

7.1.1 *Sample Probe Assembly,* including a probe liner of borosilicate glass, stainless steel, or TFE-fluorocarbon of (*1*) sufficient length to reach the gas sampling point, (*2*) of physical integrity to minimize adsorption of HCl and/or HF, and (*3*) heated and controlled to sustain the sample temperature at 350 ± 15°F (177 ± 8°C). The internal diameter of the probe liner should be between 0.25-0.5 in. (0.1-2 cm). The probe assembly shall minimize collection of particulate matter but allow gases and small particles to pass.

NOTE 5—The assembly could consist of an in-stack large pore sintered filter (>20 microns) with a shroud, or a nozzle that is positioned away from the flow stream.

NOTE 6—A specially designed probe that utilizes fore and aft independent heater and heater controllers has proven to be capable of maintaining the 350°F temperature throughout the length of the probe. This is crucial when a portion of the probe is inserted into a hot stack but the remainder of the probe is out of the stack at a much cooler relative temperature. Use of this probe design will minimize or eliminate moisture condensation and thus adsorption of HCl and HF.

7.1.2 *Particulate Filters,* rated at 0.3 µm (or less), and having an efficiency of 95 % or greater in accordance with Practice D2986. The filters are placed immediately after the heated probe in a heated and temperature-controlled compartment. A TFE-fluorocarbon-glass filter (75 % TFE-fluorocarbon, 25 % glass), or an ultra high purity quartz filter must be used to remove particulate matter.

7.1.3 *Particulate Filter Holders,* filter holders and supports should be made out of TFE-fluorocarbon or TFE-fluorocarbon coated stainless steel.

NOTE 7—The TFE-fluorocarbon filter holder and filter support must be capable of withstanding the 350°F (177°C) filter temperature.

7.1.4 *Impingers,* five midget impingers (about 50 mL volume) with straight stems and with leak-free glass connections. The first and fourth impingers in the train are empty, the second two impingers each contain 15 mL of 0.1 N H_2SO_4 absorbing solution, and the fifth contains silica gel. Silicone grease may be use to aid joining the impinger connections.

7.1.5 *Silica Gel (or equivalent),* used to protect the dry gas meter and pump. The silica gel is not part of the sample.

7.1.6 *U-Tubes,* glass or TFE-fluorocarbon connecting tubes to assemble the impinger train.

7.1.7 *Leak Free Sample Connector,* sample line to connect the silica gel impinger to the pump and gas-metering device.

7.1.8 *Rate Meter,* flow measurement device sufficient to maintain constant rate sampling at 2 L/min ±5 % or less.

7.1.9 *Volume Meter,* capable of measuring the volume of gas sample at a flow rate of 2 L/min with an accuracy of ±2 %, and a resolution of 0.01 L or better.

7.1.10 *Pump,* leak free diaphragm type or equivalent capable of maintaining a sampling rate of 2 L/min at the static pressure encountered in the stack or duct.

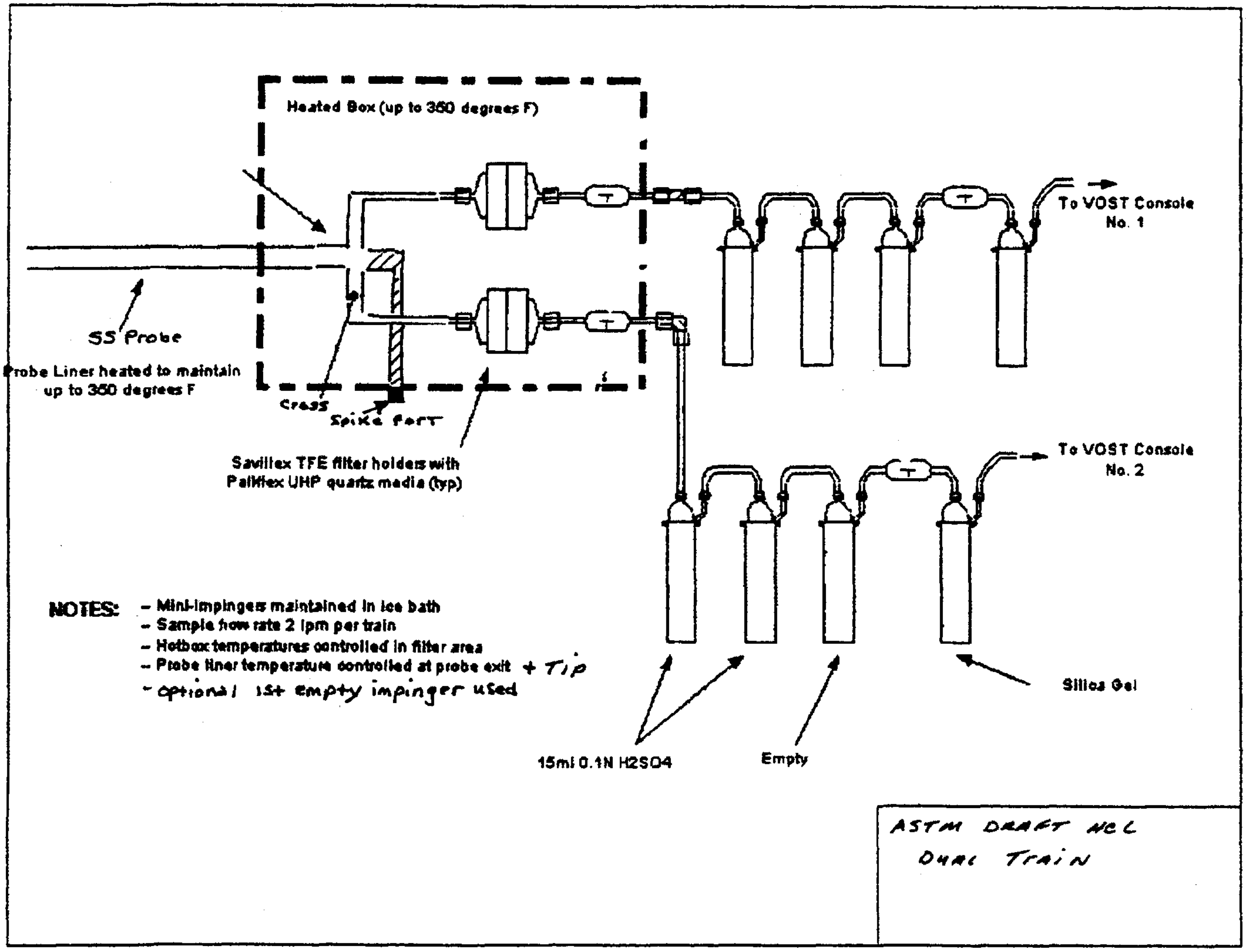

FIG. 1 Sampling Train Configuration

7.1.11 *Thermocouples or Other Temperature Measure Device,* to monitor the temperature of the probe and filter accurate to within one degree.

NOTE 8—Position thermocouples to indicate the sample gas temperature at the probe outlet. Ambient temperature or the length of probe inserted into the stack or duct should not adversely affect the accuracy of the probe temperature measurements. It is recommended that dual heaters and temperature controllers be used in the sampling probe. Determine the filter temperature by inserting a thermocouple into the filter holder behind the filter or attached directly to the exterior of the filter holder. The tester must prevent the thermocouple sensor from the direct radiant heat from the heater element, and allow sufficient time for the actual filter assembly to reach thermal equilibrium before beginning sampling.

7.1.12 *Barometer,* capable of measuring the atmospheric pressure to within 2.5 torr (0.1 in. Hg, 10.1 Kpa).

7.1.13 *Ice,* for impinger ice water bath.

7.2 *Sample Recovery:*

7.2.1 *Polyethylene Wash Bottles,* to contain the deionized water or acid impinger solution.

7.2.2 *Polyethylene Sample Storage Bottles,* to store the samples.

7.2.3 *100 mL Graduated Cylinders,* to measure the volume of the impinger samples.

7.3 *Reagent Preparation:*

7.3.1 *Class A Volumetric Flasks, Graduated Cylinders and Pipets,* to prepare the acid absorbing solution and to prepare the diluted calibration standards for the ion chromatograph.

7.4 *Instrumentation:*

7.4.1 *Ion Chromatograph,* operated under conditions that satisfy the requirements of 11.4.

8. Reagents and Materials

8.1 All reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

8.2 *Sampling:*

8.2.1 *Water,* deionized (DI), distilled. See Specification D1356.

8.2.2 *Acidic Absorbing Solution,* 0.1 N Sulfuric Acid (H_2SO_4). To prepare 100 mL of the absorbing solution for impinger solutions, slowly add 0.28 mL of concentrated H_2SO_4 to about 90 mL of water while stirring. Adjust the final volume to 100.00 mL in a volumetric flask using additional water. Shake well to mix the solution. (2.8 mL in 1 L for larger volume of reagent).

8.3 *Sample Preparation and Analysis:*

8.3.1 *Water*—Same as in 8.2.1.

8.4 *Analysis:*

8.4.1 *Halide Salt Stock Standard Solutions*—Prepare concentrated stock solutions from solid reagent grade sodium chloride (NaCl), and sodium fluoride (NaF). Dry the solid at 110°C for two or more hours and then cool to room temperature in a desiccator immediately before weighing. Weigh the solid to 0.01 mg. Prepare a nominal 1000 mg/L solution of target compound by dissolving 1650 mg of the NaCl solid (2200 for NaF) in slightly 1 L of deionized water and then bring to exactly 1 L volume. Use the following equation to calculate the actual stock solution concentration.

$$X = Y*(35.45/58.44) \tag{2}$$

where:

X = concentration of resulting salt solution in units of mg in 1 L,

Y = mg of NaCl dissolved in 1 L, and

(35.45/58.44) = the available $C1^-$ ions dissociated from a solution of NaCl.

Prepare a fluoride stock solution using this similar calculation:

$$X = Y*(18.99/41.99) \tag{3}$$

where:

X = concentration of resulting salt solution in units of mg in 1 L,

Y = mg of NaF dissolved in 1 L, and

(18.99/41.99) = the available F^- ions dissociated from a solution of NaF.

Alternately, solutions containing a certified nominal concentration of 1000 mg/L NaCl and NaF may be used.

9. Hazards

9.1 *Target Analytes*—HCl (g) and HF(g) are mucus membrane irritants. Therefore, avoid exposure to these chemicals.

9.2 *Certified Compressed Gaseous Calibration Standards*—Compressed gaseous HCl and HF are dangerous goods, are difficult to ship and to transport, can cause problems with OSHA and MSHA regulations at various mineral calciner facilities, can become airborne due to damage at the valve stem, and the contained gas is an asphyxiant. These cylinders must not be used at elevated sampling locations, and great care should be exercised during their use. Shipping compressed gases is problematic and can carry significant fines. The decision to use compressed gases in the application of this test method should be considered carefully.

9.3 *Sampling Locations*—This test method may involve sampling at locations with high positive or negative pressures, high temperature, elevated height, or high concentrations of hazardous or toxic pollutants. Exercise appropriate safety precautions to avoid accidents when working under these conditions.

9.4 *Concentrated Sulfuric Acid*—Take precaution in the handling and use. Always add the acid to the water in small quantities until thoroughly mixed.

10. Calibration and Standardization

10.1 *Ion Chromatograph*—Prepare successive dilutions from the nominal 1000 mg/L (8.4.1) stock chloride and fluoride solutions at concentration levels ranging from 0.2 mg/L to 5 mg/L (or other appropriate concentration range) using the appropriate volumetric glassware. For example:

10.0 mL of 1000 mg/L diluted to 1 L = 10 mg/L (working standard)
10 mL of 10 mg/L diluted to 500 mL = 0.2 mg/L
10 mL of 10 mg/L diluted to 200 mL = 0.5 mg/L
20 mL of 10 mg/L diluted to 200 mL = 1 mg/L

11. Procedure

11.1 *Pretest Preparations and Evaluations*—Prepare at least two sets of impinger trains to conduct paired sampling runs or a single train if sequential runs will be conducted. Preparing additional impinger trains may minimize turn around time between runs.

11.1.1 *Flow Rate and Moisture Determination*—Perform EPA Methods 1 through 4 or equivalent if effluent volumetric flow rate data are needed.

11.1.2 *Preliminary Leak Check*—Conduct a sampling system leak check from the probe tip through the entire sampling system for each sample train. Pull a vacuum equal to that expected during the sampling run. Leakage rates in excess of 1 % of the sampling rate (that is, 20 mL/min for a 2 L/min-sampling rate) are unacceptable. If a leak is determined, isolate the impinger train from the probe and filter to determine the source of the leak. If no leak is found in the impinger train, the leak is in the probe and filter assembly. Re-seat all of the connecting fittings and conduct the leak check again.

11.1.3 *Conditioning Run*—Assemble the impinger train(s) and conduct a conditioning run by collecting 120 L of gas over a one-hour period. Follow the sampling procedures outlined in 11.2.4. Ensure that the impinger train is cooled in an ice water bath to condense the stack gas HCl and HF.

NOTE 9—For the conditioning run, water can be used as the impinger solution.

11.1.4 *Conditioning Run Sample Recovery*—Remove the impinger train from the filter box. Leave the probe and filter box in position. Do not recover the filter or rinse the probe before the first run. Thoroughly rinse the impingers with DI water and discard these rinses.

NOTE 10—Leaving the probe in the stack and the filter assembly intact allows an impinger train to be easily removed and replaced with a fresh impinger train.

NOTE 11—The probe and filter assembly are conditioned by the stack gas and never recovered or cleaned until the end of the testing.

11.2 *Sampling:*

11.2.1 *Assemble Train*—Charge the second two impingers with 15 mL of 0.1 N H_2SO_4, (the first and fourth impingers should be empty at the start of each run). Place a fifth impinger containing silica gel or other applicable drying agent in front of the dry gas meter. Assemble the impinger train and connect it to the probe and filter box. Ensure that there is sufficient ice in the ice water bath.

11.2.2 *Temperature Equilibrium*—Adjust the probe and filter to 350°F (177°C). Locate the sensing thermocouple (*1*) within the filter holder behind the filter support, (*2*) by attaching directly on the exterior filter housing or on the connecting fittings at the inlet to the filter. Allow the temperature to equilibrate before beginning each run (or conditioning run).

NOTE 12—The sampling system temperature must be 350 ± 15°F (177 ± 8°C). Most test equipment is not configured to control the temperature in such a narrow range. Sampling equipment with on/off controllers should be examined carefully to determine if the required temperature tolerances of this method can be maintained. The use of proportional controllers for the probe and filter compartment heaters is usually required so that wide variations in temperature do not occur, and the temperature requirements of the method can be met.

11.2.3 *Leak-Check*—Conduct a leak check through the impinger train. A leakage rate in excess of 1 % of the sampling rate (that is, 20 mL/min for a 2-L/min sampling rate) is unacceptable. See 11.1.2 for suggestions to repair the leak.

NOTE 13—The leak check is conducted from the probe tip through the impinger train before beginning the conditioning run, and then from the impinger train back thereafter provided that the probe/filter box assembly connections remain intact at the end of each run (that is, the impinger train is removed from the filter after the run).

11.2.4 *Sample Collection:*

11.2.4.1 Ensure that the probe and filter box are equilibrated at the proper operating temperature. Record the initial dry gas meter volume. Put the probe into the stack and turn the sample pump on. Adjust the flow rate to 2 L/min.

11.2.4.2 *Record*—(*1*) the temperature of the heated components, (*2*) the sample flow rate, and (*3*) the accumulated dry gas meter volume at least every 5 min. Maintain and record the temperature and the sample rate for the duration of the run. The heated components must be maintained at 350 ± 15°F (177 ± 8°C).

11.2.4.3 At the end of the run disconnect the impinger train from the back half of the filter. Record the final dry gas meter volume.

11.2.5 *Post-Test Leak Check*—Conduct a leak check through the impinger train from the front of the first impinger through the volume meter. A leakage rate in excess of 1 % of the sampling rate (that is, 20 mL/min for a 2 L/min sampling rate) is unacceptable, and the run is invalid. The leak check vacuum must be equal to that encountered during the sampling run. Gently release the vacuum on the train, turn off the pump, and disconnect the impinger train from the meter box. Leave the probe and filter box heat on. Connect a new impinger train as soon as allowable, and conduct the leak check procedure before starting the next run.

11.2.6 Three or more sampling runs constitute a test. A test can be comprised of either three (or more) pairs of samples, or three (or more) single samples. The test specific data quality objectives determine the appropriate conditions for each test.

11.2.7 *Post-Test Analyte Spike—Quality Assurance Bias Check*—This optional procedure consists of adding a quantitative mass of either HCl or HF gas from the certified compressed gas cylinder into the sampling train upstream of the filter. For practical purposes, paired runs should be conducted if the spike procedure is performed.

11.2.7.1 *Spike Procedure*—After a successful post-test leak-check, connect the spike assembly to the impinger train so that the spike gas is delivered upstream of the particulate matter filter and into the impinger train. Connect the compressed gas standard to the inlet of the spike assembly using TFE-fluorocarbon tubing.

NOTE 14—Purge the spike assembly (TFE-fluorocarbon tubing and fittings) with the gas before completing the final connection to the sample box filter inlet.

11.2.7.2 Record the dry gas volume reading, turn on the sample pump and adjust the sample flow rate to 2 L/min. Introduce enough volume so that a mass of HCl or HF equivalent to the concentration level of interest is added. Alternately add a minimum of 0.5 to 2 mg or more (where indicated) of chloride or fluoride ions into the train.

11.2.7.3 The spike gas is delivered to the filter box at a rate greater than the 2 L/min. The spike gas is drawn into the train by the sample pump at a rate of 2 L/min, and the excess spike gas is vented through the probe into the stack. This procedure allows the sampling train to operate identically to that during actual sampling.

NOTE 15—Purge the regulator used to deliver the gas to the spike assembly with dry air or nitrogen before and after each use to avoid adsorption and corrosion of the stainless steel interior by the acid gases.

11.2.7.4 Determine the direct analysis value of the spike gas cylinder using the spike procedure (11.2.7). Flow the gas into the sampling train without the filter in place. Analyze the sample in triplicate in accordance with Sections 11 and 12 of this method.

11.2.7.5 *Calculate the Spike Delivered*—Example calculation:

$$Cyl\,(dir)\ \text{ppm}\,(v) = 100\ \text{ppm}\,(v) \tag{4}$$

$$100\ \text{ppm}\,(v)\,(\text{dry})*(36.5/24.05) = 151.8\ mg/DSCM\ \text{for HCl}$$

$$151.8\ mg/DSCM*DSCM\ \text{of spike delivered}$$

$$= mg\ \text{HCl delivered into train}$$

where:

Cyl (dir) = direct cylinder analysis from 11.2.7.4 or tag value, and

mg/DSCM = conversion from cylinder ppm (v) to mg/DSCM ppm (v) * MW/24.05 (at standard conditions).

NOTE 16—If the spike procedure is to be followed by additional runs, then the probe/filter box assembly must be purged of spike gas before beginning the next sample run. This is accomplished by connecting a sample train and sampling gas for a period of 10 min or greater. This purge train is not analyzed, and may be reused again as a purge train.

11.2.7.6 If the average value of the results provided by 11.2.7.4 and 11.2.7.5 above are within ±10 % of the certified cylinder tag value, then use the cylinder tag value as Cyl (dir).

11.3 *Sample Recovery*—After the post test leak-check, disconnect the impinger train from the heated filter compartment. Quantitatively transfer the contents of the first (water knockout) impinger, the second and third 0.1 N H_2SO_4, acid impingers, and the fourth impinger into a graduated cylinder. Rinse the impingers and the connecting u-tubes with distilled deionized water and add these rinses to the graduated cylinder. Note the sample volume on the recovery data sheet, and transfer the contents to a polyethylene bottle. Seal the bottle, label and mark the liquid level.

NOTE 17—The total contents should approximate 100 mL.

NOTE 18—The 100-mL volume is guidance, however, excessive rinse volumes will result in an increase in the apparent detection limits. The method detection limits are directly proportional to the total collected liquid volume submitted for IC analysis.

11.4 *Blanks:*

11.4.1 *Blank Train*—Assemble a sampling train. Charge the impingers with absorbing solution and allow the train to sit for one hour or more. Recover this blank train as described in 11.3. Use about the same amount of water to recover this train as that is used for actual sample trains. Acquire one blank train at each facility.

11.4.2 *Reagent Blank*—Save for analysis a portion of the acidic absorbing solution equal to that amount used in the impingers. Dilute this sample with DI water to simulate the amount of sample plus rinses collected during the actual test run. Seal the bottle and mark the liquid level. Acquire one blank for each test series and each set of reagents prepared.

11.5 *Sample Analysis*—Determine the exact sample volume (to within ±1 mL) by pouring the contents of the polyethylene sample bottle into a graduated cylinder (for sample volumes greater than 100 mL) or a 100–mL volumetric flask.

11.5.1 *Ion Chromatograph*—Operate the ion chromatograph and detector under conditions that facilitate near baseline separation of chloride and fluoride ions from each other and from other eluting anions (that is, nitrite, nitrate, phosphate, sulfate, and bromide).

11.5.2 *Instrument Stabilization*—Establish a stable baseline and analyze a deionized water blank. Analyze the blank to ensure that the analytes of interest are not present as instrument background.

11.5.3 *Instrument Calibration*—Prepare a calibration curve by conducting duplicate analysis of chloride/fluoride standards at concentration levels ranging from 0.2 mg/L to 5 mg/L (or other appropriate level). See 8.4 and 10.1 of this standard.

11.5.4 *Establish Calibration Curve*—Determine the peak area (or height) for each duplicate standard injection. The deviation from the mean for each duplicate injection should not exceed 5 %. Use either linear regression or response factors to establish the calibration. A regression coefficient of greater than 0.98 or a % RSD of the response factors of 5 % or less indicates a valid calibration curve. Report the calibration curve results in the final report.

11.5.5 *Analysis*—Analyze the field samples, quality assurance spike sample if conducted, blank train and reagent blank using the calibration curve. Analyze the QA spike sample twice and determine the percent deviation from the mean of the measurement results.

12. Calculations

12.1 *Gas Sample Volume*—Calculate the sample volume in accordance with the following equation:

$$\text{L final} - \text{L starting} = \text{Dry L Gas Sample Volume (actual conditions)} \tag{5}$$

12.2 *Total mg of HCl, HF per Sample*—Calculate the total mass of anion per sample in accordance with the following equation:

$$((IC/IV)*(SV)) - RB = \text{Total mg anion} \tag{6}$$

where:

IC = ion chromatographic results in mg,
IV = volume of sample injected into ion chromatograph in mL,
SV = sample volume in mL, and
RB = reagent blank mg value (if RB ≤ detection limit then RB in 12-2 = 0). RB must be less than 1 µg/mL for use in this equation.

12.3 *Calculate the Equivalent Flue Gas Concentration—mg/DSCM*—Calculate the equivalent flue gas concentration of HCl and HF (this assumes all gaseous chlorides and fluorides collected are HCl and HF) in accordance with the following equation:

$$\text{Total mg anion/Total sample volume } DSCM = mg/DSCM \text{ of anion} \tag{7}$$

$$mg/DSCM*K = mg/DSCM \text{ for HCl}$$

where:

K = 36.5/35.5 for the ratio of HCl to Cl^-

and:

K = 20.01/18.99 for the ratio of HF to F^-, and
$DSCM$ = dry standard cubic meters of gas collected.

To correct to standard sample volume use the following correction:

$$\text{L (dry) collected}*(Tstd/Tmeas)*(Pmeas/Pstd)*(1 \times 10^{-3}) = DSCM \tag{8}$$

where:

$Tstd$ = 293 K, and
$Pstd$ = 29.92 in. Hg (101.32 Kpa).

12.4 *Calculate the Equivalent Flue Gas Concentration—ppm (v)(dry)*—Calculate the equivalent flue gas concentration of HCl and HF in ppm (v) in accordance with the following equation:

$$[mg/DSCM*(24.05/mw)] = ppm\ (v)(dry) \text{ HCl or HF} \tag{9}$$

where:

24.05 = L/mol @ standard conditions (101.32 kPa (29.92 in. Hg) and 20°C),
MW = 36.5 g/mol for HCl, and
MW = 20.01 g/mol for HF.

12.5 *Calculate the Mass Emission Rate—g/h*—Calculate the mass emission rate (if required) in accordance with the following equation:

$$mg/DSCM*Q*(1 \times 10^{-3})*60\text{min} = \text{g/h} \tag{10}$$

where:

$mg/DSCM$ = derived from 12.3, and
Q = effluent volumetric flow rate in DSCM/min.

To convert to lb/h use to convert use 453,592 mg/lb.

NOTE 19—Concentration data may be corrected to any oxygen diluent level. For example, to correct the concentration data to 7 % O_2 use the following equation:

$$ppm\,(v)\ @\ 7\ \%\ O_2 = ppm\,(v)\ \text{actual}*((20.9 - 7)/(20.9 - \% - O_2\ \text{actual})) \tag{11}$$

12.6 *Calculate the Percent Recovery of the Optional QA Spike*—Calculate in accordance with the following equation:

$$\%\,R = CX/(CY + CZ)*100 \tag{12}$$

where:

$\%\,R$ = percent recovery of the spike,
CX = mass in mg of CI or F ions in the spiked sample,
CY = mass in mg of Cl^- or F^- ions of spike added in accordance with Eq 4, and
CZ = mass in mg of Cl^- or F^- ions in unspiked sample.

NOTE 20—The unspiked sample value is the resulting sample value from the unspiked train when conducting paired runs, or if sequential samples are acquired, the average of the unspiked runs can be used for this value. Using the second approach is only appropriate if the effluent concentration does not vary appreciably with time.

13. Report

13.1 The format of the test report is often subject to local or regional guidelines, but must contain the following information in the report body or appendices.

13.1.1 Temperature of effluent;

13.1.2 Temperature of sampling probe and filter (recorded at least every 5 min);

13.1.3 Volume of gas sampled and dry gas meter temperature and pressure;

13.1.4 Moisture content of the effluent—(if required by test);

13.1.5 Results of IC calibration—lab report;

13.1.6 Results of IC analysis—lab report;

13.1.7 Equivalent flue gas concentration in mg/DSCM and in ppm (v) dry per run;

13.1.8 Mass emission rate per run (if required by test); and

13.1.9 Results of blanks and QA analyses.

14. Precision and Bias

14.1 *Precision (Repeatability and Reproducibility):*

14.1.1 *Precision in General Use*—Based on a series of intra-laboratory tests conducted at lime plants, and application of EPA Method 301 statistical analyses to the data set, the method is able to achieve an RSD (See Appendix X1—Eq X1.1-X1.4) of from 15 to 38 % for HCl for effluent concentrations of less than 10 ppm (v) dry.

14.1.2 *Test Specific Repeatability*—An assessment of test-specific repeatability can be obtained by conducting a series of paired runs or by determining the precision from the three or more consecutive runs where temporal variations in HCl and/or HF are not present. Conduct of paired-run testing is recommended when test results are required for critical decisions at concentrations below 10 ppm (v) dry.

14.1.3 *Precision in Other Applications*—The achievable precision of this method will likely be source and source tester specific. Additional procedures to determine the method precision for applications beyond those enumerated in 14.1.1 are included in Appendix X1.

14.2 *Bias:*

14.2.1 *Bias in General Use*—Based on a series of intra-laboratory tests conducted at lime plants, and application of EPA Method 301 statistical analyses to the data set, the method had a statistically insignificant bias at sources with effluent concentrations of HCl less than 10 ppm (v) dry. The accuracy of the method based on spike recoveries for 48 sampling runs is 20 % or better for effluent concentration levels of 10 ppm (v) dry or less.

14.2.2 *Test Specific Bias*—An assessment of potential test-specific bias is provided for each test series by the "Post-Test Analyte Spike—Optional Quality Assurance Bias Check" included in 11.2.6.

14.2.3 *Bias in Other Applications*—Bias will likely be source category specific, in part, because of the reactivity of the dust for different industries. Additional procedures to determine the potential method bias for applications beyond those enumerated in 14.1.1 are included in Appendix X1.

NOTE 21—Supporting data for method precision and bias are available from the National Lime Association,[5] as provided in three separate method evaluation reports.

15. Keywords

15.1 analyte spiking; gaseous chlorides and fluorides; HCl ; HF; hydrochloric acid gas; hydrofluoric acid gas; hydrogen chloride; hydrogen fluoride; impinger method; mineral calcining; paired trains

---

[5] Available from National Lime Association, 200 North Glebe Road, Suite 800, Arlington, VA 22203.

APPENDIX

(Nonmandatory Information)

X1. ADDITIONAL OPTIONAL PROCEDURES TO DOCUMENT THE ACCURACY AND PRECISION OF THIS METHOD

INTRODUCTION

These procedures have been included as a means to generate additional data regarding the accuracy and precision of this method.

These procedures aid in determining method performance from source category to source category and will demonstrate the bias and precision of the method. Use of the statistical criteria will enable evaluation the data validity in different test applications.

Two separate procedures are described below. The quadruplet sampling approach, which has been adapted from EPA Method 301 (40 CFR part 63, Appendix A), and direct comparison to Fourier transform infrared spectrometry (FTIR) Spectroscopy (Test Method D6348 or equivalent).

X1.1 *Quadruplet Replicate Sampling System Procedure*—This procedure uses four replicate sampling trains to determine the analytical bias and precision of this method. In this application, four sampling trains are operated simultaneously. After the sampling run is completed, two of the sampling trains are spiked and two remain unspiked. A total of 6 sample runs are required using the quadruplet sampling train configuration.

X1.1.1 Assemble two separate sets of sampling trains as diagrammed in Fig. 1.

X1.1.2 Conduct six sequential one-hour runs using this quadruplet sampling arrangement. Use the procedures for pre-test and sampling as described in 11.1 and 11.2 of this method.

X1.1.3 After completing each of the six sets of runs, recover two of the four trains as described in 11.4 of this method.

X1.1.4 Conduct the QA spiking procedure described in 11.2.6 of this method using the remaining two of the four trains. Recover the trains as described in 11.4 of this method.

X1.1.5 Analyze the samples as described in 11.5 and Section 12 of this method.

X1.1.6 *Precision*—Calculate the standard deviation of unspiked results in accordance with the following equation:

$$SD_u = \left[\Sigma\left(Di^2\right)/2N\right]^{\frac{1}{2}} \tag{X1.1}$$

where:

SD_u = standard deviation of unspiked samples,
Di = the mg difference in the analytical results for each pair of unspiked samples, and
N = the number of pairs (in this case N = 6).

X1.1.7 Calculate the standard deviation of the spiked results in accordance with the following equation:

$$SD_s = \left[\Sigma\left(Di^2\right)/2N\right]^{\frac{1}{2}} \tag{X1.2}$$

where:

SD_s = standard deviation of spiked samples,
Di = the mg difference in the analytical results for each pair of spiked samples, and
N = the number of pairs (in this case N = 6).

X1.1.8 Calculate the percent relative standard deviation for the unspiked samples in accordance with the following equation:

$$\%\ RSD = \left(SD_u/M_u\right) \times 100 \tag{X1.3}$$

where:

SD_u = standard deviation of unspiked samples, and
M_u = the mean of the unspiked sample results.

X1.1.9 Calculate the percent relative standard deviation for the spiked samples in accordance with the following equation:

$$\%\ RSD = \left(SD_s/M_s\right) \times 100 \tag{X1.4}$$

where:

SD_s = standard deviation of spiked samples, and
M_s = the mean of the spiked sample results.

NOTE X1.1—If the underlying effluent concentration changes significantly during these tests, the precision may be affected adversely. This apparent imprecision should not be attributed to method imprecision.

X1.1.10 *Bias*—Calculate the numerical value of the bias using the results from the analysis of the spiked and unspiked samples in accordance with the following equation:

$$B = M_s - M_u - Cs \tag{X1.5}$$

where:

M_s = the mean of the spiked sample results in mg,
M_u = the mean of the unspiked sample results in mg, and
Cs = the mean of the spiked amount added to each spiked train in mg.

X1.1.11 Calculate the standard deviation of the mean in accordance with the following equation:

$$SDM = \left[SD_s^{\,2} + SD_u^{\,2}\right]^{\frac{1}{2}} \tag{X1.6}$$

X1.1.12 Test the bias using the t-statistic by comparing to the critical value of the two-sided t-distribution at the 95 %

confidence level and n-1 degrees of freedom in accordance with the following equation:

$$t = |B|/SDM \qquad (X1.7)$$

$$\text{Critical t} - \text{value} = 2.201 \text{ for 12 samples}$$

where:

B = bias from Eq X1.5, and
SDM = standard deviation of the mean from Eq X1.6.

X1.1.13 Compare the t value from Eq X1.7 to the critical t-value of 2.201.

X1.1.14 If the t-value from Eq X1.7 is greater than 2.201, calculate a correction factor in accordance with the equation:

$$Cf = [1/(1+(B/Cs))] \qquad (X1.8)$$

where:

B = bias from Eq X1.5, and
Cs = the mean of the spiked amount in mg.

X1.2 *Comparison to Fourier Transform Infrared Measurement Results*— This procedure provides a comparison between FTIR measurement results and the results provided by this method.

X1.2.1 Conduct the sampling and analysis procedures detailed in Sections 11 and 12 of this method. Six paired-train sample runs are required for this procedure.

X1.2.2 Simultaneously conduct FTIR measurements using either Test Method D6348 or EPA Method 321, or both. The FTIR measurements must be validated in accordance with the analyte spiking procedures contained in Annex A5 of Test Method D6348 or as prescribed in Section 9 of Method 321. The spike concentration requirements and spiking procedures must be followed.

NOTE X1.2—Test Method D6348 requires that the analyte spikes must approximate the effluent concentration within ±50 % (that is, if the native concentration is 5 ppm (v), the spike concentration level should be 5 ppm (v) ± 2.5 ppm (v) and the spike gas must represent 10 % or less of the total sample gas flow rate (volume) during the spike procedure. Method 321 requires spikes at the level of the effluent concentration or at a concentration of 5 ppm (v). The spike gas must represent 10 % or less of the total sample gas flow rate (volume) during the spike procedure. Spikes at significantly higher concentrations are not representative of the method performance at the level of concern and do not ensure that the FTIR measurements are valid.).

X1.2.3 Additional measures are required to ensure that the FTIR data are unbiased when low concentration measurements of HCl and/or HF are made. These measures include: (*1*) collecting reference spectra at concentrations bracketing or closely approximating the effluent concentrations for inclusion as FTIR calibration points, (*2*) verification of the concentration of HCl or HF calibration gas mixtures, or both by comparison to other independent gas standards, (*3*) verification of the concentration of HCl and/or HF calibration gas mixtures by wet chemical analysis, (*4*) performance checks of gas dilution systems used to dilute calibration standards to the levels necessary to approximate the effluent concentrations, and (*5*) verification of proper FTIR sampling system operating temperatures and conditions.

X1.2.4 *Precision*—Calculate the standard deviation of the six pairs of sample runs using the following equation:

$$SD = [\Sigma(Di^2)/2N]^{\frac{1}{2}} \qquad (X1.9)$$

where:

SD = standard deviation of the paired samples,
Di = the mass in mg difference in the analytical results for each pair of samples, and
N = the number of pairs (in this case N = 6).

X1.2.5 Calculate the percent relative standard deviation using the following equation:

$$\%\,RSD = (SD/M) \times 100 \qquad (X1.10)$$

where:

SD = standard deviation of the paired samples, and
M = the mean of the paired samples.

X1.2.6 *Bias*—Compare the results provided by each of the hourly average FTIR results to those provided by this method. Compare results on a ppm (v) (dry) basis.

X1.2.7 Acceptable results are indicated if the difference between the results provided with this method and the FTIR measurement results are within ±30 %, or ±5 ppm (v) (whichever is greater).

NOTE X1.3—The criteria for agreement of the two methods of ±30 %, or ±5 ppm (v), whichever is greater, reflects consideration of (*1*) the expected precision of the impinger method, (*2*) the expected bias of the impinger method of ±20 % of the mean of the measured values or ±2 ppm (v), whichever is less restrictive (*3*) the accuracy of the HCl and HF calibration gases which are no better than ±5 % of the certified tag value (*4*) the error associated with quantitative dilution of the FTIR calibration standards which is approximately 2 % (*5*) the acceptable spike recovery for the FTIR measurements of ±30 %, and, (*6*) other unquantified errors such as those associated with the FTIR linearzation procedure.

NOTE X1.4—Over the time period when both methods are in simultaneous operation the results provided by the FTIR indicate an average concentration of 5 ppm (v), and the results provided by this method are 2 ppm (v), then the percent difference is:

$$|2 - 5|/5 \times 100 = 60\,\% \text{ (this would exceed the 30 \% tolerance)} \qquad (X1.11)$$

However, the absolute difference is 3 ppm (v). Therefore, the results provided by this method would be acceptable.

ASTM International 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 International 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, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, 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 (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/