



Designation: D6735 – 01

Standard Test Method for Measurement of Gaseous Chlorides and Fluorides from Mineral Calcining Exhaust Sources—Impinger Method¹

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 Cl^- 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

¹ This test method is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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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.

D2986 Practice for Evaluation of Air Assay Media by the Monodisperse DOP (Diethyl Phthalate) Smoke Test³

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

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 Withdrawn. 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.

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 CO₂ 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 H₂SO₄ 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 H₂SO₄, 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.

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

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 associated with the test.

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 $\text{NH}_4\text{Cl}(s)$, 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.

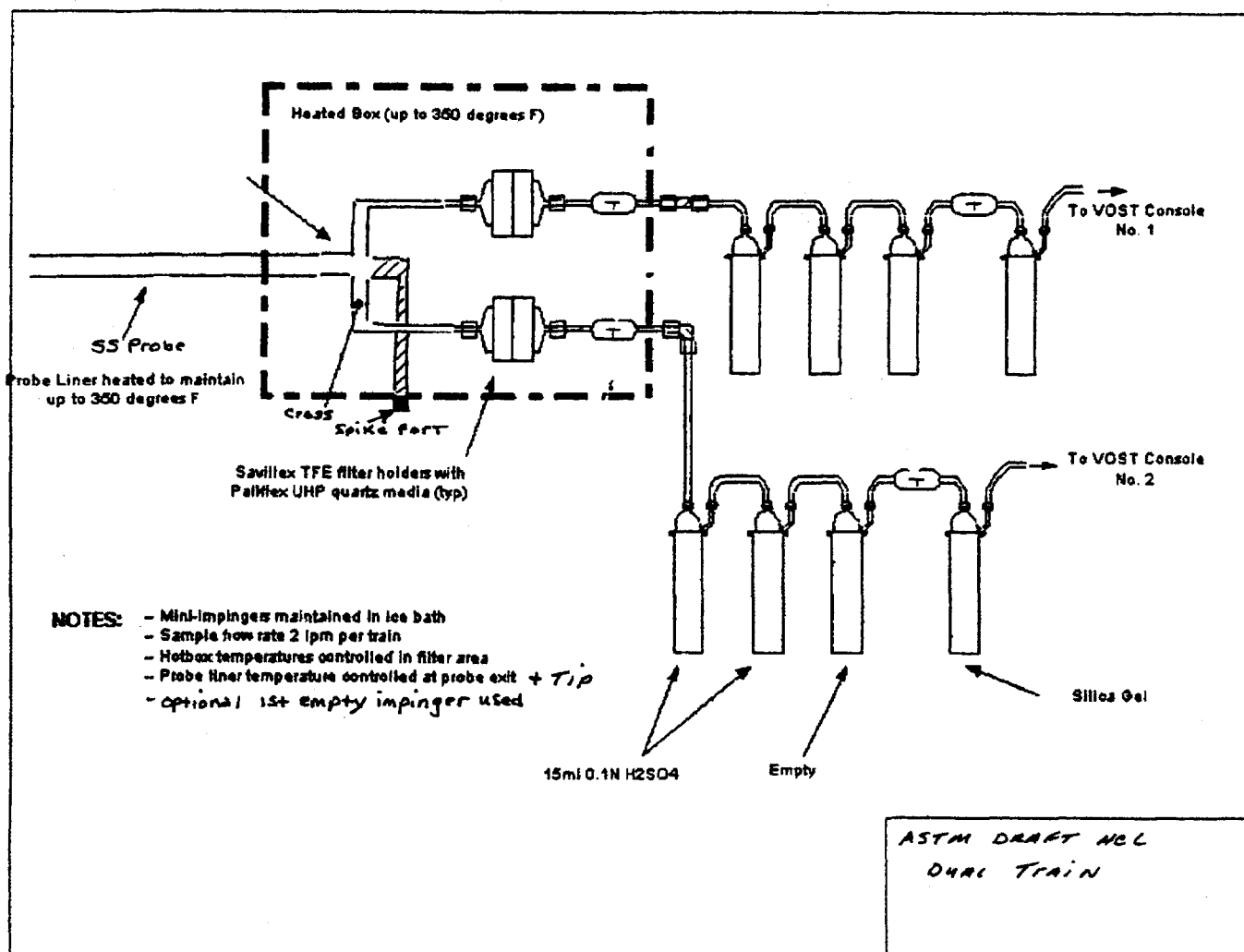


FIG. 1 Sampling Train Configuration