

Method 27—Determination of vapor tightness of gasoline delivery tank using pressure-vacuum test

Method 28—Certification and auditing of wood heaters

Method 28A—Measurement of air to fuel ratio and minimum achievable burn rates for wood-fired appliances

Method 29—Determination of metals emissions from stationary sources

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title “Test Methods and Procedures” is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. Section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless oth-

erwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as “subject to the approval of the Administrator” or as “or equivalent.” Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator’s disapproval of the alternative.

METHOD 26—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES NON-ISOKINETIC METHOD

1.0 Scope and Application

1.1 Analytes.

| Analytes                          | CAS No.    |
|-----------------------------------|------------|
| Hydrogen Chloride (HCl) .....     | 7647-01-0  |
| Hydrogen Bromide (HBr) .....      | 10035-10-6 |
| Hydrogen Fluoride (HF) .....      | 7664-39-3  |
| Chlorine (Cl <sub>2</sub> ) ..... | 7882-50-5  |
| Bromine (Br <sub>2</sub> ) .....  | 7726-95-6  |

1.2 Applicability. This method is applicable for determining emissions of hydrogen halides (HX) (HCl, HBr, and HF) and halogens (X<sub>2</sub>) (Cl<sub>2</sub> and Br<sub>2</sub>) from stationary sources when specified by the applicable subpart. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter must be sampled using Method 26A.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

2.1 An integrated sample is extracted from the source and passed through a prepurged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions which collect the gaseous hydrogen halides and halogens, respectively. The filter collects particulate matter including halide salts but is not routinely recovered and analyzed. The hydrogen halides are solubilized in the acidic solution and form chloride ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), and fluoride ( $\text{F}^-$ ) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton ( $\text{H}^+$ ), the halide ion, and the hypohalous acid ( $\text{HClO}$  or  $\text{HBrO}$ ). Sodium thiosulfate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC).

#### 3.0 Definitions [Reserved]

#### 4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide ( $\text{ClO}_2$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hydrohalous acid upon dissolution in water. However, the use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of  $\text{HBr}$  and  $\text{Cl}_2$  may cause a positive bias in the  $\text{HCl}$  result with a corresponding negative bias in the  $\text{Cl}_2$  result as well as affecting the  $\text{HBr}/\text{Br}_2$  split.

4.3 High concentrations of nitrogen oxides ( $\text{NO}_x$ ) may produce sufficient nitrate ( $\text{NO}_3^-$ ) to interfere with measurements of very low  $\text{Br}^-$  levels.

4.4 A glass wool plug should *not* be used to remove particulate matter since a negative bias in the data could result.

4.5 There is anecdotal evidence that  $\text{HF}$  may be outgassed from new teflon components. If  $\text{HF}$  is a target analyte, then preconditioning of new teflon components, by heating should be considered.

#### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide ( $\text{NaOH}$ ). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/ $\text{m}^3$  for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

#### 6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling. The sampling train is shown in Figure 26-1, and component parts are discussed below.

6.1.1 Probe. Borosilicate glass, approximately  $\frac{3}{8}$ -in. (9-mm) I.D. with a heating system to prevent moisture condensation. A Teflon-glass filter in a mat configuration should be installed to remove particulate matter from the gas stream (see Section 6.1.6).

6.1.2 Three-way Stopcock. A borosilicate-glass three-way stopcock with a heating system to prevent moisture condensation. The heated stopcock should connect to the outlet of the heated filter and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

6.1.3 Impingers. Four 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample

does not bubble through the collected condensate) should be used in front of the first impinger.

6.1.4 Drying Tube or Impinger. Tube or impinger, of Mae West design, filled with 6- to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

6.1.5 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder greater than 120 °C (248 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.6 Filter Holder and Support. The filter holder shall be made of Teflon or quartz. The filter support shall be made of Teflon. All Teflon filter holders and supports are available from Saville Corp., 5325 Hwy 101, Minnetonka, MN 55345.

6.1.7 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

6.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of 2 liters/min (0.07 ft<sup>3</sup>/min).

6.1.9 Purge Pump, Purge Line, Drying Tube, Needle Valve, and Rate Meter. Pump capable of purging the sampling probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter capable of measuring 0 to 5 liters/min (0.2 ft<sup>3</sup>/min).

6.1.10 Stopcock Grease, Valve, Pump, Volume Meter, Barometer, and Vacuum Gauge. Same as in Method 6, Sections 6.1.1.4, 6.1.1.7, 6.1.1.8, 6.1.1.10, 6.1.2, and 6.1.3.

6.1.11 Temperature Measuring Devices. Temperature sensors to monitor the temperature of the probe and to monitor the temperature of the sampling system from the outlet of the probe to the inlet of the first impinger.

6.1.12 Ice Water Bath. To minimize loss of absorbing solution.

6.2 Sample Recovery.

6.2.1 Wash Bottles. Polyethylene or glass, 500-ml or larger, two.

6.2.2 Storage Bottles. 100- or 250-ml, high-density polyethylene bottles with Teflon screw cap liners to store impinger samples.

6.3 Sample Preparation and Analysis. The materials required for volumetric dilution and chromatographic analysis of samples are described below.

6.3.1 Volumetric Flasks. Class A, 100-ml size.

6.3.2 Volumetric Pipets. Class A, assortment. To dilute samples to the calibration range of the ion chromatograph.

6.3.3 Ion Chromatograph (IC). Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, strip chart recorders, and peak height measurements may be used.

#### 7.0 Reagents and Standards

NOTE: Unless otherwise indicated, 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.

##### 7.1 Sampling.

7.1.1 Filter. A 25-mm (1 in) (or other size) Teflon glass mat, Pallflex TX40HI75 (Pallflex Inc., 125 Kennedy Drive, Putnam, CT 06260). This filter is in a mat configuration to prevent fine particulate matter from entering the sampling train. Its composition is 75% Teflon/25% borosilicate glass. Other filters may be used, but they must be in a mat (as opposed to a laminate) configuration and contain at least 75% Teflon. For practical rather than scientific reasons, when the stack gas temperature exceeds 210 °C (410 °F) and the HCl concentration is greater than 20 ppm, a quartz-fiber filter may be used since Teflon becomes unstable above this temperature.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193-77 or 91, Type 3 (incorporated by reference—see §60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). To prepare 100 ml of the absorbing solution for the front impinger pair, slowly add 0.28 ml of concentrated H<sub>2</sub>SO<sub>4</sub> to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

7.1.4 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 180 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

7.1.5 Alkaline Adsorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 100 ml of the scrubber solution for the third and fourth impinger, dissolve 0.40 g of solid NaOH in about 90 ml of water, and adjust the final solution volume to 100 ml using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5 H<sub>2</sub>O)

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in Section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of each absorbing solution to approximately the same final volume as the field samples using the blank sample of rinse water.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl<sup>-</sup> concentration using Equation 26-1 in Section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26-2 and 26-3 in Section 12.2, to calculate the Br<sup>-</sup> and F<sup>-</sup> concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/l NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Effective eluents for nonsuppressed IC using a resin- or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to pH 4.0 using a saturated sodium borate solution, and a 4 mM 4-hydroxy benzoate solution, adjusted to pH 8.6 using 1 N NaOH. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH and containing no interfering ions may be used. When using suppressed ion chromatography, if the "water dip" resulting from sample injection interferes with the chloride peak, use a 2 mM NaOH/2.4 mM sodium bicarbonate eluent.

7.3 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA regional Office or from the responsible enforcement authority.

NOTE: The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

#### 8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analyst should be trained and experienced with the procedure to ensure reliable results.

##### 8.1 Sampling.

8.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 ml of the acidic absorbing solution into each one of the first pair of impingers, and 15 ml of the alkaline absorbing solution into each one of the second pair of impingers. Connect the impingers in series with the knockout impinger first, if used, followed by the two impingers containing the acidic absorbing solution and the two impingers containing the alkaline absorbing solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or impinger at the end of the impinger train.

8.1.2 Adjust the probe temperature and the temperature of the filter and the stopcock, *i.e.*, the heated area in Figure 26-1 to a temperature sufficient to prevent water condensation. This temperature should be at least 20 °C (68 °F) above the source temperature, and greater than 120 °C (248 °F). The temperature should be monitored throughout a sampling run to ensure that the desired temperature is maintained. It is important to maintain a temperature around the probe and filter of greater than 120 °C (248 °F) since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and hence any collection of acid gases on these components would result in potential underreporting of these emission. The applicable subparts may specify alternative higher temperatures.)

##### 8.1.3 Leak-Check Procedure.

8.1.3.1 Sampling Train. A leak-check prior to the sampling run is optional; however, a leak-check after the sampling run is mandatory. The leak-check procedure is as follows: Temporarily attach a suitable [*e.g.*, 0-40 cc/min (0-2.4 in<sup>3</sup>/min)] rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

8.1.3.2 Pump. It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or pump, pull a vacuum of 250 mm (10 in) Hg, plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 sec. Other leak-check procedures may be

used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

8.1.4 Purge Procedure. Immediately before sampling, connect the purge line to the stopcock, and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A of Figure 26-1). Turn on the purge pump, and adjust the purge rate to 2 liters/min (0.07 ft<sup>3</sup>/min). Purge for at least 5 minutes before sampling.

8.1.5 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C of Figure 26-1). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate to within 10 percent during the entire sampling run. Take readings of the dry gas meter volume and temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. Shorter sampling times may introduce a significant negative bias in the HCl concentration. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak-check as described in Section 8.1.3.1.

8.2 Sample Recovery.

8.2.1 Disconnect the impingers after sampling. Quantitatively transfer the contents of the acid impingers and the knockout impinger, if used, to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle.

8.2.2 Repeat this procedure for the alkaline impingers and connecting glassware

using a separate storage bottle. Add 25 mg of sodium thiosulfate per the product of ppm of halogen anticipated to be in the stack gas times the volume (dscm) of stack gas sampled (0.7 mg per ppm-dscf).

NOTE: This amount of sodium thiosulfate includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl<sup>-</sup> ion in the alkaline solution.

8.2.3 Save portions of the absorbing reagents (0.1 N H<sub>2</sub>SO<sub>4</sub> and 0.1 N NaOH) equivalent to the amount used in the sampling train (these are the absorbing solution blanks described in Section 7.2.2); dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same amount of sodium thiosulfate solution to the 0.1 N NaOH absorbing solution blank. Also, save a portion of the rinse water used to rinse the sampling train. Place each in a separate, pre-labeled storage bottle. The sample storage bottles should be sealed, shaken to mix, and labeled. Mark the fluid level.

8.3 Sample Preparation for Analysis. Note the liquid levels in the storage bottles and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Quantitatively transfer the sample solutions to 100-ml volumetric flasks, and dilute to 100 ml with water.

9.0 Quality Control

| Section    | Quality control measure     | Effect   |
|------------|-----------------------------|--|
| 11.2 ..... | Audit sample analysis ..... | Evaluate analytical technique, preparation of standards. |

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Rate Meter, and Barometer. Same as in Method 6, Sections 10.1, 10.2, 10.3, and 10.4.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H<sub>2</sub>SO<sub>4</sub> or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the appropriate stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or heights, for the standards and plot individual values versus halide ion concentrations in µg/ml.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a

formula describing the resulting linear curve.

### 11.0 Analytical Procedures

#### 11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50  $\mu$ l sample loop, and a conductivity detector set on 1.0  $\mu$ S full scale is shown in Figure 26-2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{F}^-$  appears in the chromatogram. If any of these ions are present, repeat the load/injection procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to Section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{F}^-$  peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicate injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

#### 11.2 Audit Sample Analysis.

11.2.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of two EPA audit samples must be analyzed, subject to availability.

11.2.2 Concurrently analyze the audit samples and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

11.2.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

#### 11.3 Audit Sample Results.

11.3.1 Calculate the concentrations in mg/L of audit sample and submit results following the instructions provided with the audit samples.

11.3.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

11.3.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations. If the 10 percent specification is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

11.3.4 Failure to meet the 10 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or non-compliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

### 12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

#### 12.1 Nomenclature.

$B_{X^-}$ =Mass concentration of applicable absorbing solution blank,  $\mu$ g halide ion ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ) /ml, not to exceed 1  $\mu$ g/ml which is 10 times the published analytical detection limit of 0.1  $\mu$ g/ml.

$C$ =Concentration of hydrogen halide (HX) or halogen ( $X_2$ ), dry basis, mg/dscm.

$K=10^{-3}$  mg/ $\mu$ g.

$K_{\text{HCl}}=1.028$  ( $\mu$ g HCl/ $\mu$ g-mole)/( $\mu$ g  $\text{Cl}^-$ / $\mu$ g-mole).

$K_{\text{HBr}}=1.013$  ( $\mu$ g HBr/ $\mu$ g-mole)/( $\mu$ g  $\text{Br}^-$ / $\mu$ g-mole).

$K_{\text{HF}}=1.053$  ( $\mu$ g HF/ $\mu$ g-mole)/( $\mu$ g  $\text{F}^-$ / $\mu$ g-mole).

$m_{\text{HX}}$ =Mass of HCl, HBr, or HF in sample,  $\mu$ g.

$m_{X_2}$ =Mass of  $\text{Cl}_2$  or  $\text{Br}_2$  in sample,  $\mu$ g.

$S_{X^-}$ =Analysis of sample,  $\mu$ g halide ion ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ )/ml.

$V_{m(\text{std})}$ =Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

$V_s$ =Volume of filtered and diluted sample, ml.

12.2 Calculate the exact  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{F}^-$  concentration in the halide salt stock standard solutions using the following equations.

$$\mu\text{g Cl}^-/\text{ml} = \text{g of NaCl} \times 10^3 \times 35.453/58.44 \quad \text{Eq. 26-1}$$

$$\mu\text{g Br}^-/\text{ml} = \text{g of NaBr} \times 10^3 \times 79.904/102.90 \quad \text{Eq. 26-2}$$

$$\mu\text{g F}^-/\text{ml} = \text{g of NaF} \times 10^3 \times 18.998/41.99 \quad \text{Eq. 26-3}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Calculate the sample volume using Eq. 6-1 of Method 6.

12.4 Total  $\mu\text{g HCl}$ ,  $\text{HBr}$ , or  $\text{HF}$  Per Sample.

$$m_{\text{HX}} = K_{\text{HCl, Hbr, HF}} V_s (S_x^- - B_x^-) \quad \text{Eq. 26-4}$$

12.5 Total  $\mu\text{g Cl}_2$  or  $\text{Br}_2$  Per Sample.

$$M_{x2} = V_s (S_x^- - B_x^-) \quad \text{Eq. 26-5}$$

12.6 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K m_{\text{XH, X}_2} / V_{\text{m(std)}} \quad \text{Eq. 26-6}$$

### 13.0 Method Performance

13.1 Precision and Bias. The within-laboratory relative standard deviations are 6.2 and 3.2 percent at  $\text{HCl}$  concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit a bias to  $\text{Cl}_2$  when sampling at concentrations less than 50 ppm.

13.2 Sample Stability. The collected  $\text{Cl}^-$  samples can be stored for up to 4 weeks.

13.3 Detection Limit. A typical IC instrumental detection limit for  $\text{Cl}^-$  is 0.2  $\mu\text{g/ml}$ . Detection limits for the other analyses should be similar. Assuming 50 ml liquid recovered from both the acidified impingers, and the basic impingers, and 0.06 dscm of stack gas sampled, then the analytical detection limit in the stack gas would be about 0.1 ppm for  $\text{HCl}$  and  $\text{Cl}_2$ , respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

### 16.0 References

1. Steinsberger, S. C. and J. H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environ-

mental Protection Agency, Office of Research and Development, Report No. 600/3-89/064, April 1989. Available from the National Technical Information Service, Springfield, VA 22161 as PB89220586/AS.

2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources," March 18, 1987.

3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emissions. *J. Environ. Sci. Health. A19(3): 337-350.* 1984.

4. Stern, D. A., B. M. Myatt, J. F. Lachowski, and K. T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: *Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium*, Cincinnati, Ohio, May 2-4, 1983. Publication No. 600/9-84-015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84-234525.

5. Holm, R. D. and S. A. Barksdale. Analysis of Anions in Combustion Products. In: *Ion Chromatographic Analysis of Environmental Pollutants*. E. Sawicki, J. D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99-110.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

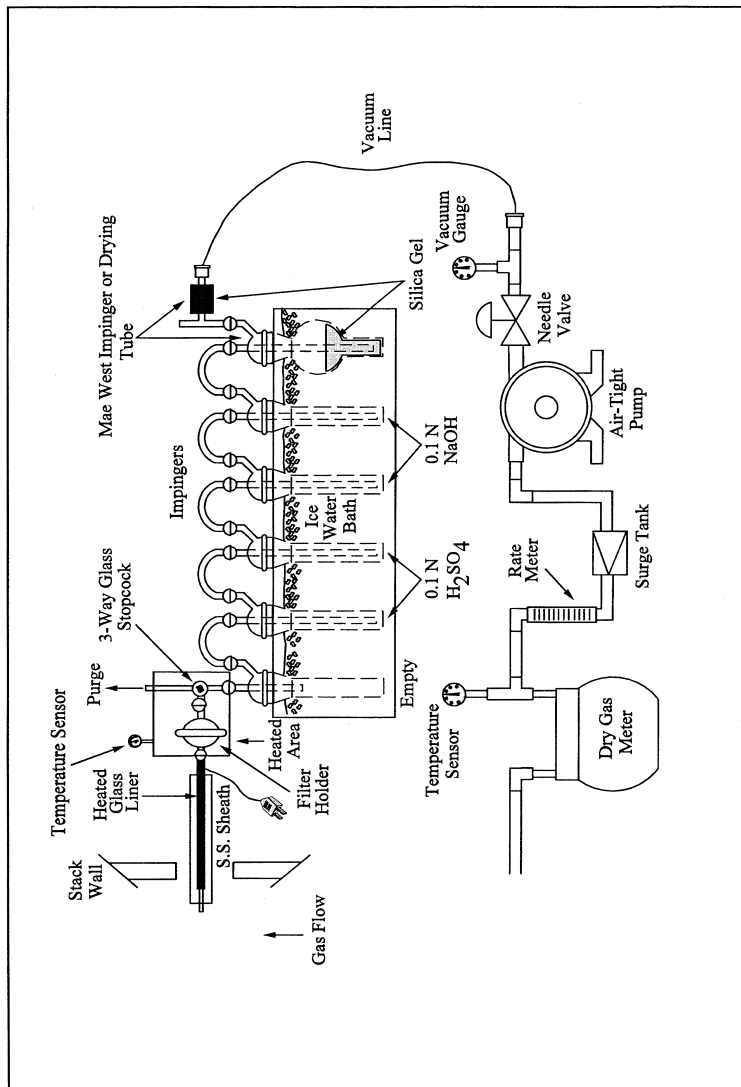


Figure 26-1. Sampling Train.

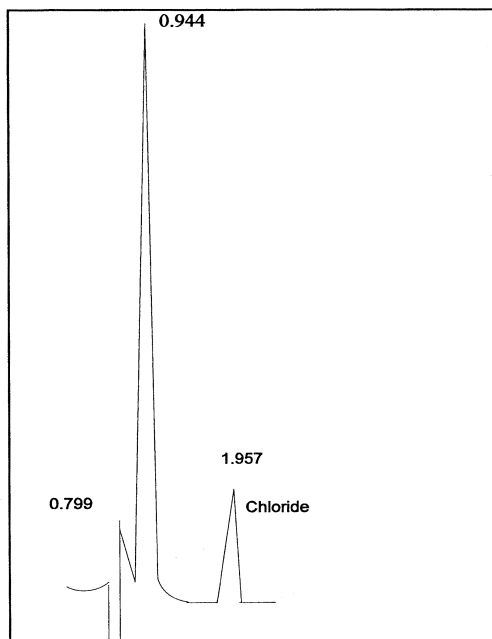


Figure 26-2. Example Chromatogram.

METHOD 26A—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES ISOKINETIC METHOD

NOTE: This method does not include all of the specifications (e.g. equipment and supplies) and procedures (e.g. sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 2, Method 5, and Method 26.

1.0 Scope and Application

1.1 Analytes.

| Analytes                          | CAS No.    |
|-----------------------------------|------------|
| Hydrogen Chloride (HCl) .....     | 7647-01-0  |
| Hydrogen Bromide (HBr) .....      | 10035-10-6 |
| Hydrogen Fluoride (HF) .....      | 7664-39-3  |
| Chlorine (Cl <sub>2</sub> ) ..... | 7882-50-5  |
| Bromine (Br <sub>2</sub> ) .....  | 7726-95-6  |

1.2 This method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X<sub>2</sub>) [Cl<sub>2</sub> and Br<sub>2</sub>] from stationary sources when specified by the applicable subpart. This method collects the emission sample isokinetically and is therefore particularly suited for sam-

pling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (e.g., hydrogen halides dissolved in water droplets).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Principle. Gaseous and particulate pollutants are withdrawn isokinetically from the source and collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain them; however, it is preferable to include the cyclone in the sampling train to protect the filter from any liquid present. The filter collects particulate matter including halide salts but is not routinely recovered or analyzed. Acidic and alkaline absorbing solutions collect the gaseous hydrogen halides and halogens, respectively. Following sampling of emissions containing liquid droplets, any halides/halogens dissolved in the liquid in the cyclone and on the filter are vaporized to gas and collected in the impingers by pulling conditioned ambient air through the sampling train. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl<sup>-</sup>), bromide (Br<sup>-</sup>),