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## 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 (Cl<sup>-</sup>), bromide (Br<sup>-</sup>), and fluoride (F<sup>-</sup>) 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 (H<sup>+</sup>), the halide ion, and the hypohalous acid (HClO or 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.  $1 \text{ mg}/\text{m}^3$  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 3/8-in. (9-mm) I.D. with a heating system capable of maintaining a probe gas temperature during sampling between 120 and 134 °C (248 and 273 °F) to prevent moisture condensation; or Teflon where stack probes are below 210 °C. If HF is a target analyte, then preconditioning of new teflon components by heating should be considered to prevent potential HF outgassing. A Teflon-glass filter in a mat configuration should be installed to remove particulate matter from the gas stream.

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 between 120 and 134 °C (248 and 273 °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 Savillex 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.

*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 must be maintained between 120 and 134 °C (248 and 273 °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 in this range 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 emissions. 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 [Reserved]

## 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 µl sample loop, and a conductivity detector set on 1.0 µS 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 Cl<sup>-</sup>, Br<sup>-</sup>, or F<sup>-</sup> 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 Cl<sup>-</sup>, Br<sup>-</sup>, and F<sup>-</sup> 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.

### 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,  $\mu\text{g}$  halide ion ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ) /ml, not to exceed 1  $\mu\text{g}/\text{ml}$  which is 10 times the published analytical detection limit of 0.1  $\mu\text{g}/\text{ml}$ .

$C$  = Concentration of hydrogen halide ( $\text{HX}$ ) or halogen ( $\text{X}_2$ ), dry basis,  $\text{mg}/\text{dscm}$ .

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

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

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

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

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

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

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

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

$V_{\text{s}}$  = 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, HBr, or HF Per Sample.

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

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

$$M_{X_2} = V_s (S_X^- - B_X^-) \quad \text{Eq. 26-5}$$

12.6 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K m_{XH,X_2} / V_{m(\text{std})} \quad \text{Eq. 26-6}$$

### 13.0 Method Performance

13.1 Precision and Bias. The within-laboratory relative standard deviations are 6.2 and 3.2 percent at 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 HCl and  $\text{Cl}_2$ , respectively.

### 14.0 Pollution Prevention [Reserved]

### 15.0 Waste Management [Reserved]

### 16.0 Alternative Procedures

Method 26A. Method 26A, which uses isokinetic sampling equipment, is an acceptable alternative to Method 26.

### 17.0 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. Environmental 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.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

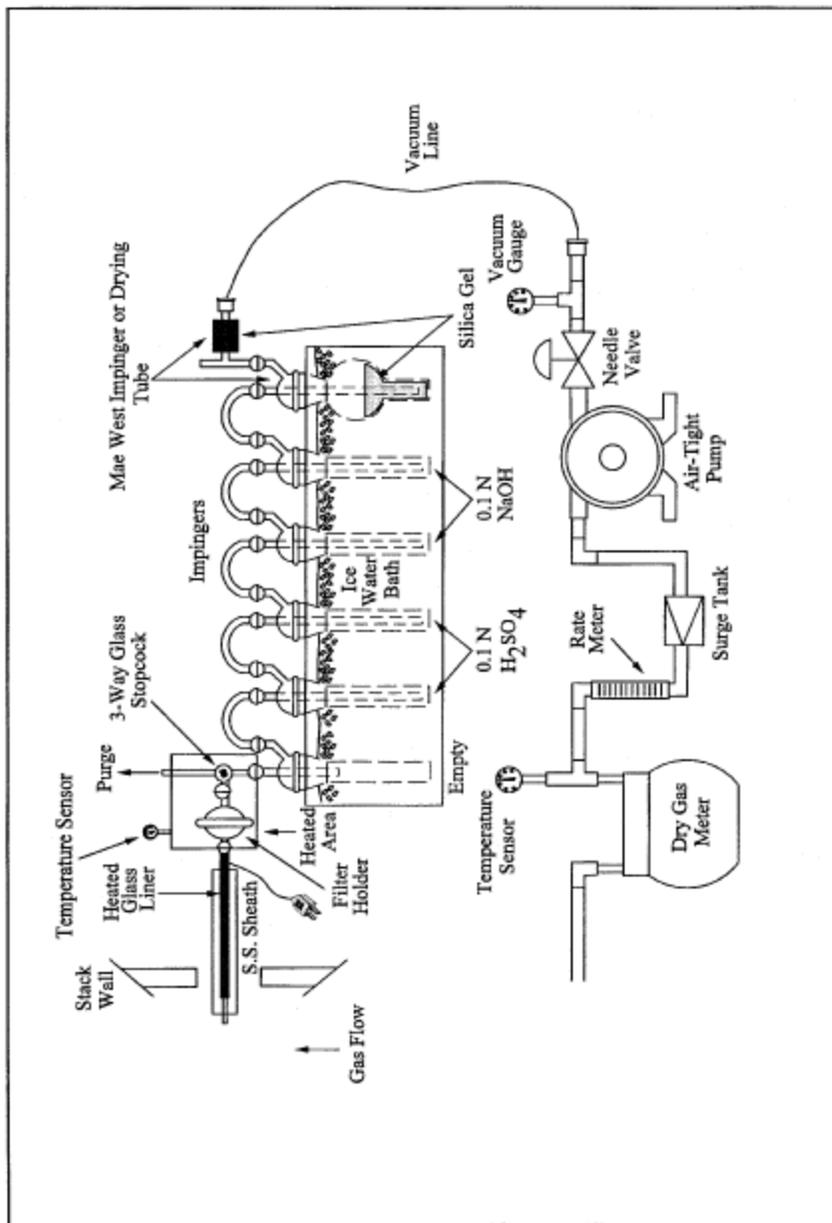


Figure 26-1. Sampling Train.

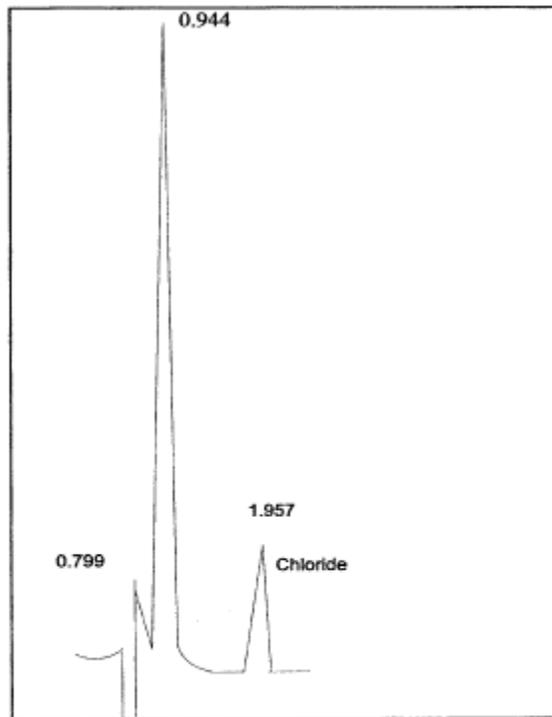


Figure 26-2. Example Chromatogram.