METHOD 0051

MIDGET IMPINGER HCl/Cl$_2$ EMISSION SAMPLING TRAIN

1.0   SCOPE AND APPLICATION

This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl$_2$, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators and municipal waste combustors. The collected samples are analyzed using Method 9057. This method is designed to collect HCl/Cl$_2$ in their gaseous forms. Use of this method is limited to the sampling of relatively dry, particulate-free gas streams. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter (e.g., HCl dissolved in water droplets) must be sampled using an isokinetic HCl/Cl$_2$ sampling train (see Method 0050). This method has potential for collection of all halogens and halogen acids, but has not been fully evaluated for that use. For analytical determination of additional halides, Method 9056 is used rather than Method 9057.

2.0   SUMMARY OF METHOD

An integrated gas sample is extracted from the stack and passes through a particulate filter, acidified water, and finally through an alkaline solution. The filter serves to remove particulate matter such as chloride salts which could potentially react and form the analyte in the absorbing solutions. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl$^-$) as follows:

$$HCl + H_2O = H_3O^+ + Cl^-$$
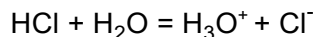
The Cl$_2$ gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H$^+$), Cl$^-$, and hypochlorous acid (HClO) as follows:

$$H_2O + Cl_2 = H^+ + Cl^- + HClO$$
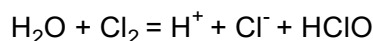
The Cl$^-$ ions in the separate solutions are measured by ion chromatography (Method 9057).

Sodium thiosulfate solution is added to the contents of the hydroxide filled impingers, in order to promote the following reaction.

$$S_2O_3^{-2} + 4OCl^- + 2OH^- = 2SO_4^{-2} + 4Cl^- + H_2O$$
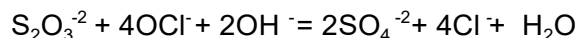
Conversion of all the original Cl$_2$ to the stable Cl$^-$ ion, and appropriate adjustment of the analysis calculations, removes the possibility of partial reduction of OCl$^-$ to Cl$^-$ and the resulting high bias to the results.

3.0   INTERFERENCES

Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl$_2$) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl$_2$ gas exhibits

a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl_2 with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4 percent in the HCl measurement.

4.0   APPARATUS AND MATERIALS

4.1   Sampling Train. The sampling train is shown in Figure 1 and component parts are discussed below.

4.1.1   Probe. Borosilicate glass, approximately 3/8-in. (9-mm) inside diameter, with a heating system to prevent condensation. When the concentration of alkaline particulate matter in the emissions is high, a 3/8-in. (9-mm) inside diameter Teflon elbow should be attached to the inlet of the probe. A 1-in. (25-mm) length of Teflon tubing with a 3/8-in. (9-mm) inside diameter should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the gas stream, thus reducing the amount of particulate entering the train. When high concentrations of particulate matter are not present, the Teflon elbow is unnecessary, and the probe inlet can be perpendicular to the gas stream. When sampling at locations where gas temperatures are greater than approximately 400°F, such as wet scrubber inlets, glass or quartz elbows must be used. In no case should a glass wool plug be used to remove particulate matter; use of such a filtering device could result in a bias in the data. Instead, a Teflon filter should be used as specified in Section 5.5.

4.1.2   Three-way stopcock. A borosilicate, three-way glass stopcock with a heating system to prevent condensation. The heated stopcock should connect directly to the outlet of the probe and filter assembly 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.

4.1.3   Impingers. Five 30-ml midget impingers with leak-free glass connectors. For sampling at high moisture sources or for extended 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.

4.1.4   Mae West impinger or drying tube. Mae West design impinger (or drying tube, if a moisture determination is not to be conducted) filled with silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump.

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

4.1.6   Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for the elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

4.1.7   Purge pump, purge line, drying tube, needle valve, and rate meter. Pump capable of purging sample probe at 2 liters/min. with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter, 0 to 5 liters/min.

4.1.8   Metering system. The following items comprise the metering system which is identical to that used for EPA Method 6 (see Reference 5).

4.1.8.1 Valve. Needle valve, to regulate sample gas flow rate.

4.1.8.2 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through train. Install a small surge tank between the pump and the rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

4.1.8.3 Rate meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of selected flow rate of 2 liters/min.

4.1.8.4 Volume meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions encountered during sampling, and equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within 3^0C (5.4^0F).

4.1.8.5 Vacuum gauge. At least 760 mm Hg (30 in. Hg) gauge to be used for leak check of the sampling train.

4.1.9   Water Bath: To minimize loss of absorbing solution

4.2   Sample Recovery.

4.2.1   Wash bottles. Polyethylene or glass, 500 ml or larger, two.

4.2.2   Storage bottles. Glass, with Teflon-lined lids, 100 ml, to store impinger samples (two per sampling run).

5.0   REAGENTS

5.1   Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2   Reagent Water. All references to water in the method refer to reagent water as defined in Chapter One unless otherwise specified. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values.

5.3   Sulfuric acid (0.05 M), H_2SO_4. Used as the HCl absorbing reagent. To prepare 100 mL, slowly add 0.28 mL of concentrated H_2SO_4 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. It is advisable to

analyze a blank sample of this reagent <u>prior</u> to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values.

5.4   Sodium hydroxide (0.1 M), NaOH. Used as the Cl_2 absorbing reagent. To prepare 100 mL, dissolve 0.40 g of solid NaOH in about 90 mL of water and adjust the final volume to 100 mL using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent <u>prior</u> to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample value.

5.5   Filter. Teflon mat Pallflex® TX40HI75 or equivalent. Locate in a glass, quartz, or Teflon filter holder with a Teflon filter support in a filter box heated to 250°F.

5.6   Sodium thiosulfate (0.5 M), $Na_2S_2O_3$. Used as the reducing agent added to the sodium hydroxide filled impingers to promote the reaction given in Section 2.0. Buy premixed reagent grade, as free of chloride as possible.

5.7   Silica gel. Indicating type, 6- to 16-mesh. 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.

6.0   SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1   Sample collection is described in this method. The analytical procedures are described in Method 9057.

6.2   Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

7.0   PROCEDURE

7.1   Calibration. Section 3.5.2 of EPA's Quality Assurance Handbook Volume III (Reference 4) may be used as a guide for these operations.

7.1.1   Dry Gas Metering System.

7.1.1.1 Initial calibration. Before its initial use in the field, first leak check the metering system (sample line, drying tube, if used, vacuum gauge, needle valve, pump, rate meter, and dry gas meter) as follows: plug the inlet end of the sampling line, pull a vacuum of 250 mm (10 in.) Hg, plug off the outlet of the dry gas meter, and turn off the pump. The vacuum should remain stable for 30 seconds. Carefully release the vacuum from the system by slowly removing the plug from the sample line inlet. Remove the sampling line (and drying tube, if applicable), and connect the dry gas metering system to a appropriately sized wet test meter (e.g., 1 liter per revolution). Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, with both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 percent from the average, the

metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

7.1.1.2   Post-test calibration check. After each field test series, conduct a calibration check as in Section 7.1.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three or more revolutions of the dry gas meter may be used, (c) only two independent runs need to be made. If the calibration factor does no deviate by more than 5 percent from the initial calibration factor (determined in Section 7.1.1.1), the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as Section 7.1.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

7.1.2   Thermometer(s). Prior to each field test, calibrate against mercury-in-glass thermometers at ambient temperature. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application. If the thermometer being calibrated reads within 2°C (2.6°F) of the mercury-in-glass thermometer, it is acceptable. If not, adjust the thermometer or use an appropriate correction factor.

7.1.3   Rate meter. The rate meter should be cleaned and maintained according to the manufacturer's instructions.

7.1.4   Barometer. Prior to each field test, calibrate against a mercury barometer. The field barometer should agree within 0.1 in. Hg with the mercury barometer. If it does not, the field barometer should be adjusted.

7.2   Sampling.

7.2.1   Preparation of collection train. Prepare the sampling train as follows: The first or knockout impinger should have a shortened stem and be left empty to condense moisture in the gas stream. The next two midget impingers should each be filled with 15 mL of 0.05 M H_2SO_4. The fourth and fifth impingers should each be filled with 15 mL of 0.1 M NaOH. It is essential that the NaOH filled impingers be maintained strongly basic throughout the sampling run. In highly acid stack environments, this may require measures such as stronger base, more volume of basic solution, or changeout of impinger liquid during the run. When in doubt the pH of the solution should be monitored frequently or continuously. Place a fresh charge of silica gel, or equivalent, in the Mae West impinger (or the drying tube). Connect the impingers in series with the knockout impinger first, followed by the two impingers containing the acidified reagent and two impingers containing the alkaline reagent, and the Mae West impinger containing the silica gel. If the moisture will be determined, weigh the impinger assembly to the nearest $\pm$ 0.5 g and record the weight.

7.2.2   Leak check procedures. Leak check the probe and three-way stopcock prior to inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds.

Place the probe in the stack at the sampling location, and adjust the filter heating system to 121°C (250°F) and the probe and stopcock heating systems to a temperature sufficient to prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to the last impinger and the needle valve. Upon completion of a sampling run, remove the probe from the stack and leak check as described above. If a leak has occurred, the sampling run must be voided. Alternatively, the portion of the train behind the probe may be leak checked between multiple runs at the same site as follows: Close the stopcock to the first impinger, and turn on the sample pump. Pull a vacuum of at least 250 mm Hg (10 in. Hg), turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Release the vacuum on the impinger train by turning the stopcock to the vent position to permit ambient air to enter. If this procedure is used, the full train leak check described above must be conducted following the final run and all preceding sampling runs voided if a leak has occurred.

7.2.3 Purge procedures. Immediately prior to sampling, connect the purge line to the stopcock and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes prior to sampling.

7.2.4 Sample collection. Turn on sample 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). Adjust the sampling rate to 2 liters/min. as indicated by the rate meter, and maintain this rate within 10 percent during the entire sampling run. Take readings of the dry gas meter, the dry gas meter temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. However, if the expected condensate catch for this sampling run duration will exceed the capacity of the sampling train, (1) a larger knockout impinger may be used or (2) two sequential half-hour runs may be conducted. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak check as described in Section 7.2.2.

7.3 Sample recovery. Following sampling, disconnect the impinger train from the remaining sampling equipment at the inlet to the knockout impinger and the outlet to the last impinger. If performing a moisture determination, wipe off any moisture on the outside of the train; weigh the train to the nearest 0.5 g and record the weight. Then disconnect the impingers from each other. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two 0.05 M H_2SO_4 impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle. The contents of the impingers and connecting glassware from the second set of impingers (containing the 0.1 M NaOH) should be recovered in a similar manner if a Cl_2 analysis is desired. Add 2 mL or more of 0.5 M $Na_2S_2O_3$. to the sodium hydroxide (Cl_2) samples. It is necessary to add sufficient $Na_2S_2O_3$ to reduce the OCl^-, but too much thiosulfate may interfere with the ion chromatography analysis. The amount needed will vary with stack emission composition. In certain situations, it may be advantageous to add the $Na_2S_2O_3$ before sampling. Consult recent references for additional suggestions. The sample bottle should be sealed, shaken to mix, and labeled; the fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Save portions of the 0.05 M H_2SO_4 and 0.1 M NaOH used as impinger reagents as reagent blanks. Take 50 ml of each and place in separate leak-free storage bottles. Label and mark the fluid levels as previously described.

7.4   Calculations. 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.

       7.4.1   Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Average dry gas meter absolute temperature, K (°R).

T_{std} = Standard absolute temperature, 293K (528°R).

V_{lc} = Total volume of liquid collected in impingers and silica gel, mL (equivalent to the difference in weight of the impinger train before and after sampling, 1 mg = 1 mL).

V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).

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

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

Y = Dry gas meter calibration factor.

p_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

       7.4.2   Sample volume, dry basis, corrected to standard conditions. Calculate as described below:

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} = K_1 Y \frac{V_m P_{bar}}{T_m} \qquad (1)$$

where:

K_1 = 0.3858 K/mm Hg for metric units.
= 17.64 °R/in. Hg for English units.

7.4.3 Volume of water vapor.

$$V_{w(std)} = V_{lc} \frac{p_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{lc} \qquad (2)$$

where:

K_2 = 0.0013333 m^3/mL for metric units.
= 0.04707 ft^3/mL for English units.

7.4.4 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad (3)$$

7.4.5 Analytical calculation of total ug HCl per sample. Calculate as described below:

$$m_{HCl} = S \times V_s \times 36.46/35.45$$

where:

m_{HCl} = Mass of HCl in sample, µg
S = Analysis of sample, µg Cl^-/mL
V_s = Volume of filtered and diluted sample, mL
36.46 = Molecular weight of HCl, µg/µg-mole
35.45 = Molecular weight of Cl^-, µg/µg-mole

7.4.6 Analytical calculation of total µg Cl_2 per sample. Calculate as described below:

$$m_{Cl2} = S \times V_2$$

where:
V_2 = Volume of filtered and diluted sample, mL
S = Analysis of sample, µg Cl^-/mL
m_{Cl2} = Mass of Cl_2 in sample, µg

7.4.7 Concentration of HCl in the flue gas. Calculate as described below:

$$C = K \times m/V_{m(std)}$$

where:
C = Concentration of HCl or Cl_2, dry basis, mg/dscm,
K = 10^{-3} mg/µg,
m = Mass of HCl or Cl_2 in sample, µg, and
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

8.0 QUALITY CONTROL

8.1 At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

8.2 Quality control check sample. Chloride solutions of reliably known concentrations are available for purchase from the National Bureau of Standards (SRM 3182). The QC check sample should be prepared in the appropriate absorbing reagent at a concentration approximately equal to the mid range calibration standard. The quality control check sample should be injected in duplicate immediately after the calibration standards have been injected the first time. The Cl^- value obtained for the check sample using the final calibration curve should be within 10 percent of the known value for the check sample.

9.0 METHOD PERFORMANCE

9.1 The in-stack limit for HCl for the method is approximately 0.08 mg/dscm of stack gas for a 1-hour sample.

9.2 The precision and bias for measurement of HCl using this sampling protocol combined with the analytical protocol, Method 9057, have been determined. The laboratory relative standard deviation is within 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at Cl_2 concentrations less than 50 ppm.

10.0 REFERENCES

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

3. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

4. U.S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods," Publication No. EPA-600/4-77-027b, August 1977.

5. U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Method 6.

6.   Steger, J.L.; Wagoner, D.E.; Bursey, J.T.; Merrill, R.G.; Fuerst, R.G. and Johnson, L.D. "Laboratory Evaluation of Method 0050 for Hydrogen Chloride," Proceedings of the 13th Annual International Incineration Conference, Houston, TX, May 1994.

7.   Johnson, L.D.,"Stack Sampling Methods for Halogens and Halogen Acids," presented at EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996.
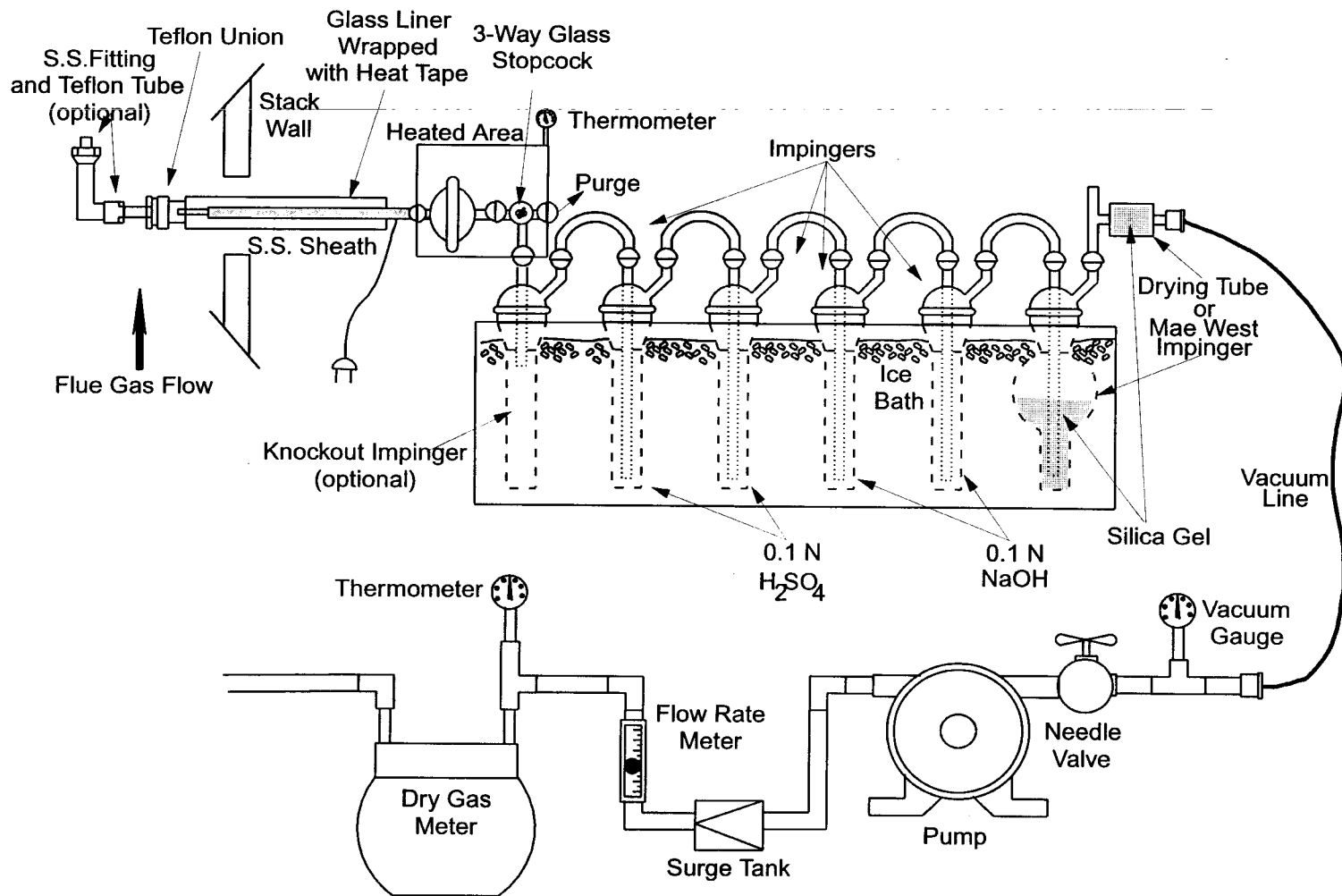
FIGURE 1. METHOD 0051 SAMPLING TRAIN

METHOD 0051
MIDGET IMPINGER HCl/Cl$_2$ EMISSION SAMPLING TRAIN

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                    │  Start  │
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    │ 7.1.1.1 Leak-check dry gas metering      │
    │ system, calculate calibration factor Y.  │
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    │ 7.1.1.2 Post test calibration            │
    │ after each test series.                  │
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    │ 7.1.2 - 7.1.4 Calibrate termometers,     │
    │ rate meter and barometer.                │
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    ┌────────────────────────────────────────┐
    │ 7.2.1 Set up sample collection train,    │
    │ connect impingers in series, and add     │
    │ reagents. If moisture is to be           │
    │ determined, weigh Mae West impinger      │
    │ with silica gel.                         │
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    │ 7.2.2 Perform leak-check on assembled    │
    │ sampling train.                          │
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    │ 7.2.3 Immediately prior to sampling,     │
    │ purge probe for 5 min. at 2 liter/min.   │
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    │ 7.2.4 Perform sample collection,         │
    │ adjust sampling rate to 2 liters/min.    │
    │ for 1 hour. Take readings for dry gas    │
    │ meter, temperature, rate meter, and      │
    │ vaccum once every 5 min.                 │
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    │ 7.3 Stop pump, disconnect impinger       │
    │ sampling train, quantitatively transfer  │
    │ contents of impingers and water rinses   │
    │ to labeled containers. Retain 50 mL      │
    │ aliquots of 0.1N H$_2$SO$_4$ and         │
    │ NaOH for blanks.                         │
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    │ 7.4 Calculate sample volume (7.4.2),     │
    │ volume of waer vapor (7.4.3), total ug   │
    │ HCL per sample (7.4.4), ug CL$_2$ per    │
    │ sample (7.4.5), and total HCL            │
    │ concentration (7.4.6).                   │
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                    │  Stop   │
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