## SUMMARY SHEET 26
### Hydrogen Halides and Halogens

| | | | Run #1 | Run #2 | Run #3 | Avg |
|---|---|---|---|---|---|---|
| Client/Plant Name | | FDS 26 | | | | |
| Job No. | | FDS 26 | | | | |
| Sampling Location | | FDS 26 | | | | |
| Run ID # | | FDS 26 | | | | |
| Test Date | | FDS 26 | | | | |
| Dry Gas Meter Calibration Factor | Y | FDS 26 | | | | |
| Barometric Pressure, mm Hg | $P_b$ | FDS 26 | | | | |
| Average DGM Temperature, °C | $t_m$ | FDS 26 | | | | |
| Volume of Metered Gas Sample, L | $V_m$ | FDS 26 | | | | |
| Volume of Metered Gas Sample, dsL | $V_{m(std)}$ | SS 26 | | | | |
| Sample Concentration, µg/mL | S | LDS 26 | | | | |
| Blank Concentration, µg/mL | B | LDS 26 | | | | |
| Sample Mass of Halide, µg | $m_{HX}$ | SS 26 | | | | |
| Sample Mass of Halogen, µg | $m_{X2}$ | SS 26 | | | | |
| Stack Concentration, mg/dscm | C | SS 26 | | | | |
| Audit Relative Error, % | RE | QA1 | | | | |
| Post test Calibration Checks | | | | | | |
| Temperature and Barometer | | CDS 2d | | | | |
| Metering System | | CDS 6 | | | | |

$$m_{HX} = k\,(S - B)$$

K = 1.028 for HCl
K = 1.013 for HBr
K = 1.053 for KF

$$m_{X2} = 200\,(S - B)$$

$$C = 10^{-3}\,\frac{m}{V_{m(std)}}$$

$$V_{m(std)} = 0.3858\,V_m\,Y\,\frac{P_b}{(t_m + 273)}$$

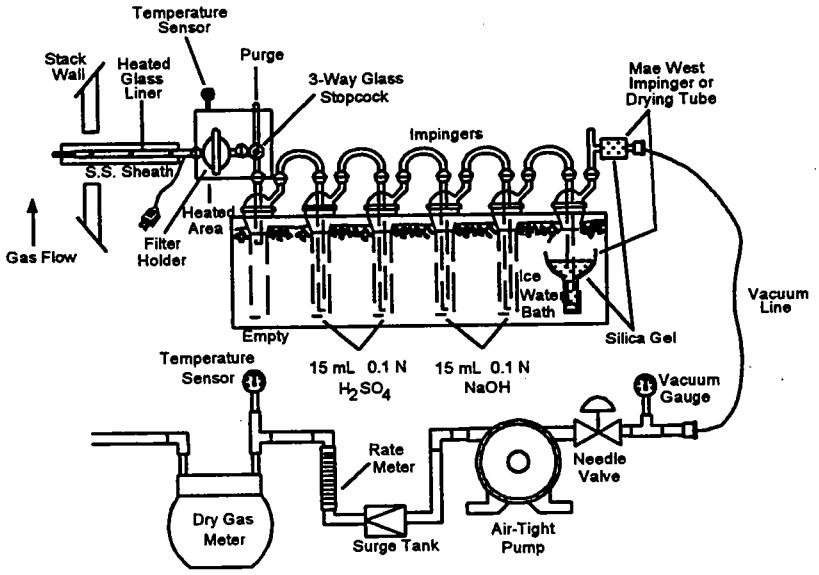


Figure F26-1. Sampling Train.

# FIELD PROCEDURE 26
## Hydrogen Halide and Halogen - Midget Impingers

### *A. Preparation of Sampling Train*

1. Prepare the sampling train shown in Figure F26-1 as follows:
   a. Pour 15 mL acidic absorbing solution into each of the first two impingers, and 15 mL alkaline absorbing solution into each of the second pair of impingers.
   b. Place fresh silica gel, or equivalent, in the drying tube or impinger at the end of the train.
   c. For high moisture sources or >1 hr sampling times, use the empty impinger as shown in Figure F26-1 before the first impinger.
2. Adjust and maintain the probe temperature and the temperature of the filter and the stopcock to ≥20°C above the source temperature, but ≤120°C.
3. ***Optional:*** Leak-check the sampling train and pump separately according to **FP 3c, sections C and D.**
4. Connect the purge line to the stopcock, and turn the stopcock to purge the probe (see Figure F26-1A), and purge at a rate of 2 L/min for ≥5 min before sampling.

### *B. Sampling*

1. Turn on the sampling pump, pull a slight vacuum of ~1 in. Hg on the impinger train, then turn the stopcock to sample stack gas through the impinger train (Figure F26-1C).
2. Adjust the sampling rate to 2 L/min, as indicated by the rate meter, and maintain within ±10% during the entire sampling run.
3. Record the data as required on FDS 26. Take appropriate readings at 5-min intervals.
4. Sample ≥1 hr. Shorter sampling times may introduce a significant negative bias in the HCl concentration.
5. *Mandatory:* Leak-check the sampling train after the sampling run **(see FP 3c, section C).**

### *C. Sample Recovery*

1. Acidic Absorbing Impingers
   a. Disconnect the impingers after sampling and quantitatively transfer the contents of the knockout impinger (if used) and acid impingers to a leak-free storage bottle.
   b. Add the water rinses of each of these impingers and connecting glassware to the storage bottle.
2. Alkaline Absorbing Impingers
   a. Quantitatively transfer the contents of the alkaline impingers to a leak-free storage bottle.
   b. Add the water rinses of each of these impingers and connecting glassware to the storage bottle.
   c. Multiply 25 mg sodium thiosulfate per "ppm" of halogen anticipated in the stack gas by the "dscm" stack gas sampled, and add this amount to storage container. [***Note:*** This amount of sodium thiosulfate includes a safety factor of ~5 to assume complete reaction with the hypohalous acid to form a second $Cl^-$ ion in the alkaline solution]
3. Blanks
   a. Save portions of both absorbing reagents equivalent to the amount used in the sampling train. Dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used.
   b. Add the same amount of sodium thiosulfate to the alkaline absorbing solution blank.
   c. Save a portion of the rinse water directly from the wash bottle.
4. Seal all sample and blank bottles, shake to mix, and label. Mark the fluid level.

**FIELD DATA SHEET 26**
**Hydrogen Halides and Halogens**

Client/Plant Name _____ Job # _____

City/State _____ Date _____

Test Location/Run # _____ Personnel _____

Train ID#/Sample Box # _____ DGM Cal Coef., Y _____ Amb Temp, °C_____

Purge Rate _____ *(2 L/min?)* Purge Time _____ *(≥5 min?)* Bar. Pressure, $P_b$ _____ mm Hg

| Clock Time | DGM Rdg (L) | Rot Rdg, R (L/min) | DGM Temp (°C) | Flow Rate Deviation | |
|---|---|---|---|---|---|
| | | | | ΔR | $\Delta R/R_{avg}$ |
| | | | | | |
| | | | | | |
| | | | | | |
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| | | | | | |
| | | | | | |
| | | | | | |
| | Average | | | | *0.90 - 1.10?* |

___ Proper probe heat (no condensation)?

| Leak-Checks ≤0.02 Avg Flow Rate at ≥10 in. Hg vac. | | | |
|---|---|---|---|
| Run # | | | |
| Pre (optional) (cc/min) | | | |
| Post (mandatory) (cc/min) | | | |
| Vacuum (≥10 in. Hg ?) | | | |

***Sample Recovery***

___ Fluid level marked?

___ Sample container sealed?

___ Sample container identified?

***Post-Test Calibrations***

*Attach CDS 2d and CDS 6. Temperature specification for the DGM thermometer is ≤ ±5.4°F.*

***QA/QC Check***

Completeness ____ Legibility ____ Accuracy ____ Specifications ____ Reasonableness ___

Checked by: _____ _____

Personnel (Signature/Date) Team Leader (Signature/Date)

# LABORATORY PROCEDURE 26
## Hydrogen Halides and Halogens

### A. *Reagents*

1. Acidic Absorbing Solution, 0.1 N Sulfuric Acid. Slowly add 0.28 mL conc. $H_2SO_4$ to about 90 mL water while stirring, and adjust the final volume to 100 mL with water. Shake well to mix the solution.
2. Alkaline Absorbing Solution, 0.1 N Sodium Hydroxide. Dissolve 0.40 g solid NaOH in about 90 mL water, and adjust the final volume to 100 mL with water. Shake well to mix the solution.
3. Blank Solution. Dilute 30 mL absorbing solution to approximately the same final volume as the field samples using the blank sample of rinse water.
4. Halide Salt Stock Standard Solutions. Dry reagent grade NaCl, NaBr, and NaF at 110°C for ≥2 hr, and cool to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g dried NaCl, 1.2 to 1.3 g dried NaBr, and 2.2 to 2.3 g dried NaF to within 0.1 mg, dissolve in water, and dilute each to 1 L. Calculate the exact $Cl^-$, $Br^-$, and $F^-$ concentrations. Refrigerate these stock standard solutions and do not use after 1 month. For $Cl^-$ standards, appropriate volumetric dilution of commercially stock solution (nominal certified 1000 mg/L NaCl) may be used.
5. Sodium Thiosulfate

### B. *Formulas*

$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44$
$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90$
$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99$

### C. *Calibration and Sample Analysis*

1. Set up and operate the ion chromatograph (IC) using the manufacturer's instruction.
2. Establish a stable baseline before sample analysis.
3. Inject a sample of water, and determine if any $Cl^-$, $Br^-$, or $F^-$ appears in the chromatogram. Repeat the load/injection procedure until they are no longer present.
4. Dilute appropriate amounts (≥1.0 mL) of stock standard solutions in 0.1 N $H_2SO_4$ or 0.1 N NaOH absorbing reagent, as applicable, to prepare at least four calibration standards for each absorbing reagent having concentrations within the linear range of the field samples.
5. Ensure adequate baseline separation for the peaks of interest using one of the standards in each series.
6. Quantitatively transfer the sample solution to a 100-mL volumetric flask, and dilute the solution to 100 mL with water. (Suggest beginning with 50-mL.)
7. For each series, inject the calibration standards, starting with the lowest concentration standard.
8. Inject in duplicate the reagent blanks, quality control sample, field samples, and (if applicable) audit samples. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard. Duplicate injects must agree within 5% of their mean.
9. Inject the calibration standards again, beginning with the lowest concentration.
10. Measure the areas or heights of the $Cl^-$, $Br^-$, and $F^-$ peaks.
11. For the standards, plot individual values versus halide ion concentrations in $\mu g$/mL. Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.
12. Determine the concentrations of the field samples and reagent blanks from the mean response using the linear calibration curve.

### D. *Notes*

1. Effective eluents for nonsuppressed IC using a resinor 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.
2. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate.
3. When suppressed ion chromatography is used and if the "water dip" resulting from sample injection interferes with the chloride peak, use a 2 mM NaOH/2.4 mM sodium bicarbonate eluent.

**LABORATORY DATA SHEET 26**
**Hydrogen Halides and Halogens**

Client/Plant Name _____ Job No. _____

City/State _____ Sampling Location _____

Ion Chromatograph ID # _____ Analyst _____ Date _____

QC Sample Conc, μg/mL: $Cl^-$ _____ $Br^-$ _____ $F^-$ _____ Abs Soln: Acidic ___ Alkaline ___

| Sample No. | Sample ID # | Peak Height (H) or Area (A) | | | Concentration, μg/mL | | |
|---|---|---|---|---|---|---|---|
| | | $Cl^-$ | $Br^-$ | $F^-$ | $Cl^-$ | $Br^-$ | $F^-$ |
| | Cal. Standard 1 | | | | | | |
| | Cal. Standard 2 | | | | | | |
| | Cal. Standard 3 | | | | | | |
| | Cal. Standard 4 | | | | | | |
| | Blank | | | | | | |
| | QC Sample | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | Audit #1 | | | | | | |
| | Audit #2 | | | | | | |

___ Plot of peak height or area vs. halide concentration (μg/mL) attached?

___ Injections done in duplicate and agree within ±5% of average?

___ Average response from duplicate injections used to determine concentration?

___ Audit samples within ±10% of actual concentration? ***Note:*** Samples that are analyzed to demonstrate compliance must include a set of two audit samples.

***QA/QC Check***

Completeness ____ Legibility ____ Accuracy ____ Specifications ____ Reasonableness ____

Checked by: _____ _____

Personnel (Signature/Date) Team Leader (Signature/Date)

## SUMMARY SHEET 26A
### Hydrogen Halides and Halogens

| | | | Run #1 | Run #2 | Run #3 | Avg |
|---|---|---|---|---|---|---|
| Client/Plant Name | | FDS 5 | | | | |
| Job No. | | FDS 5 | | | | |
| Sampling Location | | FDS 5 | | | | |
| Run ID # | | FDS 5 | | | | |
| Test Date | | FDS 5 | | | | |
| Run Start Time | | FDS 5 | | | | |
| Run Finish Time | | FDS 5 | | | | |
| Net Traverse Points | | FDS 1 | | | | |
| Traverse Matrix (Rectangular) | | FDS 1 | | | | |
| Net Run Time, min | $\theta$ | FDS 5 | | | | |
| Nozzle Diameter, in. | $D_n$ | FDS 5 | | | | |
| Dry Gas Meter Calibration Factor | Y | CDS 5 | | | | |
| Average $\Delta H$ (orifice meter), in. $H_2O$ | $\Delta H$ | FDS 5 | | | | |
| Barometric Pressure, in. Hg | $P_b$ | FDS 5 | | | | |
| Stack Static Pressure, in. $H_2O$ | $P_g$ | FDS 5 | | | | |
| Abs Stack Pressure ($P_b + P_g/13.6$), in. Hg | $P_s$ | SS 5 | | | | |
| Average Stack Temperature, °F | $t_s$ | FDS 5 | | | | |
| Avg Abs Stack Temperature ($t_s + 460$), R | $T_s$ | FDS 5 | | | | |
| Carbon Dioxide, % dry | $\%CO_2$ | FDS 3 | | | | |
| Oxygen, % dry | $\%O_2$ | FDS 3 | | | | |
| Carbon Monoxide + Nitrogen, % dry | $\%(CO+N_2)$ | FDS 3 | | | | |
| Dry Molecular Weight, lb/lb-mole | $M_d$ | FDS 3 | | | | |
| Average DGM Temperature, °F | $t_m$ | FDS 5 | | | | |
| Volume of Metered Gas Sample, dcf | $V_m$ | FDS 5 | | | | |
| Volume of Metered Gas Sample, dscf | $V_{m(std)}$ | SS 5 | | | | |
| Volume Water Condensed, mL | $V_{lc}$ | FDS 5 | | | | |
| Volume of Water Vapor, scf | $V_{w(std)}$ | SS 5 | | | | |
| Moisture Content, fraction | $B_{ws}$ | SS 5 | | | | |
| Pitot Tube Coefficient | $C_p$ | CDS 2a | | | | |
| Average Velocity Pressure, in. $H_2O$ | $\Delta p$ | FDS 5 | | | | |
| Average $[(t_{si} + 460)\ \Delta p]^{1/2}$ | $[T_{si}\ \Delta p]^{1/2}$ | FDS 5 | | | | |
| Velocity, ft/sec | $v_s$ | SS 5 | | | | |
| Stack Area, $ft^2$ | A | FDS 1 | | | | |
| Isokinetic Sampling Rate, % | %I | SS 5 | | | | |
| Sample Concentration, $\mu$g/mL | S | LDS 26 | | | | |
| Blank Concentration, $\mu$g/mL | B | LDS 26 | | | | |
| Volume of Diluted Sample, mL | $V_s$ | LDS 26 | | | | |
| Sample Mass of Halide, $\mu$g | $m_{HX}$ | SS 26A | | | | |
| Sample Mass of Halogen, $\mu$g | $m_{X2}$ | SS 26A | | | | |
| Stack Concentration, mg/dscf | C | SS 26A | | | | |
| Audit Relative Error, % | RE | QA 1 | | | | |

| | | Run #1 | Run #2 | Run #3 | Avg |
|---|---|---|---|---|---|
| Post-test Calibration Checks | | | | | |
| Temperature and Barometer | CDS 2d | | | | |
| Differential Pressure Gauges | CDS 2d | | | | |
| Metering Systems | CDS 5 | | | | |

$$m_{HX} = k\,(S - B)$$

k = 1.028 for HCl
k = 1.013 for HBr
k = 1.053 for HF

$$m_{X2} = 2\,V_s\,(S - B)$$

$$C = \frac{10^{-3}\,m}{V_{m(std)}}$$

**FIELD PROCEDURE 26A**
**Hydrogen Halides and Halogens**
**(Isokinetic Procedure)**

***Note:*** *This procedure is the same as that for Method 5, except for the variations noted below (see also Figure F26A-1 for variations in the sampling train). The hydrogen halides (HX) include hydrogen chloride (HCl), hydrogen bromide (HBr), and hydrogen fluoride (HF)] and the halogens ($X_2$) include chlorine ($Cl_2$) and bromine ($Br_2$). Ground glass stoppers, plastic caps, serum caps, Teflon tape, Parafilm, or aluminum foil may be used to close openings of train component after preparation, before sampling, during transport to and from the sampling site, and prior to sample recovery.* ***Use FDS 5.***

***A. Sampling***

1. Particulate matter may also be determined concurrently with this method. If so, do not use the alternative Teflon probe liner, cyclone and filter holder, but use the Teflon filter support. If a particulate is not to be determined, do not desiccate or weigh the filter.
2. When the stack temperature >410°F, use a one-piece glass nozzle/liner assembly.
3. Add the following reagents (see Figure F26A-1).
   a. 50 mL 0.1 N $H_2SO_4$ to the condensate impinger, if used.
   b. 100 mL 0.1 N $H_2SO_4$ in each of the next two impingers.
   c. 100 mL 0.1 N NaOH in each of the following two impingers.
   d. 200-300 g of preweighed silica gel from its container to the last impinger.
4. Maintain a temperature >248°F around the filter and (cyclone, if used).
5. If the condensate impinger becomes too full, recover condensate for moisture and HX analysis. Recharge impinger with 50 mL 0.1 N $H_2SO_4$, and replace impinger into sampling train. Conduct required leak-checks. Subtract leak-check volume from total volume.
6. Before disassembling the train, visually inspect the probe liner and filter for signs of moisture. If any moisture is visible, or whenever the optional cyclone is used (even if moisture is not visible), perform the following procedure. Upon completing the test run, connect the ambient air conditioning tube at the probe inlet and purge the train with the filter heating system at 248°F at a low flow rate (e.g., $\Delta H$ = 1 in. $H_2O$) for 30 min. Remove the conditioning tube, and examine the cyclone and filter for any visible moisture. If moisture is still visible, repeat this step for 15 min, and observe again. Keep repeating until the cyclone is completely dry (critical step).

***B. Sample Recovery***

After recovery, seal the lids of all storage containers around the circumference with Teflon tape. Recover the samples as follows:

1. Container No. 1 (Optional: Filter Catch). Same as **FP 5, step E3.**
2. Container No. 2 (Optional: Front Half Rinse. Same as **FP 5, step E4.**
3. Container No. 3 (Knockout and Acid Impinger Catch for Moisture and Hydrogen Halide Determination). Same as **FP 5, step E6,** except:
   a. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers and connecting glassware including the back portion of the filter holder (and flexible tubing, if used) with water and add these rinses to the storage container.
   b. Seal the container, shake to mix, and label. Mark the fluid level.
4. Container No. 4 (Alkaline Impinger Catch for Halogen and Moisture Determination). Same as **FP 5, step E6,** except:
   a. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container.
   b. Add 25 mg sodium thiosulfate per ppm halogen-dscm of stack gas sampled. Seal the container shake to mix, and label: mark the fluid level. Retain alkaline absorbing solution blank and analyze with the samples.
5. Container No. 5 (Silica Gel for Moisture Determination). Same as **FP 5, step E5.**

6. Container Nos. 6 through 9 (Reagent Blanks). Save portions of the absorbing reagent (0.1 N $H_2SO_4$ and 0.1 N NaOH) equivalent to the amount used in the sampling train; dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same ratio of sodium thiosulfate solution used in container No. 4 to the 0.1 N NaOH absorbing reagent blank. Also, save a portion of the rinse water alone and a portion of the acetone equivalent to the amount used to rinse the front half of the sampling train. Place each in a separate, labeled sample container.

7. Shipment. Prior to shipment, recheck all sample containers to ensure that the caps are well-secured. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.

### *C. Alternatives*

1. Do not use metal liners. Water-cooling of the stainless steel sheath is recommended at temperatures exceeding 500°C. Teflon may be used in limited applications for stack temperatures between 250°F and 410°F (point where Teflon is estimated to become unstable).

2. The first impinger shown in Figure F26A-1 (knockout or condensate impinger) is optional and is recommended as a water knockout trap for high moisture conditions.

3. Teflon impingers are an acceptable alternative.

4. When the stack gas temperature is 410°F, a quartz fiber filter may be used instead of the Teflon mat (e.g., Pallflex TX40H145) filter.

### *D. Notes*

1. The acidic absorbing solution is for the HX, and the alkaline for the $X_2$. 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 ($H^+$), the halide ion, and the hypohalous acid (HClO or HBrO).

2. The post-test purge with conditioned air is to vaporize any halides/halogens dissolved in condensed moisture or liquid droplets in the cyclone and on the filter and transfer the gases to the absorbing solutions.

3. Sodium thiosulfate is added 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.

4. Interferences

   a. Chlorine dioxide ($ClO_2$) and ammonium chloride ($NH_4Cl$), which produce halide ions upon dissolution, are potential interferences.

   b. The halogen gases that disproportionate to HX and an hypohalous acid upon dissolution in water interfere with the halides measurement, but the acidic absorbing solution greatly reduces the dissolution of any halogens.

   c. Simultaneous presence of both HBr and $Cl_2$ may cause a positive bias in HCl and a negative bias in $Cl_2$ and affect the $HBr/Br_2$ split between the acid and caustic impingers.

   d. High concentrations of nitrogen oxides ($NO_X$ may produce sufficient nitrate ($NO_3^-$) to interfere with measurements of very low $Br^-$ levels.

   e. When HX $<20$ ppm, a negative bias may result, perhaps due to reaction with small amounts of moisture in the probe and filter.

5. The in-stack detection limit for HCl is approximately 0.02 $\mu$g/L of stack gas; the analytical detection limit for HCl is 0.1 $\mu$g/mL. Detection limits for the other analyses should be similar.

6. The 25 mg sodium thiosulfate/ppm halogen includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second $Cl^-$ ion in the alkaline solution.

# LABORATORY PROCEDURE 26A
## Hydrogen Halides and Halogens

*Note: This procedures for analyzing Containers Nos. 1 and 2 and Acetone Blank (Optional particulate matter determination) and Container No. 5 (silica gel) are the same as that in Method 5 and the rest of the samples are the same as that in Method 26, with the following variations (attach appropriate data sheets, i.e. **LDS 5 and LDS 26**).*

### *A. Reagent Preparation*

Prepare separate reagent blanks of each absorbing reagent for analysis with the field samples as follows:

1. Dilute 200 mL of each absorbing solution (250 mL of the acidic absorbing solution, if a condensate impinger is used) to the same final volume as the field samples using the blank sample of rinse water.
2. If a particulate is determined, collect a blank sample of acetone.

### *B. Analysis*

1. Analyze the Cl samples within 4 weeks after collection for HCl and $Cl_2$.
2. <u>Container Nos. 3 and 4 and Absorbing Solution and Water Blanks</u>. Quantitatively transfer each sample to a volumetric flask or graduated cylinder and dilute with water to a final volume within ±50 mL of the largest sample.
3. If the values from duplicate injections are not within ±5% of their mean, repeat the duplicate injections and use all four values to determine the average response.