

State of California
Air Resources Board

Method 421

Determination of Gaseous Chloride and
Fluoride in Emissions from Stationary Sources

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Method 421

Determination of Gaseous Chloride and Fluoride In Emissions From Stationary Sources

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability

This method is applicable to the quantitative determination of gaseous chloride and fluoride in emissions from stationary sources. It detects gaseous chloride and fluoride compounds which can be absorbed and ionized in a mildly basic buffer solution, and also detects volatile chloride and fluoride compounds in aerosol mists. Hydrochloric acid (HCl) and hydrofluoric acid (HF) are assumed to be the principle compounds detected when testing combustion processes.

1.2 Principle

Gas with entrained aerosols is extracted isokinetically from the stack with a heated glass or quartz probe and passed through a heated filter to a series of chilled impingers where gaseous chlorides and fluorides are absorbed in a solution of sodium bicarbonate and sodium carbonate. This impinger solution is analyzed for chloride and fluoride by ion chromatography with conductivity detection. The chloride and fluoride peaks are identified by characteristic retention times and quantified by reference to external standards.

2. RANGE, SENSITIVITY, AND PRECISION

2.1 Range and Sensitivity

Range and sensitivity will vary depending on analytical instrumentation and other factors including composition of the stack gas sampled. Quantitative measurement of HCl and HF concentrations from fractional ppmv levels to a few percent is achievable.

2.2 Precision

Precision expressed as sample standard deviation and accuracy expressed as average percent recovery are determined as specified in section 7.3 and will vary depending on various factors including operator and instrumentation capabilities and composition of the stack gas sampled.

3. INTERFERENCES

The chromatographic columns and the corresponding operating parameters herein described normally provide a high degree of resolution but interferences may be encountered from some sources.

3.1 Adjacent Anion Peaks

Any anion with a retention time similar to that of chloride or fluoride can interfere. Large amounts of an adjacent anion can interfere with the peak resolution for the chloride or fluoride anion. Sample dilution and/or spiking can solve most interference problems.

3.2 Contamination

Contaminants in the reagent water, reagents, glassware and other sample processing apparatus can cause discrete artifacts or elevated baseline in ion chromatograms.

3.3 Particulate Material

Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns must be filtered to prevent damage to instrument columns and flow systems.

3.4 "Water Dip" Negative Peak

The "water dip" or negative peak elutes near the fluoride peak and can interfere. Some "early eluting" ions also elute near the water dip including acetate, propionate and formate. When the nature of the source or the appearance of chromatograms suggest such interferences an alternate eluent or operating conditions may give better peak resolution.

3.5 Corrective Action

The analyst may select column and operating parameters best suited to the particular analytical problem provided that the operator describes any modifications, demonstrates that the technique is capable of accurate and reproducible measurements by methods outlined in section 7.3, and makes supporting data available for review and approval by the Executive Officer. In this test method, the term "Executive Officer" means the Executive Officer of the Air Resources Board or the Executive Officer (Air Pollution Control Officer) of the Air Pollution Control District/Air Quality Management District. Data generated by alternate methods may be disapproved by the Executive Officer in the absence of adequate assurances of data quality.

4. APPARATUS

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board.

4.1 Sampling Train

The following sampling apparatus is required. The tester may use an alternative sampling apparatus only after the Executive Officer determines that it is equivalent to the required sampling apparatus for the purposes of this test method.

A schematic diagram of the sampling train is shown in Figure 1. The equipment required for this train is the same as described in Method 5 except as follows:

NOTE: Except where otherwise indicated, references to other supporting test methods such as "Method 5" or "Method 2" are to those test methods adopted by the California Air Resources Board.

4.1.1 Probe Liner

Same as described in Method 5 except use only quartz or borosilicate glass liners.

4.1.2 Impingers

Four impingers are connected in series with leak-free glass ball joint fittings or similar leak-free, non-contaminating, inert fittings such as Teflon. The first, third, and fourth impingers are of the Greenburg-Smith design modified by replacing the tip with a 1-cm (0.5 in.) I.D. glass tube extending to 1 cm from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip. A silica gel cartridge may be substituted for the fourth impinger.

As described in section 6.1.3 the first and second impingers will each contain 100 ml of impinger solution (see section 5.1.3). The third will be empty, and the fourth will contain a known weight of silica gel or equivalent dessicant.

A thermometer which measures temperatures to within 1°C (2°F), should be placed at the outlet of the fourth impinger.

4.2 Sample Recovery

The following items are needed:

4.2.1 Brushes and Implements

Probe liner and nozzle brushes, petri dishes, plastic storage containers, funnel and rubber policeman as in Method 5. Used only in equipment cleanup, not in sample recovery.

4.2.2 Wash Bottles

Used only in equipment cleanup, not in sample recovery.

4.2.3 Sample Storage Containers

Chemically resistant, borosilicate glass bottles for impinger solutions and washes, 1000 mL. Teflon or high-density polyethylene or polypropylene bottles may be used. Use screw-cap liners that are either rubber-backed Teflon or leak-free, impermeable and resistant to chemical attack. (Narrow mouth bottles are less prone to leakage).

4.2.4 Graduated Cylinder and/or Balance

To measure condensed water to within 2 mL or 1 g. Graduated cylinder, if used, should be glass, 500 ml (or larger), with subdivisions no greater than 5 mL.

4.2.5 Funnel

To aid in sample recovery. Only a glass funnel may be used.

4.3 Analysis

The following equipment is needed:

4.3.1 Balance –Analytical

Capable of accurately weighing to the nearest 0.0001 g.

4.3.2 Sample bottles

Glass, Teflon, or high-density polyethylene or polypropylene. The capacity should be sufficient to allow replicate analyses of the anion of interest.

4.3.3 Pipettes

An assortment of sizes.

4.3.4 Volumetric Flasks

100-mL, 250-mL and 1000-mL.

4.3.5 Ion Chromatograph

Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed air, detector, and strip chart recorder and/or data system. A data system is recommended for peak integration. The ion chromatograph should have at least the components listed below. The analyst may use alternative components provided that there is adequate resolution of peaks and there is no impairment of precision and accuracy as demonstrated by the methods outlined in section 7.3.

4.3.5.1 Anion guard column

An appropriate anion guard column shall be selected (e.g., Dionex model AG4A or equivalent).

4.3.5.2 Anion separator column

An appropriate anion separator column shall be selected (e.g., Dionex model AS4A or equivalent).

4.3.5.3 Anion Suppressor

An appropriate anion suppressor shall be selected (e.g., Dionex Anion Micromembrane Suppressor or equivalent).

4.3.5.4 Pump

Capable of maintaining a steady flow as required by the system.

4.3.5.5 Flow gauges

A gauge may be necessary for measuring the specified system flow rate; metering pump systems may be used in place of gauges.

4.3.5.6 Detector

Conductivity cell. Approximately 6 uL volume, (e.g., Dionex, or equivalent).

4.3.6 Filtering System

0.45 micron Millipore filter and Millipore vacuum filtration unit or equivalent.

5. REAGENTS

Unless otherwise specified, use American Chemical Society reagent grade (or equivalent) chemicals throughout.

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board.

5.1 Sampling

The following reagents are needed:

5.1.1 Miscellaneous Technical Materials

Filters, silica gel, and crushed ice as specified in Method 5.

5.1.2 Water

Deionized, distilled water which conforms to ASTM Specification D1193-77, Type 3. If high concentrations of organic matter are not expected to be present, the analyst may omit the potassium permanganate test for oxidizable organic matter.

5.1.3 Impinger Solution

A solution of 1.7 mM sodium bicarbonate and 1.8 mM sodium carbonate. Dissolve 0.5712 g sodium bicarbonate (NaHCO_3) and 0.7631 g of sodium carbonate (Na_2CO_3) in reagent water (5.1.2), and dilute to 4 liters. A portion of the impinger solution used for the test must be reserved for use as a reagent blank.

Note: Bacteria can grow in the carbonate/bicarbonate solutions described above and it is good practice to make up fresh stocks frequently and filter before use to protect the chromatographic column.

5.2 Sample Recovery

5.2.1 Recovery Rinse Solution

Same as impinger solution (5.1.3).

5.3 Analysis

The following reagents are needed:

5.3.1 Reagent water

Same as 5.1.2 above. Verify that the conductance is 1 micro-Mho or less.

5.3.2 Eluent solution

A solution of 1.7 mM sodium bicarbonate and 1.8 mM sodium carbonate (see Section 5.1.3) or other eluent recommended by the manufacturer for use with the ion chromatograph equipment described in Section 6.4.

5.3.3 Sulfuric Acid

Concentrated.

5.3.4 Anion Suppressor Regeneration Solution

Follow ion chromatograph manufacturer's recommendations. Sulfuric acid, 0.025 N, is recommended for use with the Dionex equipment described in section 4.3.5.3. Dilute 2.8 mL concentrated sulfuric acid (H_2SO_4) to 4 liters with reagent water.

5.3.5 Stock Chloride Standard Solution, 1000 mg/L

This may be purchased as a certified solution or prepared from ACS reagent grade materials (dried at 105°C for 30 min.) as follows: Dissolve 1.6485 g sodium chloride (NaCl) in reagent water (5.1.2) and dilute to 1 liter. Stock standards are stable for at least one month when stored at 4°C.

NOTE: Chloride and fluoride standards may be combined in solutions containing both ions if desired. Section 5.3.8 describes the procedure for the preparation of fluoride standards.

5.3.6 Intermediate Stock Chloride Standard

Pipet 200 mL of the stock standard (5.3.5) into a 1000-mL volumetric flask, and dilute to volume with eluent solution (5.1.3).

5.3.7 Chloride Calibration Standards

Add accurately measured volumes of the intermediate standard (5.3.6) to a volumetric flask and dilute to volume with eluent solution (5.1.3). Prepare standards at at least three concentration levels (see section 7.2).

5.3.8 Stock Fluoride Standard Solution, 1000 mg/L

This may be purchased as a certified solution or prepared from ACS reagent grade materials (dried at 105°C for 30 min.) as follows: Dissolve 2.210 g sodium fluoride (NaF) in reagent water (5.1.2) and dilute to 1 liter. Stock standards are stable for at least one month when stored at 4°C.

5.3.9 Intermediate Stock Fluoride Standard

Pipet 200 mL of the stock fluoride standard (5.3.8) into a 1000-mL volumetric flask , and dilute to volume with eluent solution (5.1.3).

5.3.10 Fluoride Calibration Standards

Add accurately measured volumes of the intermediate fluoride standard (5.3.9) to a volumetric flask and dilute to volume with eluent solution (5.1.3). Prepare standards of at least three concentration levels (see section 7.2).

6. PROCEDURE

6.1 Sampling

Because of the complexity of this method, testers should be trained and experienced with the test procedures in order to ensure reliable results.

6.1.1 Pretest Preparation

Follow the same general procedure described in Method 5, except the filter need not be weighed.

6.1.2 Preliminary Determinations

Follow the same general procedure described in Method 5.

6.1.2.1 Sampling Time Selection

Considering the nature of the source, select a sampling time period estimated to yield quantifiable concentrations in the impinger solution without overloading the filter with particulate matter or the impingers with condensed moisture.

6.1.2.2 Sampling Run Requirements

Requirements specifying the minimum number of sampling runs, total volume of gas sampled, and total sampling time may be imposed by regulation or by the authority requiring testing. In the absence of such requirements, the test program should be planned so that the test results are representative of emissions during normal operating conditions. At a minimum, three sampling runs must be performed in sequence for a minimum sampling time of 1 hour each.

6.1.3 Preparation of Collection Train

Follow the same general procedure given in Method 5 except substitute impinger solution (5.1.3) for deionized water. Assemble the train as shown in Figure 1.

NOTE: One sampling train must be used as a field blank (6.2.2). Charge the impingers with impinger solution, assemble the train and perform the leak check but do not draw sample gas through the train. Recover the field blank according to section 6.2.

6.1.4 Leak-Check Procedures

Follow the general leak-check procedures given in Method 5 (Pretest Leak Check, Leak Checks During the Sample Run, and Post-Test Leak Check).

6.1.5 Sampling Train Operation

Follow the same general procedure given in Method 5. For each run, record the data required on a data sheet such as the "Field Data Record" form shown in Method 5.

6.1.6 Calculation of Percent Isokinetic

Calculate as in Method 5.

6.2 Sample Recovery

Allow the probe to cool. Inspect the train prior to and during disassembly and note any abnormal conditions. Disconnect the impingers, and treat them in the following manner:

6.2.1 Container No. 1 (Impingers)

If the volume of liquid is large, the tester may place the impinger solutions in several containers. Dismantle each of the first three impingers and connecting glassware in the following manner:

1. Disconnect and cap the ball joints.
2. Rotate and agitate each impinger to remove condensate from impinger walls.
3. Transfer the contents of the impingers to a 500-mL graduated cylinder. Remove each outlet ball joint's cap and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the cylinder. Measure the liquid volume to within ± 2 mL. Alternatively, determine the weight of the liquid to within ± 0.5 g. Record in the log the volume or weight of the liquid present, and the occurrence of any color or film in the impinger catch. The liquid volume or weight is needed, along with the silica gel data, to calculate the stack gas moisture content (see Method 5).
4. Transfer the contents, once measured, to Container No. 1.

NOTE: In steps 5 and 6 below, measure and record the total amount of recovery rinse solution used for rinsing.

5. Pour a measured amount, approximately 30 mL, of recovery rinse solution (5.2.1) into each of the first three impingers and agitate the impingers. Drain the recovery rinse solution through the outlet of each impinger into Container No. 1. Repeat this operation a second time; inspect the impingers for any abnormal conditions.

6. Rinse each piece of glassware connecting the impingers twice with a measured amount of recovery rinse solution, adding this rinse into Container No. 1.

Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

NOTE: Do NOT add any particulate material or cleanup rinse from the probe, filter or filter holder to Container No. 1; rather, DISCARD any such material if not required for other analysis.

6.2.2 Field Blank

At least one field blank must be collected. The field blank must be treated the same as the samples except that no sample gas is drawn through the sampling train. The blank must be analyzed as a contamination check for the solutions and apparatus used in the field.

6.2.3 Container No. 2 (Silica Gel)

Check the color of the indicating silica gel to determine if it has been completely spent, and note its condition. Transfer the silica gel from the fourth impinger to the original container and seal. The tester may use a funnel to pour the silica gel, and rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or any other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow the procedure for weighing Container No. 2 under section 6.4.3.

6.3 Sample Preparation

6.3.1 Container No. 1 (Impingers)

Check the liquid level to determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or determine the volume lost from the difference between the initial and final solution levels, and use this value to adjust the final results. Adjustments must be reported with test results and adjusted results are subject to approval by the Executive Officer.

Filter the sample through a Millipore membrane filter (4.3.6) into a volumetric flask, and dilute to volume with deionized distilled water.

6.3.2 Field Blank

Filter through a Millipore membrane filter (4.3.6) into a volumetric flask. Dilute to the same volume as the sample (see section 6.3.1).

6.4 Analysis

The analysis should be done only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting chromatograms. Each analyst should demonstrate the ability to generate acceptable results with this method using the procedure described in section 7.3.2.

6.4.1 Chromatograph Conditions

The following operating conditions are recommended for the ion chromatograph. Other columns, chromatograph conditions, or detectors may be used if the conditions of section 7.3.2 are met.

6.4.1.1 Columns

As specified in 4.3.5.

6.4.1.2 Detector

As specified in 4.3.5. Select the sensitivity required for the analysis based on estimated sample concentration. Follow the manufacturer's instructions for obtaining the optimum temperature compensating factor for each column set and eluent batch. This is especially important when operating at high sensitivities.

6.4.1.3 Eluent

As specified in 5.3.2.

6.4.1.4 Sample Loop

100 μ L.

6.4.1.5 Pump Volume

2.30 mL/min.

6.4.1.6 Calibration

Calibrate the ion chromatograph, and prepare a calibration curve as described in section 7.2.

6.4.2 Chromatographic Analysis

Load and inject a fixed amount of well mixed sample (at least 10 loop volumes). The first samples to be analyzed should be a reagent blank (5.1.3) and calibration standards followed by a quality control sample. Use the same size loop for standards and samples. Flush the injection loop thoroughly with each new sample. An automated constant volume injection system may also be used.

For each sample, record the injection time, injection volume, flow rate, detector sensitivity setting, recorder chart speed, peak height or area, and retention time.

It is recommended that all injections of field samples be duplicated. At least 10% of field sample injections must be duplicated (see section 7.3.5 below).

If a peak response exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and re-analyze. Calculate a dilution factor (≤ 1) for use in the final calculations.

Run a reagent blank (5.1.3) and a standard after every 10 samples to check the chromatograph calibration. Recalibrate as necessary.

The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for an anion. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

If any chromatogram fails to produce adequate resolution, or if identification of an anion is questionable, spike the sample with an appropriate amount of standard, and reanalyze.

6.4.3 Container No. 2 (Silica Gel)

The tester may conduct this step in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

7. CALIBRATION AND QUALITY CONTROL

7.1 Sampling Train Calibration

Calibrate the sampling train components according to the requirements of Method 5.

7.2 Standard Calibration Curves

Establish the ion chromatographic operating parameters indicated in section 6.4.1 above. Prepare a sufficient number of fluoride and chloride standards (sections 5.3.7 and 5.3.10), or combined chloride and fluoride standards, to construct an accurate calibration curve for each ion. This should include a minimum of four concentrations each for chloride and fluoride and a reagent blank (5.1.3). The concentration of the lowest standard should be near, but above the method detection limit or the low end of the concentration range for the attenuator setting. The other standards should correspond to the range of concentrations expected in the sample. Additional standards may be needed to define any non-linear regions.

7.2.1 Preliminary Adjustment

Pump eluent through the column. After the system is equilibrated and the detector baseline is stable adjust zero to approximately 10 percent of chart. Inject the highest calibration standard. As the highest calibration standard elutes, adjust the largest peak to approximately 90 percent of chart.

7.2.2 Calibration Injections and Data

Inject 0.01 to 1.0 mL (determined by injection loop volume) of each calibration standard starting with the highest concentration.

For each peak record the anion (chloride or fluoride), concentration of the standard, peak height or area, the injection time (the position of the pen on the chart at the time of sample injection), injection volume, flow rate, attenuator setting, and recorder chart speed. Measure the distance on the chart from the injection time to the

time at which the peak maximum occurs. This distance divided by the chart speed is defined as the anion retention time.

It is recommended that injections of standards be duplicated. Plot the peak height or area of each standard (y-axis) versus the corresponding calibration standard's concentration (x-axis).

7.2.3 Analytical Limit of Detection (LOD)

The analytical limit of detection (LOD) should be calculated at least once every six months, or whenever there is a change in operator or instrumentation. No data shall be reported below the LOD.

Calculate the LOD by the following equation:

$$\text{LOD} = |A| + 3S$$

Where:

A is the least squares intercept from the multipoint calibration curve.

S is the standard deviation of replicate determinations of the lowest concentration standard. At least 7 replicates are required. The lowest concentration standard must be approximately 1 to 5 times the estimated LOD.

7.3 Quality Control

7.3.1 Minimum Requirements

The minimum quality control requirements are an initial demonstration of analytical performance (as described in section 7.3.2), daily analysis of quality control samples for determination of percent recovery, and analysis of duplicates, calibration standards and blanks after every ten field samples as a continuing check on performance. The laboratory should maintain performance records to provide assurance of the quality of data that are generated.

Whenever changes in method as permitted herein are made or when there is a change in operator, instrumentation or reagents, performance should be rechecked by the procedure described in section 7.3.2 below.

7.3.2 Initial Demonstration of Capability

Before performing any analyses, the analyst should demonstrate the ability to generate acceptable accuracy and precision with this method using quality control samples.

7.3.2.1 Preparation of Quality Control Samples

Select a representative spike concentration of 2 mg/L or more for each anion. Use the stock standard to prepare a quality control sample with concentration in eluent solution that is 100 times greater than the values selected above. Use a pipet to add 1.00 mL of this solution to each of four 100-mL volumetric flasks. Fill the flasks with eluent solution to produce four 100 mL aliquots. Samples used for percent recovery checks must not be used to construct or correct the calibration curve.

7.3.2.2 Analysis of Quality Control Samples

Analyze the aliquots according to the procedure in section 6.4.2.

7.3.2.3 Calculation of Percent Recovery

Calculate percent recovery for each anion in each aliquot as $100 \% \times (\text{result})/(\text{expected result})$. Calculate the average percent recovery (R), and the sample standard deviation (s) of the percent recovery, for each anion.

7.3.2.4 Performance Criteria

An average percent recovery between 95.0% and 105% and a sample standard deviation for percent recovery not greater than 15% should be feasible for a competent analyst with appropriate equipment and materials when analyzing concentrations of 2 mg/L or greater in samples prepared as above. If performance is outside these limits, review potential problem areas and repeat the performance test. More restrictive performance criteria may be appropriate when dictated by special testing objectives or when the limits above are outside statistical control limits (usually set at ± 3 standard deviations) based on a laboratory's past performance.

7.3.3 Records of Performance

Results of quality control checks including percent recovery checks and injection of quality control samples as specified in section 7.3.5 below should be kept in an ongoing file maintained and available for continuing reference.

7.3.3.1 Control Charts

Control charts may optionally be used to follow trends in performance for quality control samples in a particular concentration range. For concentrations of 2.0 mg/L or above, control limits should be at least as restrictive as the limits set out in section 7.3.2.4.

7.3.4 Daily Check of Percent Recovery

Each day samples are analyzed, and after every 40 field samples (including field blanks) have been analyzed, and after any change in reagents or instrumentation, the percent recovery "R" shall first be determined for each anion by analyzing in duplicate a spiked sample prepared as described in 7.3.2.1 prior to analysis of samples from the field.

7.3.5 Blanks, Calibration Checks and Duplicates

After every 10 field sample (including field blank) injections and at the end of the day, quality control samples shall be analyzed including a reagent blank, a calibration standard and (if all field samples are not duplicated as recommended) a duplicate of at least one of the preceding field samples. If duplicates or calibration standards deviate more than 5% from expected value or if reagent blanks produce a response greater than 10% of the average field sample concentration, the analyst must attempt to identify and correct analytical problems and reanalyze the field samples.

7.3.6 Additional Quality Assurance Practices

The laboratory may adopt additional quality assurance practices for use with this method including those suggested below.

7.3.6.1 Field Duplicates

Field duplicates (duplicate sampling runs) may be used to monitor the overall precision of the sampling and analysis technique.

7.3.6.2 Confirmation Checks

When there is doubt about the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and spiking must be used.

7.3.6.3 Interlaboratory Performance Checks

Whenever possible the laboratory should analyze quality control samples from other laboratories and agencies such as EPA and NIST.

8. CALCULATIONS

8.1 Nomenclature

C_{Cl} = Chloride concentration (ug/mL) from the calibration curve.

C_F = Fluoride concentration (ug/mL) from the calibration curve.

C_{sHCl} = Concentration of equivalent HCl in the stack gas (mg/m^3), dry basis, corrected to standard conditions of 760 mm Hg (29.92 in. Hg) and 293°K (528°R).

C_{sHF} = Concentration of gaseous fluorides as equivalent HF in the stack gas (mg/m^3), dry basis, corrected to standard conditions of 760 mm H (29.92 in. Hg) and 293°K (528°R).

f = Dilution factor ≤ 1 (required only if sample dilution was needed to reduce the concentration into the range of calibration)

V_s = Total volume of sample solution (mL) (from section 6.3.1).

m_{tHCl} = Total equivalent HCl (mg) in sample volume V_s .

m_{tHF} = Total equivalent HF (mg) in sample volume V_s .

$V_{m(std)}$ = Dry Gas Volume, dscm (dscf). See section 8.2 below.

8.2 Dry Gas Volume

Using the data from this test, calculate $V_{m(\text{std})}$, the total volume of dry gas metered corrected to standard conditions (20°C and 760 mm Hg), by using the appropriate equation specified in Method 5. If necessary, adjust $V_{m(\text{std})}$ for leakages as outlined in Method 5. See the field data sheet for the average dry gas meter temperature and average orifice pressure drop.

8.3 Volume of Water Vapor and Moisture Content

Using data obtained in this test and appropriate equations in Method 5, calculate the volume of water vapor $V_{w(\text{std})}$ and the moisture content B_{ws} of the stack gas.

8.4 Concentrations

8.4.1 Total Equivalent HCl and HF in Sample

Use the following equations to calculate the mass of equivalent HCl and HF in the sample volume V_s :

$$m_{\text{tHCl}} = C_{\text{Cl}} \times 10^{-3} \times V_s \times 1.028 / f \quad \text{Eq. 1a}$$

and

$$m_{\text{tHF}} = C_{\text{F}} \times 10^{-3} \times V_s \times 1.053 / f \quad \text{Eq. 1b}$$

Where:

1.028 = the conversion from chloride anion to equivalent HCl

1.053 = the conversion from fluoride anion to equivalent HF

8.4.2 Equivalent HCl and HF Concentrations in Stack Gas

Use the following equations to calculate HCl and HF concentrations in the stack gas:

$$C_{\text{sHCl}} = K \times m_{\text{tHCl}} / V_{m(\text{std})} \quad \text{Eq. 2a}$$

and

$$C_{\text{sHF}} = K \times m_{\text{tHF}} / V_{m(\text{std})} \quad \text{Eq. 2a}$$

Where:

$K = 35.31 \text{ ft}^3/\text{m}^3$ if $V_{m(\text{std})}$ is expressed in cubic feet

$K = 1.00 \text{ m}^3/\text{m}^3$ if $V_{m(\text{std})}$ is expressed in cubic meters

8.5 Isokinetic Variation and Acceptable Results.

Same as in Method 5. To calculate the average stack gas velocity, use the appropriate equation in Method 2 and the data from this field test.

9. REPORTING REQUIREMENTS

9.1 Report of Analytical Laboratory

The report of the laboratory performing analysis of field samples should include at least the following (nomenclature and units as defined in section 8):

V_s for each field sample and field blank;

C_{Cl} and C_F for each field sample and field blank including results of duplicate injections;

f for each field sample and field blank;

Results for all associated quality control samples required by sections 7.3.4 and 7.3.5, indicating for each the type of sample, the concentration found and the concentration expected;

Nature and results of any corrective action related to quality control samples.

9.2 Report of Source Tester to Data User

The report submitted or published by the source tester should include at least the following (nomenclature and units as defined in section 8):

All data required above in the report of the analytical laboratory;

m_{tHCl} and m_{tHF} for each field sample and field blank;

Volume of water vapor and moisture content for each field sample;

Percent Isokinetic for each field sample;

$V_{m(std)}$ for each field sample;

C_{sHCl} and C_{sHF} for each field sample.

10. ALTERNATIVE TEST METHODS

Alternative test methods may be used provided that they are equivalent to Method 421 and approved in writing by the Executive Officer of the Air Resources Board. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

11. BIBLIOGRAPHY

American Society for Testing and Materials. Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. Philadelphia, Pa. 1974. pp. 40-42.

O'Dell, J.W., Pfaff, J.D., Gales, M.E., and McKee, G.D. "Test Method: The determination of Inorganic Anions in Water by Ion Chromatography – Method 300.0. U.S. Environmental Protection Agency/Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. Jan., 1984.

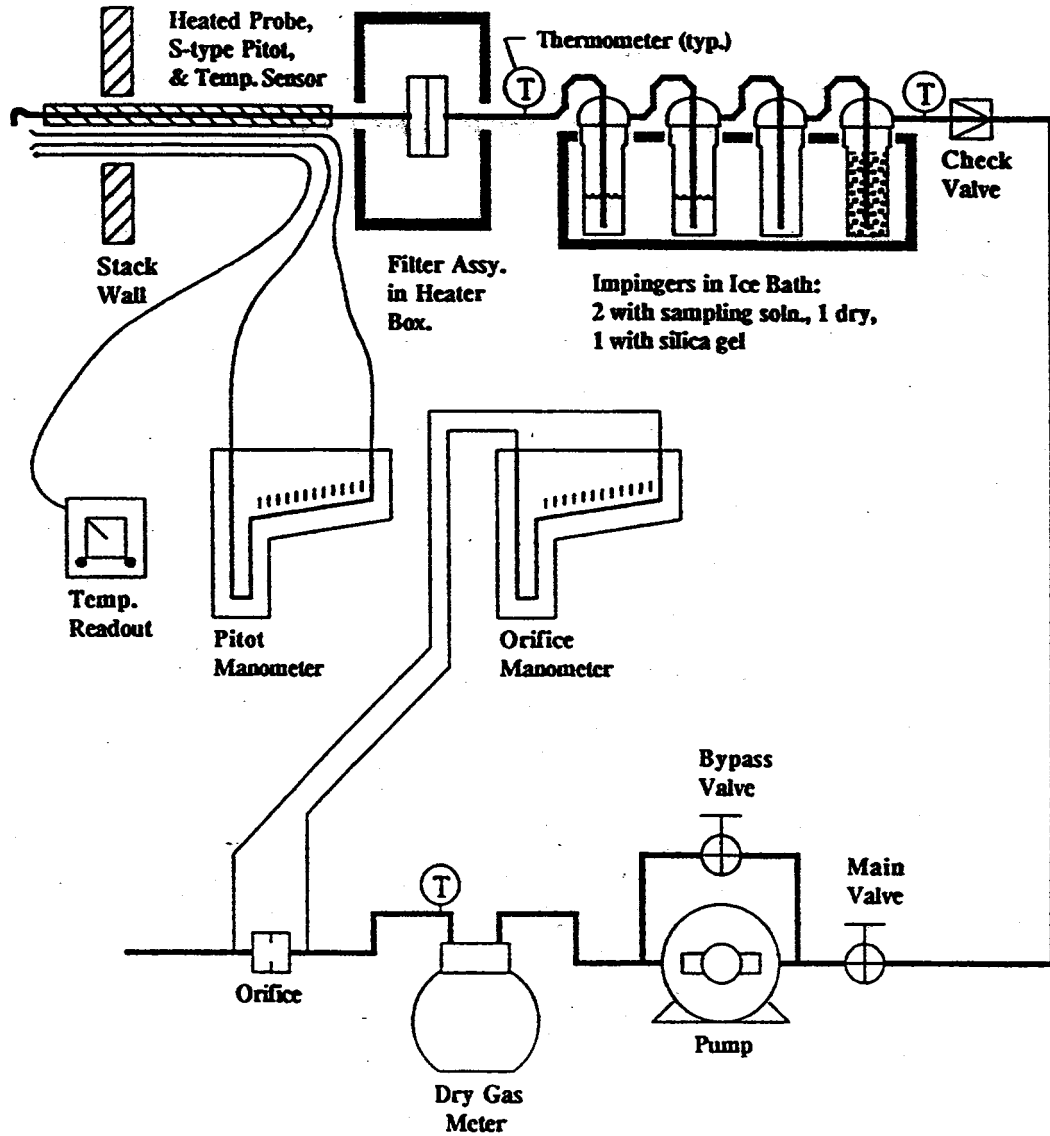
U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., Method 9250. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1982).

NIOSH Manual of Analytical Methods, 3rd ed., Method 7903, Acids, Inorganic. U.S. Department of Health and Human Services DHHS (NIOSH) Publ. No. 84-100. Feb, 1984.

Cheney, J.L., and Fortune, C.R., 1979. Evaluation of a method for measuring hydrochloric acid in combustion source emissions. The Science of the Total Environment. 13: 9-16.

Stationary Source Test Methods – Volume 1 – Methods for Determining Compliance with District Nonvehicular (Stationary Source) Emission Standards. State of California, Air Resources Board, Monitoring and Laboratory Division.

FIGURE 1



Method 421 Sampling Train