An EPA Method 0050 HCl/Cl₂ Train (SW-846 Method 0050) configuration is used to collect samples from stack gas for the assessment of particulate matter, hydrogen chloride (HCl), and chlorine (Cl₂). Other acid gases such as hydrogen fluoride (HF), hydrogen bromide (HBr), nitric acid (HNO₃), nitrous acid (HNO₂), nitrate (NO₃⁻), and nitrite (NO₂⁻) emissions can also be measured. The Method 0050 sample components are collected from the train after the completion of each run. A particulate filter with an attendant acetone probe rinse is collected for the determination of stack gas particulate. A composite sample containing the contents of the first three (3) impingers of the train is collected. The first impinger is empty at the beginning of the sampling run, and serves as a condensate knockout impinger (CKI) for the collection of the majority of the condensate formed in the train. The second and third impingers are initially charged with 100 mL each of 0.1N H₂SO₄. These acidic impingers allowed for the dissociation and collection of HCl and other acid gases from the stack gas. A second composite sample of the fourth and fifth impingers is collected, each initially charged with 100 mL of 0.5N NaOH, and analyzed for Cl⁻ (and F⁻, NO₃⁻, and NO₂⁻).

The main feature of this assessment is the determination of chlorine gas separately from HCl acid gas. Chlorine gas (Cl₂) present in the emissions does not desorb in the acidic H₂SO₄ medium. Chlorine passes through the first three impingers as an unreacted gas, but is trapped by chemical reaction when it comes in contact with the NaOH solution. The reaction is as follows:

\[ \text{Cl}_2 + 2\text{OH}^- \xrightarrow{\text{NaOH}} \text{OCl}^- + \text{Cl}^- + \text{H}_2\text{O} \]

Both of the chlorine products of this reaction dissociate into their respective base forms (Cl⁻ and OCl⁻). Consequently, the Method 0050 sampling train collects the Cl₂ gas (0.5N NaOH impingers) as a separate
species from HCl gas (0.1N H₂SO₄). Note that both the 0.1N H₂SO₄ and the 0.5N NaOH impinger composites are analyzed in the lab for chloride (Cl⁻) anion content, but the HCl and Cl₂ off-gas concentrations are acquired from the data. The 0.5N NaOH samples are treated in the laboratory (not in the field) with sodium thiosulfate (Na₂S₂O₃) as a reducing agent to convert the hypochlorite (OCl⁻) ion to chloride (Cl⁻). Conversion of OCl⁻ to Cl⁻ is performed to ensure that an accurate assessment of the Cl₂ content is made. The chemical equation for the conversion of OCl⁻ is as follows:

\[
S_2O_3^{2-} + 4OCl^- + 2OH^- \rightarrow 2SO_4^{2-} + 4Cl^- + H_2O
\]

Oxidizing species like hypochlorite (OCl⁻) are chemically reduced by thiosulfate to convert it to the chloride anion. By the addition of thiosulfate, the measured concentration of chloride is equal to the exact concentration of chlorine that was trapped by the NaOH impinger solution with no possible bias due to a partial conversion.

The 0.1N H₂SO₄ (condensate samples) and 0.1N NaOH impinger samples are analyzed by ion chromatography using SW-846 Method 9056/9057. The calibration range of the lab application extends from 0.5 mg/L to 20 mg/L for all of the target anions. In order to quantify the target anions, several analyses are typically conducted at different dilution factors that range from 1 to 10, since the various anions are present at several concentration levels. Dilutions are performed to bring the sample concentrations within the instrument calibration range, as well as to overcome any deleterious matrix effects. Optimum values are chosen for reporting, with the lowest detection limits achievable, reported in each case. The final data for each anion are based on analyses that are within the calibration range of the instrument.
Method 0050/Method 26 or 26A

HCl and Cl₂ Emissions in Stack Gas

SAMPLE PRESERVATION AND HOLDING TIMES

The holding times and preservation techniques are either those recommended in Title 40 CFR Section 136.3, Table 11, "Required Containers, Preservation Techniques, and Holding Times," or those presented by EPA in Table 3-1 of the Handbook - Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration (EPA-625/6-89-023).

The 0.5N NaOH impingers should always be individually checked for pH by using pH test strips at the conclusion of each sampling run. The pH should be maintained above pH = 9 during the run, otherwise Cl₂ will not be trapped by the solution, and the results will be biased low.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Matrix</th>
<th>Preservation⁹</th>
<th>Holding Time¹⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate Matter</td>
<td>Particulate Filter</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Hydrogen Chloride and Chlorine (HCl &amp; Cl₂)</td>
<td>0.5N Sodium Hydroxide</td>
<td>pH &gt; 10</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td></td>
<td>0.1N Sulfuric Acid</td>
<td>pH &lt; 2</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td>Hydrogen Fluoride (HF)</td>
<td>0.5N Sodium Hydroxide</td>
<td>pH &gt; 10</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td></td>
<td>0.1N Sulfuric Acid</td>
<td>pH &lt; 2</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td>Hydrogen Bromide and Bromine (HBr &amp; Br₂)</td>
<td>0.5N Sodium Hydroxide</td>
<td>pH &gt; 10</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td></td>
<td>0.1N Sulfuric Acid</td>
<td>pH &lt; 2</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td>Hydrogen Nitrate and Hydrogen Nitrite (HNO₃ &amp; HNO₂)</td>
<td>0.5N Sodium Hydroxide</td>
<td>Cool, 4°C ± 2°C, pH &gt; 10</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td></td>
<td>0.1N Sulfuric Acid</td>
<td>Cool, 4°C ± 2°C, pH &lt; 2</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td>Sulfuric Acid (H₂SO₄)</td>
<td>0.5N Sodium Hydroxide</td>
<td>Cool, 4°C ± 2°C, pH &gt; 10</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td></td>
<td>0.1N Sulfuric Acid</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Phosphorous Acid (H₃PO₃)</td>
<td>0.5N Sodium Hydroxide</td>
<td>Cool, 4°C ± 2°C, pH &gt; 10</td>
<td>28 days to analysis</td>
</tr>
<tr>
<td></td>
<td>0.1N Sulfuric Acid</td>
<td>Cool, 4°C ± 2°C, pH &lt; 2</td>
<td>28 days to analysis</td>
</tr>
</tbody>
</table>

⁹ CPT samples requiring refrigeration will be preserved on ice from the time of collection through delivery to the analytical laboratory.

¹⁰ Holding times are calculated from the date of collection.
Sodium Thiosulfate Addition to 0.1 N Sodium Hydroxide Impingers:  
*In the Field or In the Lab?*

In an effort to optimize service to our customers, TestAmerica has reviewed the sampling and analysis objectives regarding Method 0050 (also Method 26A) to provide recommendations of best practice. The particular issue before us is the addition of sodium thiosulfate (Na$_2$S$_2$O$_3$) to the sodium hydroxide (NaOH) impinger composite to achieve the complete conversion of the impinger species to chloride (Cl$^-$). Some additional development of the issue is helpful.

TestAmerica strongly recommends that **No Sodium Thiosulfate** be added in the field, but that the lab be instructed to add the right amount at the time of analysis. Sodium Thiosulfate is **not** a preservative. The article below explains why.

Both Method 0050 (from SW-846) and Method 26A (from CFR 40) include procedures for the recovery of the NaOH impingers in the field instructing the stack sampling technicians to add Na$_2$S$_2$O$_3$ to the sample composite. Method 0050 prescribes the addition in Section 7.6.13, and Method 26 places the requirement in Section 8.2.4. Specifically, the instructions say to add 25 mg of Na$_2$S$_2$O$_3$ to the composite for every ppm of halogen anticipated to be in the stack gas. The fact that this instruction is ambiguous is obvious since these measurements have to be made first in order to know the ppm in the stack gas. Additionally, the volume of stack gas actually pulled through the impinger train defines the absolute amount of Na$_2$S$_2$O$_3$ required to treat the samples. All of this simply to say that a stack sampling technician is probably **not** going to be equipped with either the information or the tools to establish the ppm levels of chlorine in the stack on site.

Therefore, the amount of Na$_2$S$_2$O$_3$ that needs to be added to the samples will not be known until the samples are analyzed. The problem typically manifests itself when samplers attempt to add sodium thiosulfate with no knowledge of the sample needs and place well over the amount needed to convert the contents of the sample. Thiosulfate (S$_2$O$_3^{2-}$) is an anion just like chloride, and gives a characteristic chromatographic peak downfield of sulfate (SO$_4^{2-}$). If placed in the samples in milligram quantities, a huge chromatographic peak is placed in the samples that typically interferes with chloride (Cl$^-$). Dilutions are effective in bringing the interference under control, but often dilute out the chloride peak at the same time. We receive samples so loaded with the Na$_2$S$_2$O$_3$ that
the only anion peak defined after the required dilutions are applied is the superfluous thiosulfate peak. This chemical should not be put into these samples with no knowledge of the required amounts.

How then should the sodium thiosulfate treatment be handled? Note that sodium thiosulfate is not a preservative. It does not serve to prolong the holding time for 0.5N NaOH impingers, nor prevent the loss of chloride. Sodium thiosulfate is a reducing agent applied to these samples to convert an oxidized form of chlorine to chloride. In the impinger during sampling the following hydrolysis reaction takes place to trap the chlorine gas:

\[
\text{Cl}_2 + \text{H}_2\text{O} \xrightarrow{\text{NaOH}} \text{H}^+ \text{Cl}^- + \text{H}^+ \text{OCl}^- \quad \text{(Equation 1)}
\]

The simplified presentation of this reaction is:

\[
\text{Cl}_2 \xrightarrow{\text{NaOH}} \text{Cl}^- + \text{OCl}^- \quad \text{(Equation 2)}
\]

The products are chloride (Cl\(^-\)) and hypochlorite ion (OCl\(^-\)). The Na\(_2\)S\(_2\)O\(_3\) is used to convert the hypochlorite (OCl\(^-\)) to chloride (Cl\(^-\)) as follows:

\[
\text{S}_2\text{O}_3^{2-} + 4\text{OCl}^- + 2\text{OH}^- \rightarrow 2\text{SO}_4^{2-} + 4\text{Cl}^- + \text{H}_2\text{O} \quad \text{(Equation 3)}
\]

Note that the reaction requires basic conditions to be favored and that [OCl\(^-\)] will always be less than or equal to the [Cl\(^-\)] in these impingers (Equation 2).

At the bench, the analyst removes a portion of the impinger sample composite and prepares to inject it onto the column of a calibrated ion chromatograph. At this time the analyst places enough Na\(_2\)S\(_2\)O\(_3\) into the aliquot portion to fully reduce hypochlorite for any level of chloride concentration below the top calibration point. Figure 1 displays a calibration curve for chloride (Cl\(^-\)) and the
calibration range that all analyses are to be bracketed within. Table 1 displays the stoichiometric amounts of Na$_2$S$_2$O$_3$ required for conversion within the calibration range. The reducing reagent is applied with a 2-fold excess relative to the top calibration point. If chloride is present above the calibration point, dilutions are required to bring it under the top point, assuring that the reaction with thiosulfate will be complete.

Table 1.
Micrograms of Sodium Thiosulfate Required to Convert Hypochlorite at Concentrations Within the Anion Calibration Scale

<table>
<thead>
<tr>
<th>Calibration Point</th>
<th>Parts-per Million (ppm)</th>
<th>Total μg Cl$^-$ (50 mLs)</th>
<th>μMoles of Chloride (Cl$^-$)</th>
<th>μMoles of Sodium Thiosulfate (S$_2$O$_3^{2-}$)</th>
<th>Micrograms of Thiosulfate* (Na$_2$S$_2$O$_3^{2-}$ • 5 H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>25</td>
<td>0.705</td>
<td>0.176</td>
<td>43.68</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>50</td>
<td>1.410</td>
<td>0.323</td>
<td>80.16</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>125</td>
<td>3.526</td>
<td>0.882</td>
<td>218.89</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>250</td>
<td>7.052</td>
<td>1.763</td>
<td>437.54</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>500</td>
<td>14.103</td>
<td>3.526</td>
<td>875.08</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>750</td>
<td>21.155</td>
<td>5.289</td>
<td>1,312.62</td>
</tr>
</tbody>
</table>

The weight indicated is the stoichiometric amount of sodium thiosulfate required for the conversion of OCl$^-$ present at the concentration of the calibration point. Theoretically the concentration of OCl$^-$ is less than or equal to the concentration of Cl$^-$ in the sample.

\[
\text{Cl}_2 + \text{OH}^- \rightarrow \text{Cl}^- + \text{OCl}^- 
\]

Molecular Weight of Sodium Thiosulfate: Na$_2$S$_2$O$_3$ • 5 H$_2$O (248.18 gm/mole or 248.18 μg/μmole)

Molecular Weight of Chlorine: Cl$^-$ (35.453 gm/mole or 35.453 μg/μmole)

Equation: S$_2$O$_3^{2-}$ + 4 OCl$^-$ + 2OH$^-$ $\rightarrow$ 2 SO$_4^{2-}$ + 4 Cl$^-$ + H$_2$O
TestAmerica’s Approach at the Bench

In conclusion, TestAmerica recommends that the lab be instructed to carry out the treatment of 0.5N NaOH impinger composites with sodium thiosulfate. In the controlled environment of the lab, we can discern the amount that needs to be added without applying the huge excesses that are heaped upon these samples in an information vacuum.
Calculation Showing the Microliters of Sodium Thiosulfate Spike Added by TestAmerica Procedure:

1) TestAmerica sodium thiosulfate solution concentration:
   \[ 1.0\text{N } S_2O_3^{2-} = 1.0 \text{ eq/L} = 1.0 \text{ moles/L} = 1.0 \mu\text{moles/\muL} \]

2) A 20 microliter spike converted to micromoles:
   \[ 1.0 \mu\text{moles/\muL} \cdot (20 \mu\text{L}) = 20 \mu\text{moles} \]

3) Micromoles converted to micrograms:
   \[
   (20 \mu\text{moles}) \cdot \left( \frac{248.18 \mu\text{g/\mu mole}}{1 \mu\text{mole}} \right) = 4963.6 \mu\text{g} \\
   = 4.96 \text{ mg of } Na_2S_2O_3
   \]

* For classical oxidation-reduction (redox) chemical equations, the normality of a solution depends on the number of oxidation state changes that take place for a chemical in a given reaction. The normality of Na$_2$S$_2$O$_3$ is four (4) times the molarity in the current application. However, it has been ascribed a normality of 1.0 by the supplying vendor, and affirmed by them to likewise have a molarity of 1.0, even though the number of equivalence in this application is four (4). The calculation above uses the vendor supplied information.

Calculation Showing the Microliters of 0.1N Sodium Thiosulfate Required for a Five-Fold Excess:

1) From Table #1 the stoichiometric weight of sodium thiosulfate is increased five-fold:
   \[ 1.313 \text{ mg } Na_2S_2O_3 \times 5 = 6.57 \text{ mg} \]

2) The millimoles of reagent are calculated as follows:
   \[
   (6.57 \text{ mg}) \cdot \left( \frac{1.0 \text{ millimoles}}{248.18 \text{ mg}} \right) = 0.026 \text{ millimoles of } Na_2S_2O_3
   \]

3) The spike volume of a 1.0N Na$_2$S$_2$O$_3$ solution is calculated as follows:
   \[
   (0.026 \text{ millimoles}) \cdot \left( \frac{\text{mL}}{1.0 \text{ millimoles}} \right) = 0.026 \text{ mL} \\
   = 26 \mu\text{L} \text{ or } \approx 25 \mu\text{L} \text{ of a 1.0N } Na_2S_2O_3 \text{ solution required for a nominal 5-fold excess to convert } OCl^- \text{ to } Cl^- \text{ at the top calibration point.}
# Method 0050/Method 26 or 26A

**HCl and Cl₂ Emissions in Stack Gas**

## Recommended Quality Measurements for a 3 Run CPT

<table>
<thead>
<tr>
<th>Analytical Parameter (Analysis)</th>
<th>Sample Name or Type</th>
<th>Total No. of Field Samples</th>
<th>Analytical Procedure Description (Method)</th>
<th>Laboratory QC Measurement Type</th>
<th>Frequency of Applied QC Measurement Type</th>
<th>Total No. of Laboratory QC Measurements</th>
<th>Field QC Measurement Type</th>
<th>Total No. of Field QC Samples</th>
<th>Total No. of Laboratory Analyses²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate</td>
<td>M5 Train (particulate filter and acetone probe rinse)</td>
<td>3 filters, 3 acetone probe rinses</td>
<td>Gravimetric (EPA Method 5, Method 26A)</td>
<td>Replicate weighing to constant weigh</td>
<td>Every particulate sample</td>
<td>3 filters, 3 acetone probe rinses</td>
<td>Field blank (1 particulate filter, 1 acetone probe rinse)</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>M5 Train (0.1N sulfuric acid impinger composite)</td>
<td>3</td>
<td>Ion chromatography (SW-9056/SW-9057)</td>
<td>MS/MSD</td>
<td>One set per test condition</td>
<td>2</td>
<td>Reagent blank (0.1N sulfuric acid impinger solution)</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Chlorine</td>
<td>M5 Train (0.5N sodium hydroxide impinger composite)</td>
<td>3</td>
<td>Ion chromatography (SW-9056/SW-9057)</td>
<td>MS/MSD</td>
<td>One set per test condition</td>
<td>2</td>
<td>Reagent blank (0.5N sodium hydroxide impinger solution)</td>
<td>1</td>
<td>6</td>
</tr>
</tbody>
</table>
## Analytical Quality Control Checks, Frequencies, Target Acceptance Criteria, and Corrective Action

<table>
<thead>
<tr>
<th>Parameter/Method</th>
<th>QC Check</th>
<th>Frequency</th>
<th>Target Criteria</th>
<th>Corrective Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate Matter</td>
<td>Replicate weighings of samples and blanks</td>
<td>Every filter, 6 hour intervals</td>
<td>Repeat filter weighing to constant weight; agreement of last three replicates within ± 0.5 mg</td>
<td>Perform additional measurements</td>
</tr>
<tr>
<td>Chloride by Ion Chromatography (Methods SW-9056 and SW-9057)</td>
<td>Initial Calibration (minimum four (4) standards and one (1) blank)</td>
<td>Daily</td>
<td>Fit of standard curve • Correlation coefficient ≥ 0.995</td>
<td>(1) Repeat linearity check (2) Prepare new standard (3) Service instrument</td>
</tr>
<tr>
<td></td>
<td>Initial Calibration Verification (ICV/ICB)</td>
<td>Beginning of analysis sequence</td>
<td>ICV • 90 to 110% recovery ICB • Concentration &lt; RL</td>
<td>Repeat calibration</td>
</tr>
<tr>
<td></td>
<td>Continuing Calibration Verification (CCV/CCB)</td>
<td>After every 10 samples</td>
<td>CCV • 90 to 110% recovery CCB • Concentration &lt; RL</td>
<td>(1) Repeat initial calibration (2) Reanalyze affected samples</td>
</tr>
<tr>
<td>Laboratory Method Blank</td>
<td>Once per sample batch (maximum 20 samples)</td>
<td></td>
<td>Target Analyte Concentration &lt; RL</td>
<td>Flag associated sample data</td>
</tr>
<tr>
<td>Laboratory Control Sample/Laboratory Control Sample duplicate (LCS/LCSD)</td>
<td>Once per sample batch (maximum 20 samples) LCSD not required if MSD performed</td>
<td></td>
<td>Accuracy • %Recovery: 90 – 110% Precision (if applicable) • RPD ≤ 20%</td>
<td>(1) Rerun Entire Batch (2) If not rerun, or results are still unacceptable, flag data (3) Discuss in final report</td>
</tr>
<tr>
<td>Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis</td>
<td>Recommend one set per 0.1N H₂SO₄, and one set per 0.5N NaOH client batch</td>
<td></td>
<td>Accuracy • %Recovery: 80 – 120% Precision (if applicable) • RPD ≤ 35%</td>
<td>Flag data</td>
</tr>
</tbody>
</table>
Method 0050/Method 26 or 26A
Method for Determining HCl and Cl₂ Emissions in Stack Gas

**Sampling and Field Procedures for HCl, Cl₂, and Particulate in Stack Gases**

**Sample Name:** Stack HCl/Cl₂/Particulate  
**Note:** The recommended sample names for these samples are:
- 0.1N H₂SO₄ Impinger Composite  
- 0.5N NaOH Impinger Composite  

Please use these names on the Chain-of-Custody documentation.

**Sampler:** Stack Sampling Engineer  
**Process Sample Location:** Stack Sampling Platform  
**Sampling & Health & Safety Equipment:** Sampling and safety equipment is as follows:
- Method 0050 Sampling Train  
- Petri Dish with tared weighed Particulate Filter  
- 250 mL amber Boston Round - Acetone Probe Rinse  
- 1 Liter amber Boston Round* - 0.1N H₂SO₄ Impinger Contents  
- 500 mL amber Boston Round* - 0.5N NaOH Impinger Contents  
- Graduated Cylinder  
- Acetone  
- Wash bottles  
- Safety glasses or face shield  
- Latex gloves and other safety equipment as required  

*Note: A smaller Boston Round bottle is recommended if volume of final sample allows.

**Sample Collection Frequency:** Continuously during each sampling run. Sampling volume will be one (1) m³ (or larger) at a rate not to exceed 0.75 m³ per hour.

**Sampling Procedures:** Particulate Filter Preparation -- A set of quartz fiber filters will be individually prepared by weighing to a constant weight on a calibrated analytical balance capable of measuring 0.0001 g. The filter will then be sealed with Teflon® tape in a numberered, clean glass petri dish for transport to the field.
HCl/Cl₂/Particulate Train Operation -- The sampling train will be assembled with a tared particulate filter; with a heated glass probe and empty first impinger for the collection of condensate. Note that if large amounts of condensate moisture is expected, the first impinger volume should be considered such that bumping of the contents of impinger #1 into impinger #2 is avoided. The accumulation of condensate in Impinger #2 affects the 0.1N H₂SO₄ solution by dilution. The second and third impingers will contain 100 ml of 0.1N H₂SO₄, and the fourth and fifth impinger will contain 100 ml of 0.5N NaOH. A sixth impinger is a silica gel moisture trap which is pre-weighed for the purpose of moisture gain. The impinger train will be connected to a control box, which contains flow controls, thermocouple readouts and a dry gas meter capable of accurately measuring the gas sample volume. After assembly, the train will be leak checked prior to and following each sampling run.

An initial traverse is made with a pitot tube at each sample port following EPA Methods 1 and 2 to establish the stack velocity profile, temperature, and flow rate, and to check for cyclonic air flow. Sample point location will be in accordance with EPA Method 1. The total sampling time during a run will be approximately 1½ hours with a nominal two (2) dry standard cubic meter (dscm) of stack being sampled. EPA Method 5 procedures are followed for pre-test and post-test leak checks, isokinetic sampling rate, and filter changeouts (if needed), and data recording.

HCl/Cl₂/Particulate Train Sample Recovery -- The impinger section of the sampling train is moved intact to the cleanup area for sample recovery as follows:

- The particulate filter is removed from its holder and carefully placed into its original glass petri dish which is then sealed with Teflon® tape and further sealed in a Zip-lock® bag.

- The internal surfaces of the nozzle, probe, and front half of the filter holder are cleaned by first rinsing, brushing, and final rinsing with acetone. These acetone rinsates are collected together into a pre-labeled, numbered 250 ml Boston Round glass sample bottle.

- The samples will be recovered from the sampling train by disconnecting the first three impingers, volumetrically measuring their individual catches, and transferring the catches into a single one (1) Liter Boston Round amber glass sample bottle with a Teflon® lined lid. The impingers will be then rinsed with 0.1N H₂SO₄ and this rinse will be combined with the impinger sample. The total H₂SO₄ impinger sample and rinse volumes will be recorded on the sample collection sheet. The pH of the final sample will also be measured using appropriate pH test strips and recorded on the sample collection sheet. The samples will be packed and shipped to the laboratory where they will be analyzed for chloride by ion chromatography. No cooling to 4°C is required for this sample.
The pH of the individual 0.5N NaOH impingers will also be measured using appropriate pH test strips and recorded on the sample collection sheet. The impingers will then be volumetrically measured and transferred to a separate, numbered, pre-labeled one (1) liter Boston Round amber glass sample bottle. These impingers will be rinsed with 0.5N NaOH and the rinsate will be combined with the NaOH impinger sample. The total NaOH impinger sample and rinse volume will be recorded on the sample collection sheet. The samples will be packed and shipped to the laboratory where they will be analyzed for chloride by ion chromatography. No cooling to 4°C is required for this sample.

Documentation and Record Keeping:
Before sampling is commenced, each bottle will be labeled with a specific sample number, the project name, the run number, the sample description, and an area for the date of sampling. The sampling coordinator will also record all samples collected into a field logbook. This logbook will serve as the master document listing of all of the trial burn samples collected.

Quality Assurance:
During one run of the test, reagent blank samples will be collected of the stock 0.1N sulfuric acid and 0.5N sodium hydroxide impinger solutions, the acetone probe rinse solution, and the particulate filter media.

All equipment, including the thermocouples, rotameters and dry gas meter will be calibrated before the tests and their calibrations verified after the completion of each test run.

Method References:
EPA Methods 1, 2, 3, 4 and 5, Appendix A, Reference Methods, New Source Performance Standards, 40 CFR 60.


Analysis of HCl/Cl₂ and Particulate in M-5 Train Samples

Sample Name: Particulate Filter
Acetone Probe Rinse
0.1N H₂SO₄ Impinger Contents
0.5N NaOH Impinger Contents

Sample Holding Time: Particulate Determinations: none, but perform in a timely manner.
Chlorine or Chloride Analysis: analyze within 30 days of sample collection.

Analysis Procedures:

Particulate Sample: Condition the particulate filter sample by oven drying for 24 hours at 105°C followed by 2 hours of desiccation. Conduct replicate weighings of the filter every 6 hours while continuing to desiccate between weighings until a constant weight has been achieved. Weigh the filter sample using a calibrated analytical balance capable of weighing to the nearest 0.0001 g.

Acetone Probe Rinse: Evaporate the acetone probe rinse sample to near dryness and prepare the residue by oven drying at 105°C for 24 hours. Weigh the dried residue to a constant weight on a calibrated analytical balance capable of weighing to the nearest 0.0001 g.

Impinger Samples: Analyze H₂SO₄ and NaOH impinger samples separately for chloride using an ion chromatograph. Report results as HCl and Cl₂ catches respectively.

Method References:


Method 26A - 40CFR 60 Appendix A, "Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources -- Isokinetic Method ".