Other Test Method – 40: Determination of Hydrogen Chloride Emissions from Coal-Fired Combustion Sources Using Sorbent Traps

NOTE: Please submit a copy, either electronic or paper, of any test report from application of this OTM to EPA's Measurement Technology Group. **Electronic copies should be submitted via email with the subject line "OTM-40" to: EMC@epa.gov Paper copies should be mailed to:**
>   **Measurement Technology Group**
>   **Office of Air Quality Planning and Standards**
>   **U.S. Environmental Protection Agency (Mail Code E143-02)**
>   **Research Triangle Park, NC 27711**

This method takes the sampling technique and approach to performance specifications found in the sorbent based measurement method for mercury emissions (EPA Method 30B, 40 CFR 60, Appendix A) and applies them to the measurement of hydrogen chloride (HCl) emissions.

This method was submitted by the Energy and Environmental Research Center (EERC) on behalf of the Electric Power Research Institute (EPRI) to EPA's Office of Air Quality, Planning and Standards, Air Quality Assessment Division, Measurement Technology Group (MTG) for (1) inclusion into the Other Test Method (OTM) category on EPA's Air Emission Measurement Center (EMC) website at: https://www.epa.gov/emc/emc-other-test-methods and (2) consideration as a broadly applicable alternative test method. OTM-40 has now been approved for use at coal-fired utility steam generating units subject to 40 CFR Subpart UUUUU, see https://www.epa.gov/sites/production/files/2018-05/documents/alt129.pdf

The posting of a test method on the OTM portion of the EMC website is neither an endorsement by EPA regarding the validity of the test method nor a regulatory approval of the test method. The purpose of the OTM portion of the EMC website is to promote discussion of developing emission measurement methodologies and to provide regulatory agencies, the regulated community, and the public at large with potentially helpful tools.

Other Test Methods are test methods which have not yet been subject to Federal rulemaking. Each of these methods, as well as the available technical documentation supporting them, have been reviewed by the EMC staff and have been found to be potentially useful to the emission measurement community. The types of technical information reviewed include field and laboratory validation studies; results of collaborative testing; articles from peer-reviewed journals; peer-review comments; and quality assurance (QA) and quality control (QC) procedures in the method itself. A table summarizing the available technical information for each method can be found at the link below. As noted above, the EPA strongly encourages the submission of additional supporting field and laboratory data as well as comments in regard to these methods.

These methods may be considered for use in federally enforceable State and local programs (e.g., Title V permits, State Implementation Plans (SIP)) provided they are subject to an EPA Regional SIP approval process or permit veto opportunity and public notice with the opportunity for comment. The methods may also be considered to be candidates to be alternative methods to

meet Federal requirements under 40 CFR Parts 60, 61, and 63; <u>however, they must be approved as alternatives through a separate action under §§60.8(b), 61.13(h), or 63.7(f) before a source may use them for this purpose.</u> Consideration of the applicability of an OTM for a particular purpose should be based on the stated applicability, the supporting technical information outlined in the table, or regulatory actions including approval as an alternative test method or inclusion in a SIP. These methods are available for application without EPA oversight for other non-EPA program uses including state permitting programs and scientific and engineering applications.

As many of these methods are submitted by parties outside the Agency, the EPA staff may not necessarily be the technical experts on these methods. Therefore, technical support from EPA for these methods is limited, but the table contains contact information for the developers so that you may contact them directly. Also, be aware that these methods are subject to change based on the review of additional validation studies or on public comment as a part of adoption as a Federal test method, the Title V permitting process, or inclusion in a SIP.

Method History

Initial Posting – 05/31/2018

EPA advises all potential users to review the method and all appendices carefully before application of this method.

***OTHER TEST METHOD 40 (OTM – 40) Determination of Hydrogen Chloride
Emissions from Coal-Fired Combustion Sources Using Sorbent Traps***

1.0   *Scope and Application*

Other Test Method 40 is a method designed to measure hydrogen chloride (HCl) in emissions
from coal-fired electric utility steam generating units with "dry" flue gas (i.e., no entrained water
droplets). The method uses sorbent traps and an extractive sampling system to collect a
representative sample. The total chloride collected in the sorbent traps is then measured using ion
chromatography (IC) for chloride which is reported as HCl.

1.1 Analytes

This method is intended to measure HCl (CAS No. 7647-01-0) in micrograms per dry standard
cubic meter (µg/dscm). The measurable concentration range will depend on the sample time
(longer sample collection time for lower concentrations) or sample dilution (higher-concentration
samples can be diluted). For the purposes of this method, standard temperature and pressure are
defined as 20°C and 760 mm Hg, respectively. This method is applicable for determining
emissions of HCl from coal-fired electric generating units that emit a "dry" flue gas. This method
does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g.,
sampling and analytical) essential to its performance. Some material is incorporated by reference
from other methods in this part. Therefore, to obtain reliable results, persons using this method
should have a thorough knowledge of additional U.S. Environmental Protection Agency (EPA)
test methods, which are found in 40 CFR 60, Appendices A-1, A-3, and A-6.

a.   Method 1—Sample and Velocity Traverses for Stationary Sources.
b.   Method 4—Determination of Moisture Content in Stack Gases.
c.   Method 5—Determination of Particulate Matter Emissions from Stationary Sources.
d.   Methods 26 and 26A—Determination of Hydrogen Halide and Halogen Emissions from
     Stationary Sources.
e.   Method 30B—Determination of Total Vapor Phase Mercury Emissions from Coal-Fired
     Combustion Sources Using Carbon Sorbent Traps.

1.2 Applicability

*Note: The use of OTM-40 for performance tests used to show compliance with federal emission
standards or monitoring requirements must be approved by the EPA Administrator.*

This method is intended for measuring HCl emissions for the purposes of conducting compliance
tests, performing relative accuracy test audits (RATAs) of HCl continuous emissions monitoring
systems, and similar emission measurements. The method is designed for relatively low
particulate matter applications and should only be applied at sampling location after all pollution
control devices. The method shall not be used at stationary sources where moisture droplets may
be present (e.g., after a wet scrubber). In addition, sampling at sources that contain high

ammonia (NH₃) environments should be avoided. At present, this method has been approved by the EPA Administrator for application to coal-fired electric utility steam generating units subject to 40 CFR 63, Subpart UUUUU with low moisture combustion gases at temperatures above 100 C with no entrained water droplets. Regulatory applications this method beyond this source category must be approved by the appropriate regulatory authority.

1.3 Data Quality Objectives (DQO)

OTM-40 is designed to provide data of known quality for measuring HCl emissions from coal-fired combustion systems. The principle objective is to ensure the accuracy of the data at the actual emission levels and in the actual emissions matrix encountered. To meet this objective, National Institute of Standards and Technology (NIST) traceable calibration and spiking standards must be used and method performance tests are required. Quality assurance and quality control requirements are included in this method to assure that the data collected is of known and acceptable quality for each testing program. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 *Summary of Method*

Known volumes of flue gas are extracted from a stack or duct through paired, in-stack sorbent media traps at an appropriate flow rate. For each test run, paired train sampling is required to determine measurement precision and verify acceptability of the measured emissions data. A field recovery test which assesses recovery of a gaseous HCl spike to determine measurement bias is also used to verify data acceptability. The sorbent traps are recovered from the sampling system, prepared for analysis as needed, and analyzed by ion chromatography.

3.0 *Definitions*

3.1 Analytical System. The combined equipment and apparatus used to perform sample analyses. This includes any associated sample preparation apparatus (e.g., digestion equipment, spiking systems, reduction devices, etc.) as well as an analytical instrumentation such as IC (ion chromatography).

3.2 Calibration Standards. The chloride-containing solutions prepared from NIST-traceable standards and are used to calibrate analytical systems.

3.3 Independent Calibration Standard. NIST-traceable standard obtained from a source or supplier independent of that for the calibration standards. It is used to confirm the integrity of the calibration standards used.

3.4 Interference. A compound or material in the sample matrix other than HCl whose characteristics may bias the measurement (positively or negatively). The interference may not prevent the sample measurement but could increase the analytical uncertainty in the measured HCl concentration.

3.5 Liquid Evaporative Standard. A reference gas produced by vaporizing NIST-traceable liquid standards of known HCl concentration and quantitatively diluting the resultant vapor with a carrier gas. Liquid evaporative standards must be certified using gravimetrically based procedures of the latest version of the EPA Traceability Protocol for Quantification and Certification of Evaporative HCl Gas Standards and Humidification of HCl Gas Standards from Cylinders (see Section 7.7 of Reference 1).

3.6 Method Detection Limit. The lowest mass of HCl greater than zero that can be estimated and reported by the candidate analytical technique. The method detection limit (MDL) is statistically derived from replicate low-level measurements near the analytical instrument's detection level.

3.7 Reference Gas Standard. A NIST-traceable reference gas containing a known concentration of HCl certified in accordance with an EPA traceability protocol. Alternative gas standards which have been certified using alternative approved traceability protocols (i.e., ALT-114) may also be used.

3.8 Sorbent Trap. A cartridge or sleeve containing a sorbent media with multiple sections separated by an inert material such as quartz wool. These sorbent traps are optimized for the quantitative capture of HCl.

3.9 NIST. The National Institute of Standards and Technology is the U.S. National Metrological Institute responsible for establishing reference materials and standards.

3.11 NIST Traceable. A reference material with a well-defined traceability linkage to NIST reference materials or standards. This traceability linkage is established via an unbroken chain of comparisons to a stated NIST reference material.

3.12 Run. One of a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.13 Test. Refers to the series of runs required by the applicable regulation.

3.14 Ion (ion-exchange) Chromatography. An analytical process that allows the separation of ions and polar molecules based on their affinity to the ion exchanger or ion-exchange column. An IC is the instrument utilized to measure ions and polar molecules based on the ion-exchange principle.

3.15 Anions. A negatively charged ion.

3.16 Conductivity. The degree to which a specified material conducts electricity.

3.17 Electrical Conductivity. The amount of electrical charge a material can carry or its ability to carry a current. International System of Units (SI) units of Siemens per meter (S/m).

3.18 Electrolytic Conductivity Detection. The eluate from the suppressor passes through a flow cell with two to four electrodes, between which an AC potential is applied. When the sample

ions enter the cell, the capability of the solution to conduct electrons increases. The increase in current is proportional to the increase in conductivity, which is in turn a linear function of the ion concentration.

3.20 Analyte. A component or chemical species of a substance or chemical constituent that is being identified and measured as part of an analytical procedure.

3.21 Eluent or Eluant. Liquid solution of a salt or combination of several salts in water that transports the sample through the chromatography system (i.e., ion-exchange column) and contributes to the selectivity of the separation. The eluent solution also acts as a buffer and provides a stable pH for analysis. The eluent is referred to as the mobile phase or "carrier" in IC.

3.22 Suppressor. Electrolytic or chemical suppressive device that decreases the conductivity of the eluent from the ion-exchange column while increasing the analyte ion signals.

3.23 Molarity. A concentration unit of a solution expressed as the number of moles of a solute per liter of solution.

3.24 Retention Time. A measure of the time taken for a solute to pass through a chromatography column (i.e., ion exchanger). It is calculated as the time from injection to detection.

3.25 Elution. The process of extracting one material or chemical component from another by washing with a solvent, eluent, or other mobile phase, as in washing of a loaded ion-exchange resin to extract captured ions of interest.

3.26 Eluate. The analyte material that emerges from the chromatograph and inherently includes both the analytes and solutes passing through the column.

3.27 Ion-Exchange Column. An equilibrated stationary phase consisting of ionizable functional groups where the targeted molecules of a mixture to be separated and quantified can bind while moving through the mobile phase within the column.

4.0   *Interferences*

Interferences may result from the sorbent trap material used as well as from the measurement environment itself. Volatile materials, such as molecular chlorine (Cl_2), chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce chloride ions during the dissolution of the HCl from the sorbent traps are potential interferents that may result in a positive bias. For this reason, this method should not be performed in flue gas streams where any of these compounds are expected. Other interferences may be present that interfere with sample analyses. Potential analytical interferences are assessed by performing the analytical matrix interference, analytical bias, and field recovery tests.

High concentrations of other anions and other halogen salts may cause interferences in the analysis of HCl sorbent traps due to "peak tailing" and/or the overloading of the analytical column. Interferences may be caused by ions with retention times that overlap those of the anion

of interest. Large concentrations of an ion can interfere with the peak resolution of an adjacent anion. It is suggested a stationary phase (ion-exchange column) with maximum capacity be used to minimize this. Sample dilution and/or fortification can be used to mitigate most interference problems.

Chloride and chloride salts found on coal ash, coal dust and other coal material, human hands, human sweat and secretions, city water or other ionized water, and other surfaces may also be significant interferences by way of chloride contamination. Clean technique during sample collection, recovery, dilution, and subsequent analysis is vitally important. Additionally, method interferences may be caused by contaminants in the reagent water, reagents, glassware, leaching containers, transfer pipettes, and other sample-processing apparatus that lead to discrete artifacts or elevated baselines in chromatograms. All materials must be demonstrated to be free from interferences under the conditions of analysis by recovering and analyzing method blanks in the same manner as test samples. Specific selection of reagents and reagent water is required.

Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent blockage and damage to instrument columns and flow systems. If any samples or reagents have undergone filtration, the associated method blanks must also be filtered. Fibers from laboratory cleaning wipes can be sufficient to block narrow-bore instrument tubing, thus filtration should be considered.

The recovery procedure utilized to extract the captured chloride from the HCl in the flue gas stream should result in all captured chloride being present in solution only as the chloride ion upon IC analysis. When all sorbent material has been dissolved in solution, the chloride will remain as the chloride ion (Cl^-) and not convert to hypochlorite (ClO^-), chlorite (ClO_2^-), chlorate (ClO_3^-), or perchlorate (ClO_4^-). Bias testing was conducted during the development of the method, including bias by chlorine gas, to ensure the captured HCl gas was converted to only the chloride ion. As a result of the bias testing, chlorine gas did not result in chloride ion bias by the oxoacids: hypochlorous acid, chlorous acid, chloric acid, and perchloric acid.

High-purity water is required in every step of the sampling, recovery, dilution, and analytical procedure to eliminate contamination and/or other interferences. It is suggested ASTM Type 1 reagent water or water with a specific resistance of 18.0 mega-ohm or greater from an ultrapure water system be utilized. Water with a specific resistance of 18.1 or higher, if possible, is preferred. To aid in achieving low detection limits, the same ultrapure water purification system should be utilized for wash and rinse water, dilution water, standard preparation water, blank preparation, spike preparation, and every other possible instance water is utilized. Maintaining consistency across all steps of the method is crucial to achieving low detection limits while eliminating potential interferences and contaminants.

5.0   *Safety*

This method may require handling of hazardous materials and work in hazardous conditions. This method may not address all of the safety issues associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicable regulatory limitations prior to performing these procedures.

5.1 Site Hazards. Prior to applying these procedures/specifications in the field, the potential hazards at the test site should be considered; advance coordination with the site is critical to understand the conditions and applicable safety policies. At a minimum, portions of the sampling system will be hot, requiring appropriate gloves, long sleeves, and caution in handling this equipment. In addition, the plant may require the use of personal protection equipment (PPE), including but not limited to safety glasses, hard hats, and steel-toed boots.

5.2 Laboratory Safety. Although the chemicals used (primarily distilled water) are not hazardous, it is expected that policies will be in place to minimize risk of chemical exposure and to properly handle waste disposal in the laboratory. Personnel shall wear appropriate laboratory attire according to a chemical hygiene plan established by the laboratory.

5.3 Reagent Toxicity/Carcinogenicity. The toxicity and carcinogenicity of any reagents used must be considered. Depending upon the sampling and analytical technologies selected, this measurement may involve hazardous materials, operations, and equipment, and this method does not address all of the safety problems associated with implementing this approach. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performance. Any chemical should be regarded as a potential health hazard, and exposure to these compounds should be minimized. Chemists should refer to the Safety Data Sheet (SDS) for each chemical used.

6.0   *Equipment and Supplies*

The following list is presented as an example of key equipment and supplies likely required to measure HCl using a sorbent trap sampling system. It is recognized that additional equipment and supplies may be needed. Collection of paired samples is required.

6.1 Sampling System. A typical sorbent trap sampling system is shown in Figure 17-1. The sorbent trap sampling system shall include the following components.

6.1.1 Sorbent Traps. The sorbent media used to collect HCl must be configured in a trap with at least two distinct segments or sections connected in series that are amenable to separate analyses. Section 1 is designated for primary capture of HCl. Section 2 is designated as a backup section to measure any potential HCl breakthrough. Each sorbent trap must be inscribed or otherwise permanently marked with a unique identification number, for tracking purposes. The sorbent media may be any collection material capable of quantitatively capturing and recovering HCl from the source emissions for subsequent analysis. Selection of the sorbent media shall be based on the material's ability to achieve the performance criteria contained in this method. The sorbent media must be obtained from a source that can demonstrate its quality assurance and quality control (see Section 7.2). The paired sorbent traps are supported on a probe and inserted directly into the flue gas stream.

6.1.2 Sampling Probe Assembly. A single probe assembly capable of operating paired sampling traps must be used and shall have a leak-free attachment to the sorbent trap(s). Each sorbent trap must be mounted at the entrance of the probe (See Figure 30B-1). The entrance of the sorbent

trap must make direct contact with the stack gas without interference such that the gas sampled enters the trap(s) directly. Each probe/sorbent trap assembly must be either heated or cooled if the stack temperature is outside the temperature range of 120°–134°C (248°–273°F). Use a calibrated thermocouple to monitor the temperature of the stack and the temperature of the sorbent traps.

6.1.3 Moisture Removal Device. A moisture removal device or system shall be used to remove water vapor from the gas stream prior to entering the flow metering devices.

6.1.4 Vacuum Pump. A leak-tight, vacuum pump capable of operating within the system's flow range.

6.1.5 Gas Flowmeter. A gas flowmeter (such as a dry gas meter, thermal mass flowmeter, or other suitable measurement device) shall be used to determine the total sample volume on a dry basis, in units of standard cubic meters. The meter must be sufficiently accurate to measure the total sample volume to within 2% and must be calibrated at selected flow rates across the range of sample flow rates at which the sampling train will be operated. The gas flowmeter shall be equipped with any necessary auxiliary measurement devices (e.g., temperature sensors, pressure measurement devices) needed to correct the sample volume to standard conditions.

6.1.6 Sample Flow Rate Meter and Controller. A flow rate indicator and controller for maintaining necessary sampling flow rates.

6.1.7 Temperature Sensor. Same as Section 6.1.1.7 of Method 5.

6.1.8 Barometer. Same as Section 6.1.2 of Method 5.

6.2 Gaseous HCl Sorbent Trap Spiking System. A known mass of gaseous HCl must be spiked onto the first section of sorbent traps in order to perform the HCl analytical bias test and the field quality control tests. Any approach capable of quantitatively delivering NIST-traceable masses of gaseous HCl onto sorbent traps is acceptable. Several spiking technologies or devices are available to meet this objective. Their practicality is a function of HCl mass spike levels. Liquid evaporative standards or reference gas standards (see Section 3.0 of this method) are suitable.

6.3 Sample Preparation and Analysis. The following list is of key equipment and supplies likely required to quantitatively recover and analyze HCl from sorbent trap media. It is recognized that additional equipment and supplies may be needed.

6.3.1 Analytical Balance. Capable of weighing to the nearest 0.0001 g.

6.3.2 Pipets, Class A Volumetric Flasks, Beakers. Assorted sizes.

6.3.3 Ion Chromatograph. An analytical chromatography system capable of delivering 1 to 10 mL of eluent per minute at a pressure of 1000 to 5000 psi (6.5 to 34.5 MPa). The chromatograph must be equipped with an injection valve and a 100-µL sample loop, and set up with the following components: precolumn, analytical (or separator) column, conductivity suppressor,

conductivity detector, pump, syringe (or auto-sampler), and all appropriate data collection equipment. An example of a suitable IC system and set-up used during the evaluation of this method is found in the table below:

Table 6-1. Example Ion Chromatogragh Set-up

Equipment	Example
Ion Chromatograph	ThermoFisher™ Dionex™ ICS-3000
Guard Column	ThermoFisher™ Dionex™ IonPac™ AG23
Anion Exchange Column	ThermoFisher™ Dionex™ IonPac™ AS23
Conductivity Suppressor	ThermoFisher™ Dionex™ ASRS 300
Data Collection System	ThermoFisher™ Dionex™ Chromeleon

6.4 Moisture Measurement System. If correction of the measured HCl emissions for moisture is required, either Method 4 or other moisture measurement methods approved by the Administrator will be needed to measure stack gas moisture content.

7.0   *Reagents and Standards*

7.1 Reagents and Standards. Only NIST-traceable calibration standards, standard reference materials, and reagents shall be used for the tests and procedures required by this method (see Section 3.0). Reagent-grade chemicals must be used in all tests. It is intended that the highest-purity salts commercially available be utilized in all tests and all reagents that conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other grades of reagent may be used, provided the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1 Reagent Water. ASTM International (ASTM) Type 1 reagent water or equivalent. Prior to use, all reagent water must be verified to have a specific resistance of 18.0 MΩ-cm or greater.

7.1.2 Eluent. Use only high-purity, reagent-grade chemicals and water (18.0 MΩ-cm, minimum) to create the appropriate chromatographic eluent according to the manufacturer's guidance for the proper mobile phase for the specific column set in use. A concentrated stock solution of the eluent may be prepared and diluted subsequent to analysis to allow for improved day-to-day reproducibility and ensure accurate quantifications. Eluent concentrates may also be purchased from the column manufacturer that ensures reproducibility and a higher degree of accuracy due to consistency of eluent strength.

Note: An example of a suitable commercially available concentrated eluent is the ThermoFisher™ Dionex™ AS23 Sodium Carbonate/Bicarbonate Eluent Concentrate (250 mL, 100x) from ThermoScientific™ for the IonPac™ AS23 column set. The AS23 Eluent Concentrate is a 100x concentrated solution of 0.45 M Na_2CO_3/0.08 M $NaHCO_3$ which is diluted to create the appropriate eluent strength mobile phase according to the manufacturer guidelines.

7.1.3 Stock Solutions (1000 mg/L). NIST-Certified standards may be purchased and utilized as stock solutions. Alternatively, you may prepare stock solutions from reagent grade sodium chloride (NaCl). Prepare the stock solution by first drying the reagent for 1 hour at 600°C, cooling in a desiccator, then dissolving 1.2877 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask. Stock solutions are stable for at least 1 month when stored at 6 °C.

7.1.4 Chloride Calibration Standards. Prepare a blank and at least three chloride calibration standards. If not purchased commercially, the chloride standards must be prepared in Class A volumetric flasks. Calibration standards should be prepared weekly. The validity of the existing standard can be confirmed through the analysis of a freshly prepared ICV standard. At a minimum, prepare three concentrations of standards at a high-range, intermediate-range, and low-range by diluting the stock solution in a Class A volumetric flask with the appropriate amount of reagent water to achieve the desired concentration. A sufficient number of standards must be analyzed to allow an accurate calibration curve to be established while ensuring the test samples measured fall within the linear range of the calibration. It may be useful to prepare a low-range and high-range calibration to allow for a wider dynamic range of concentrations from test samples.

7.2 Sorbent Trap Media. The sorbent trap media shall be prepared such that the material used for testing is of known and acceptable quality. Sorbent supplier quality assurance/quality control measures to ensure appropriate and consistent performance such as sorptive capacity, uniformity of preparation treatments, and background levels shall be considered.

8.0   *Sample Collection and Handling*

This section presents the sample collection and handling procedures along with the pretest and on-site performance tests required by this method. Since different options may be chosen to comply with certain performance criteria, each test report must identify the specific options selected and document the results with respect to the performance criteria of this method.

8.1 Sample Point Selection. When this method is used to determine compliance with an emission standard or limit, use the appropriate sampling points located according to Table 1–1 or Table 1–2 of Method 1. If this test method is used for relative accuracy test audits of an HCl CEMS, use the appropriate sampling point described in Section 11.9.3 of Performance Specification 18 (Reference 1).

8.2 Measurement System Performance Tests. The following laboratory and field procedures and associated criteria of this section are designed to ensure 1) selection of a sorbent and analytical technique combination capable of quantitative collection and analysis of HCl, 2) collection of an adequate amount of HCl on each sorbent trap during field tests, and 3) adequate performance of the method for each test program. The primary objectives of these performance tests are to characterize and verify the performance of the intended analytical system and associated sampling and analytical procedures and to define the minimum amount of HCl (as the sample collection target) that can be quantified reliably.

(a) Analytical Matrix Interference Test
(b) Determination of Minimum Sample Mass
(c) HCl Analytical Bias Test
(d) Determination of Nominal Sample Volume
(e) Field Recovery Test – spiked field samples

8.2.1 Analytical Matrix Interference Test and Minimum Sample Dilution. The analytical matrix interference test is a laboratory procedure. The purpose of the test is to verify the presence or absence of known and potential analytical matrix interferences. The analytical matrix interference test determines the minimum dilution (if any) necessary to mitigate matrix effects on the sample digestate solutions. The analytical matrix interference test is sorbent material-specific and shall be performed for each sorbent material intended for field sampling and analysis. The test shall be performed using a mass of sorbent material comparable to the sorbent mass typically used in the first section of the trap for sampling. Similar sorbent materials from different sources of supply are considered to be different materials and must be tested individually. An analytical matrix interference test must be conducted for each sorbent material prior to the analysis of field samples.

8.2.1.1 Analytical Matrix Interference Test Procedures. Digest/leach and prepare for analysis a representative mass of sorbent material (unsampled) according to the intended laboratory techniques for field samples. Analyze the digestate according to the intended analytical conditions at the least diluted level intended to be used for sample analysis (e.g., undiluted, 1 in 10 dilution, etc.). Determine the HCl concentration of the undiluted digestate solution. Prepare a series of solutions with a fixed final volume containing graduated aliquots of the sample digestate and a fixed aliquot of a calibration standard (with the balance being HCl-free reagent or H_2O) to establish solutions of varied digestate dilution ratio (e.g., 1:2, 1:5, 1:10, 1:100, etc.). One of these solutions should contain only the aliquot of the calibration standard in HCl-free reagent or H_2O. This will result in a series of solutions where the amount of HCl is held relatively constant and only the volume of digestate diluted is varied. Analyze each of these solutions following the intended sample analytical procedures and conditions, determining the concentration for each solution.

8.2.1.2 Analytical Matrix Interference Test Acceptance Criteria. Compare the measured concentration of each solution containing digestate to the measured concentration of the digestate-free solution. The lowest dilution ratio of any solution having an HCl concentration within ±5% of the digestate-free solution is the minimum dilution ratio required for analysis of all samples. If you desire to measure the digestate without dilution, the ± 5% criterion must be met at a dilution ratio of ≥ 90% digestate.

8.2.1.3 Example Analytical Matrix Interference Test. An example analytical matrix interference test is presented below. Additional information on the conduct of the analytical matrix interference test will be posted at www.epa.gov/emc. Determine the most sensitive working range for the analyzer to be used. This will be a narrow range of concentrations. Digest and prepare for analysis a representative mass of sorbent material (unsampled) according to your intended laboratory techniques for sample preparation and analysis. Prepare a calibration curve

for the most sensitive analytical region, e.g., 0.0, 0.01, 0.05, 0.5, 1.0 ppm. Using the highest calibration standard, e.g., 1.0 ppm, prepare a series of solutions by adding successively smaller increments of the digestate to a fixed volume of the calibration standard and bringing each solution to a final fixed volume with HCl-free deionized water (DI H_2O). To 2.0 mL of the calibration standard add 18.0, 10.0, 4.0, 2.0, 1.0, 0.2, and 0.0 mL of the digestate. Bring the final volume of each solution to a total volume of 20 mL by adding 0.0, 8.0, 14.0, 16.0, 17.0, 17.8, and 18.0 mL of DI H_2O. This will yield solutions with dilution ratios of 9:10, 1:2, 1:5, 1:10, 1:20, 1:100, and 0:10, respectively. Determine the HCl concentration of each solution. The dilution ratio of any solution having a concentration that is within ±5% of the concentration of the solution containing 0.0 mL of digestate is an acceptable dilution ratio for analyzing field samples. If more than one solution meets this criterion, the one with the lowest dilution ratio is the minimum dilution required for analysis of field samples. If the 9:10 dilution meets this criterion, then no sample dilution is required.

8.2.2 Determination of Minimum Sample Mass. The minimum mass of HCl that must be collected per sample must be determined. This information is necessary in order to effectively perform the HCl Analytical Bias Test, to estimate target sample volumes/sample times for test runs, and to ensure the quality of the measurements. The determination of minimum sample mass is a direct function of analytical technique, measurement sensitivity, dilutions, etc. This determination is required for all analytical techniques. Based on the analytical approach you employ, you should determine the most sensitive calibration range. Based on a calibration point within that range, you must consider all sample treatments (e.g., dilutions) to determine the mass of sample that needs to be collected to ensure that all sample analyses fall within your calibration curve.

8.2.2.1 Determination of Minimum Calibration Concentration or Mass. Based on your instrument sensitivity and linearity, determine the calibration concentrations or masses that make up a representative low-level calibration range. Verify that you are able to meet the multipoint calibration performance criteria in Section 11.0 of this method. Select a calibration concentration or mass that is no less than 2 times the lowest concentration or mass in your calibration curve. The lowest point in your calibration curve must be at least 5, and preferably 10, times the MDL, which is the minimum amount of the analyte that can be detected and reported. The MDL must be determined at least once on an annual basis for each analytical system using the MDL study found in Section 15.0 of EPA Method 301. You must report the MDL results in each test report

Note: While it might be desired to base the minimum calibration concentration or mass on the lowest point in the calibration curve, selecting a higher concentration or mass is necessary to ensure that all analyses of the field samples will fall within the calibration curve. Therefore, it is strongly recommended that a minimum calibration concentration or mass be selected that is sufficiently above the lowest point of the calibration curve.

Based on the minimum calibration concentration or mass and other sample treatments including, but not limited to, final digestate volume and minimum sample dilution, determine the minimum sample mass. Consideration should also be given to the HCl levels expected to be measured in Section 2 of the sorbent traps and to the breakthrough criteria presented in Table 17.1.

8.2.3 HCl Analytical Bias Test. Before analyzing any field samples, the laboratory must demonstrate the ability to recover and accurately quantify HCl from the chosen sorbent media by performing the following analytical bias test for sorbent traps spiked with HCl. The analytical bias test is performed at a minimum of two distinct sorbent trap HCl loadings that will 1) represent the lower and upper bound of sample HCl loadings for application of the analytical technique to the field samples and 2) be used for data validation.

8.2.3.1 HCl Analytical Bias Test Procedures. Determine the lower and upper-bound mass loadings. The minimum sample mass established in Section 8.2.2.2 can be used for the lower-bound HCl mass loading although lower HCl loading levels are acceptable. The upper-bound HCl loading level should be an estimate of the greatest mass loading that may result as a function of stack concentration and volume sampled. As previously noted, this test defines the bounds that actual field samples must be within in order to be valid. The test is performed by analyzing the front section of three sorbent traps containing HCl at the lower bound mass loading level and the front section of three sorbent traps containing HCl at the upper bound mass loading level. In other words, analyze each mass loading level in triplicate. You may refer to Section 6.2 for spiking guidance. Prepare and analyze each spiked trap, using the same techniques that will be used to prepare and analyze the field samples. The average recovery for the three traps at each mass loading level must be between 90% and 110%. If multiple types of sorbent media are to be analyzed, a separate analytical bias test is required for each sorbent material. Report the results of the analytical bias test for each sorbent material used for testing.

Note: Document the sample preparation procedures (i.e., digestion/leaching) and analytical matrix test results in a Standard Operation Procedure (SOP), which may be made available to the regulatory authority upon request.

8.2.4 Determination of Target Sample Volume. The target sample volume is an estimate of the sample volume needed to ensure that valid emission data are collected (i.e., that sample mass HCl loadings fall within the analytical calibration curve and are within the upper and lower bounds set by the analytical bias tests). The target sample volume and minimum sample mass can also be determined by performing a diagnostic test run prior to initiation of formal testing.

Example: If the minimum sample mass of HCl determined in Section 8.2.2 is 20 µg and the concentration of HCl in the stack gas is estimated to be 1 ppmv, then the following calculations would be used to determine the target sample volume:

1) 1 ppmv HCl = (1 g HCl x 1 g-mole/24.04 L x 36.5 g HCl/g-mole)/10^6 L flue gas = 1.52 µg/L

2) Target Sample Volume = (20 µg)/(1.52 µg/L) = 13.2 L

8.2.5 Determination of Sample Run Time. Sample run time will be a function of minimum sample mass (see Section 8.2.2), target sample volume (see Section 8.2.4), and nominal equipment sample flow rate. The minimum sample run time for conducting RATAs of HCl monitoring systems is 30 minutes and for emissions testing to characterize an emission source is 1 hour, unless otherwise specified in an applicable regulation.

Example: If the target sample volume has been determined to be 13.2 L, then the following formula would be used to determine the sampling time necessary to acquire 13.2 L of gas when sampling at a rate of 0.4 L/min.

Sampling time (min) = 13.2 L/0.4 L/min = 33 minutes

8.2.6 Field Recovery Test – Spiked Field Traps. The field recovery test provides a test program-specific verification of the performance of the combined sampling and analytical approach. Three sets of paired traps are used to collect samples. One of each pair is spiked with a known mass of HCl before the samples are collected and analyzed. The average recovery of the spiked samples is used to verify performance of the measurement system under field conditions during that specific test program. Conducting this test requires an estimate or confirmation of the stack HCl concentrations at the time of testing.

8.2.6.1 Calculation of Presampling Spiking Level. Determine the sorbent trap spiking level for the field recovery test using estimates of the stack HCl concentration, the target sample flow rate, and the planned sample duration. First, determine the HCl mass expected to be collected in Section 1 of the sorbent trap. The presampling spike must be within 50% to 150% of this expected mass.

Example calculation: For an expected stack HCl concentration of 1 ppmv (1.52 ug/L) a target sample rate of 0.50 L/min, and a sample duration of 60 minutes:

(0.50 L/min) * (60 min) * (1.52 ug/L) = 46 ng
A Hg spike of 23 to 69 ng (50%–150% of 46 ng) would be appropriate.

8.2.6.2 Field Recovery Test Procedures. Set up two identical sampling trains. One of the sampling trains shall be designated the spiked train and the other the nonspiked train. Spike HCl onto the front section of the sorbent trap in the spiked train before sampling. The mass of HCl spiked shall be 50% to 150% of the mass expected to be collected with the nonspiked train. Sample the stack gas with the two trains simultaneously, using the same procedures as for the field samples (see Section 8.3). The total sample volume must be within ±20% of the target sample volume for the field sample test runs. Analyze the sorbent traps from the two trains utilizing the same analytical procedures and instrumentation as for the field samples (see Section 11.0). Determine the fraction of spiked HCl recovered (R) using the equations in Section 12.7. Repeat this procedure for a total of three runs. Report the individual R values in the test report; the average of the three R values must be between 85% and 115%.

Note: It is acceptable to perform the field recovery test concurrent with actual test runs (e.g., through the use of a quad probe).

8.3 Sampling. This section describes the procedures and criteria for collecting the field samples for analysis. As noted in Section 8.2.6, the field recovery test samples are also collected using these procedures.

8.3.1 Pretest Leak Check. Perform a leak check of the sampling system with the sorbent traps in place. For each of the paired sampling trains, draw a vacuum in the train, and adjust the vacuum to ~15 in. Hg; and, using the gas flowmeter, determine leak rate. The leak rate for an individual train must not exceed 4% of the target sampling rate. Once the leak check passes this criterion, carefully release the vacuum in the sample train, seal the sorbent trap inlet until the probe is ready for insertion into the stack or duct, and record the results of the leak check.

8.3.2 Determination of Flue Gas Characteristics. Determine or measure the flue gas measurement environment characteristics (gas temperature, static pressure, gas velocity, stack moisture, etc.) in order to determine ancillary requirements such as probe heating requirements (if any), initial sampling rate, moisture management, etc.

8.3.3 Sample Collection. Using a gloved hand, remove the plug from the end of each sorbent trap, store each plug in a clean sorbent trap storage container, and position each trap in the end of the sampling probe via a Teflon union. Remove the stack or duct port cap and insert the probe(s). Secure the probe(s) and ensure that no leakage occurs between the duct and environment. Sampling can begin when the probe temperature measured by the probe thermocouple reaches the target range of 120°–134°C (248°–273°F). Record initial data including the HCl sorbent trap ID, date, and the run start time. Record the initial gas flowmeter reading, stack temperature, sorbent trap temperatures, meter temperatures (if needed), temperatures of heated equipment such as the vacuum lines and the probes (if heated), the sampling system vacuum readings, and any other appropriate information, before beginning sampling. Begin sampling and target the desired sample rate to ensure at minimum the calculated minimum gas sample is collected over the selected test time. Adjust the sampling flow rate as necessary to maintain the initial sample flow rate. Ensure that the total volume sampled for each run is within 20% of the total volume sampled for the field recovery test. At regular intervals (≤5 minutes) during the sampling period, record the date and time, the sample flow rate, the gas meter reading, the stack temperature, sorbent trap temperature, the flowmeter temperatures (if using a dry gas meter), temperatures of heated equipment such as the vacuum lines and the probes (if heated), and the sampling system vacuum readings. Adjust the sampling flow rate as necessary to maintain the initial sample flow rate.

Note: Because of the high potential for HCl/chloride contamination from outside sources, care should be taken at any point the sorbent trap is physically handled. It is recommended that all sampling and field personnel use nitrile, latex, or other inert gloves when handling the traps to prevent contamination.

8.3.4 Data Recording. Obtain and record any essential operating data for the facility during the test period, e.g., the barometric pressure must be obtained for correcting sample volume to standard conditions when using a dry gas meter. At the end of the data collection period, record the final gas flowmeter reading and the final values of all other essential parameters.

8.3.5 Posttest Leak Check. When sampling is completed, turn off the sample pump, remove the probe(s) with sorbent traps from the port, and carefully seal the end of each sorbent trap using a gloved hand. Perform another leak check of each sampling train with the sorbent traps in place, at the maximum vacuum reached during the sampling period. Record the leakage rates and

vacuums. The leakage rate for each train must not exceed 4% of the average sampling rate for the data collection period. Following each leak check, carefully release the vacuum in the sample train.

8.3.6 Sample Recovery. Using a gloved hand, recover each sampled sorbent trap by removing it from the probe and sealing both ends. Wipe any deposited material from the outside of the sorbent trap. Place the sorbent trap into an appropriate sample storage container and store/preserve in an appropriate manner (see Section 8.3.8). Use nitrile, latex, or other inert gloves when handling the traps to prevent contamination.

8.3.7 Stack Gas Moisture Determination. If the moisture basis of the measurements made with this method (dry) is different from the moisture basis of the applicable emission limit, you must determine the moisture content of the flue gas and correct for moisture using Method 4 procedures. If correction of the measured HCl for moisture is required, at least one Method 4 moisture determination shall be made during each test run.

8.3.8 Sample Handling, Preservation, Storage, and Transport. While the performance criteria of this approach provide for verification of appropriate sample handling, it is still important that the user consider, determine, and plan for suitable sample preservation, storage, transport, and holding times for these measurements. Therefore, procedures in ASTM D6911-15 "Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis" shall be followed for all samples, where appropriate. To avoid HCl/chloride contamination of the samples, special attention should be paid to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the sorbent cartridges. Collection and analysis of blank samples (e.g., reagents, sorbent media, field blanks etc.) are critical in verifying the absence or potential sources of HCl/chloride contamination, including all solutions used for recovery, digestion, dilution, and analysis (see Section 9.0, Quality Assurance and Quality Control).

8.3.9 Sample Custody. Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. The chain of custody procedures in ASTM D4840-99 "Standard Guide for Sampling Chain-of-Custody Procedures" shall be followed for all samples (including field samples and blanks).

9.0   *Quality Assurance and Quality Control (QA/QC)*

Table 17.1 summarizes the quality assurance/quality control performance criteria that are used to validate the HCl emissions data from the sorbent trap measurement system.

10.0   *Calibration and Standardization*

Only NIST-traceable calibration standards (i.e. calibration gases, solutions, etc.) shall be used for the spiking and analytical procedures in this method.

10.1 Gas Flow Meter Calibration

10.1.1 Preliminaries. The manufacturer or equipment supplier of the gas flowmeter should perform all necessary setup, testing, programming, etc., and should provide the end user with any necessary instructions, to ensure that the meter will give an accurate readout of dry gas volume in standard cubic meters for this method.

10.1.2 Initial Calibration. Prior to its initial use, a calibration of the gas flow meter shall be performed. The initial calibration may be done by the manufacturer, by the equipment supplier, or by the end user. If the flowmeter is volumetric in nature (e.g., a dry gas meter), the manufacturer or end user may perform a direct volumetric calibration using any gas. For a mass flow meter, the manufacturer, equipment supplier, or end user may calibrate the meter using either 1) a bottled gas mixture containing $12\pm0.5\%$ CO_2, $7\pm0.5\%$ O_2, and balance N_2 (when this method is applied to coal-fired boilers); 2) a bottled gas mixture containing CO_2, O_2, and N_2 in proportions representative of the expected stack gas composition; or 3) the actual stack gas.

10.1.2.1 Initial Calibration Procedures. Determine an average calibration factor (Y) for the gas flow meter by calibrating it at three sample flow rate settings covering the range of sample flow rates at which the sampling system will be operated. You may either follow the procedures in Section 10.3.1 of Method 5 or in Section 16 of Method 5. If a dry gas meter is being calibrated, use at least five revolutions of the meter at each flow rate.

10.1.2.2 Alternative Initial Calibration Procedures. Alternatively, the initial calibration of the gas flow meter may be performed using a reference gas flow meter (RGFM). The RGFM may be 1) a wet test meter calibrated according to Section 10.3.1 of Method 5, 2) a gas flow metering device calibrated at multiple flow rates using the procedures in Section 16 of Method 5, or 3) a primary volumetric standard calibration device capable of measuring volumetric flow to an accuracy of 1%. To calibrate the gas flowmeter using the RGFM, proceed as follows: While the system is sampling the actual stack gas or a compressed gas mixture that simulates the stack gas composition (as applicable), connect the RGFM to the discharge of the system. Care should be taken to minimize the dead volume between the gas flow meter being tested and the RGFM. Concurrently, measure dry stack gas volume with the RGFM and the flow meter being calibrated for at least 10 minutes at each of three flow rates covering the typical range of operation of the sampling system. For each set of concurrent measurements, record the total sample volume, in units of dry standard cubic meters (dscm), measured by the RGFM and the gas flow meter being tested.

10.1.2.3 Initial Calibration Factor. Calculate an individual calibration factor, Yi, at each tested flow rate from Section 10.1.2.1 or 10.1.2.2 of this method (as applicable) by taking the ratio of the reference sample volume to the sample volume recorded by the gas flowmeter. Average the three Yi values, to determine Y, the calibration factor for the flowmeter. Each of the three individual values of Yi must be within ±0.02 of Y. Except as otherwise provided in Sections 10.1.2.4 and 10.1.2.5 of this method, use the average Y value from the initial 3-point calibration to adjust subsequent gas volume measurements made with the gas flowmeter.

10.1.2.4 Pretest On-Site Calibration Check (Optional). For a mass flow meter, if the most recent 3-point calibration of the flow meter was performed using a compressed gas mixture, you may want to conduct the following on-site calibration check prior to testing, to ensure that the flow meter will accurately measure the volume of the stack gas: While sampling stack gas, check the calibration of the flow meter at one intermediate flow rate setting representative of normal operation of the sampling system. If the pretest calibration check shows that the value of Yi, the calibration factor at the tested flow rate, differs from the current value of Y by more than 5%, perform a full 3-point recalibration of the meter using stack gas to determine a new value of Y, and (except as otherwise provided in Section 10.1.2.5 of this method) apply the new Y value to the data recorded during the field test.

10.1.2.5 Posttest Calibration Check. Check the calibration of the gas flowmeter following each field test at one intermediate flow rate setting, either at, or in close proximity to, the average sample flow rate during the field test. For dry gas meters, ensure at least three revolutions of the meter during the calibration check. For mass flowmeters, this check must be performed before leaving the test site, while sampling stack gas. If a one-point calibration check shows that the value of Yi at the tested flow rate differs by more than 5% from the current value of Y, repeat the full 3-point calibration procedure to determine a new value of Y, and apply the new Y value to the gas volume measurements made with the gas flowmeter during the field test that was just completed. For mass flowmeters, perform the 3-point recalibration while sampling stack gas.

10.2 Thermocouples and Other Temperature Sensors. Use the procedures and criteria in Section 10.3 of Method 2 to calibrate in-stack temperature sensors and thermocouples. Dial thermometers shall be calibrated against NIST-traceable thermometers. Calibrations must be performed prior to initial use and before each field test thereafter. At each calibration point, the absolute temperature measured by the temperature sensor must agree to within ±1.5% of the temperature measured with the reference sensor, otherwise the sensor may not continue to be used.

10.3 Barometer. Calibrate against a NIST-traceable barometer as per Section 10.6 of Method 5. Calibration must be performed prior to initial use and before each test program, and the absolute pressure measured by the barometer must agree to within ±10 mm Hg of the pressure measured by the NIST-traceable barometer, otherwise the barometer may not continue to be used.

10.4 Other Sensors and Gauges. Calibrate all other sensors and gauges according to the procedures specified by the instrument manufacturer(s).

10.5 Analytical System Calibration. See Section 11.1 of this method.

11.0 *Analytical Procedures*

The analysis of HCl sorbent traps and quality control samples may be conducted using any instrument or technology capable of quantifying total HCl from the sorbent media and meeting the performance criteria in this method. Although halogens can be measured using a multitude of techniques, the description of the analytical approach in this method is directed at IC. Other analytical techniques such as Fourier transform infrared spectroscopy may be used; however, it is

not possible to provide detailed, technique-specific analytical procedures for all of them. It is critical that the operational procedures as specified by the instrument manufacturer be followed.

11.1 Analytical System Calibration. Perform a multipoint calibration of the IC system at three or more upscale points over the desired quantitative range. Multiple calibration ranges shall be calibrated, if necessary. The field samples analyzed must fall within a calibrated, quantitative range and meet the performance criteria specified below. The calibration curve range(s) shall be determined such that the levels of HCl mass expected to be collected and measured will fall within the calibrated range. The calibration curve may be generated by directly introducing standard solutions into the analyzer or by spiking the standards onto the sorbent media and then introducing into the analyzer after preparing the sorbent/standard according to the particular analytical technique. For each calibration curve, the value of the square of the coefficient of determination, i.e., R^2, must be ≥0.99, and the analyzer response must be within ±5% of the reference value at each upscale calibration point. Calibrations must be performed on the day of the analysis, before analyzing any of the samples. Following calibration, an independent calibration verification standard shall be analyzed (see Section 11.1.3 below). The measured value of the independently prepared standard must be within ±10% of the expected value. You should also empirically verify the MDL by preparing a standard at the calculated MDL, and analyze it. The measured value should be within 50% of the true value to verify the MDL. *Note: A sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration approximately five times the MD (see Section 11.1.5 of this method). The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. It may be useful to prepare a low-range and high-range calibration to allow for a wider dynamic range of concentrations from test samples.*

11.1.1 Calibration Standards. After a stable baseline is obtained (typically 30 min to 1 hr), begin to inject standards starting with the lowest concentration standard and increasing in concentration to the highest standard. Use a fixed injection volume of 100 µL (determined by injection loop volume) for each calibration standard. Record and report the peak area responses, retention times of chloride, and chromatographs for each standard.

11.1.2 Chloride Calibration Curve. Establish the chloride calibration curve by plotting the peak area response for each standard against the corresponding concentration. Use a least-squares linear regression to calculate the calibration curve formula. The linear correlation coefficient should be equal to or greater than 0.99. A weighted least-squares regression may also be performed using 1/concentration or 1/(concentration)^2 as the weighting factor, so long as the correlation coefficient criterion of Section 11.1 of this method is met.

11.1.3 Independent Calibration Verification Standard. Verify the accuracy of the initial calibration curve by analyzing an independent calibration standard. This standard must be prepared from an independent material (second source or separate manufacturer) at or near the mid-range of the calibration curve. The measured value for this standard must be within 10% of its true value. Record the peak area responses, retention times of chloride, and chromatograph for each standard. If the calibration curve cannot be verified within the specified limits, the cause must be determined and the instrument recalibrated before samples are analyzed.

11.1.4 Continuing Calibration Verification. Verify the accuracy of the calibration curve on each day prior to conducting sample analysis, and for every 10 or fewer samples, through the analysis of a continuing calibration verification (CCV) standard. The CCV should be made from the same material as the initial calibration standards at or near mid-range. The measured value for the CCV standard must be within 10% of its expected value for the calibration to be considered valid. Record and report the peak area responses, retention times of chloride, and chromatograph for each standard. If the CCV standard result does not meet the acceptance criterion, sample analysis must be discontinued, the cause determined, and the instrument recalibrated. Results from any samples analyzed after the last acceptable CCV shall be invalidated and the samples reanalyzed.

11.1.5 Method Detection Limit. The MDL (or limit of detection) for your analytical approach must be determined according to Section 15.0 of Method 301.

11.1.6 Low Level Quantification. Some samples (e.g., the mass collected in trap Section 2) may have HCl levels so low that it may not be possible to quantify them in the analytical system's calibrated range. Because reliable estimates of these very low level HCl measurements are necessary to fully validate the emissions data, the MDL is used to establish the minimum amount that can be detected and reported. If the measured mass (or concentration) is below the lowest calibration point but above the MDL, the analyst must estimate the mass or concentration of the sample based on the analytical instrument response relative to an additional calibration standard prepared at a mass or concentration between the MDL and the lowest calibration point in the calibration curve. This is accomplished by establishing a response factor (e.g., area counts per mass) for the additional calibration standard and estimating the HCl present in the sample based on its response and the response factor.

11.2 Sample Preparation. A sampling tube typically consists of three quartz wool plugs and two sections of sorbent material. The HCl measured in the first and second quartz wool plugs are combined with the results from the sorbent material of Section 1. The quartz wool plugs and the Section 1 sorbent may be analyzed separately, or if a digestion/leaching procedure is used, they can be combined. For Section 2, the analytical results from the sorbent material and the third plug of quartz wool are combined, but the sorbent and quartz wool plug may be analyzed together or separately.

11.3 Field Sample Analyses. Analyze the sorbent trap samples following the same procedures that were used for conducting the HCl analytical bias tests. Record and report the peak area responses, retention times of chloride, and chromatograph for each sample. The individual sections of the sorbent trap and their respective components must be analyzed separately as described above in Section 11.2. All sorbent trap Section 1 sample analyses must be within the calibrated range of the analytical system. For wet analyses, the sample can simply be diluted to fall within the calibrated range. However, for analytical procedures where the sample is completely consumed or destroyed during preparation and analysis, if the sample is not within the calibrated range, it cannot be reanalyzed. As a result, the sample cannot be validated, and another sample must be collected. It is strongly suggested that the analytical system be calibrated over multiple ranges so that all samples fall within the calibrated range.

The total mass of HCl measured in each sorbent trap Section 1 must also fall within the lower and upper mass limits established during the initial HCl analytical bias test. If a sample is analyzed and found to fall outside of these limits, it is acceptable for an additional HCl analytical bias test to be performed that now includes this level. However, some samples (e.g., the mass collected in trap Section 2 or the mass collected in trap Section 1 when the stack gas concentration is <0.01 ppmv), may have HCl levels so low that it may not be possible to quantify them in the analytical system's calibrated range. Because a reliable estimate of these low-level HCl measurements is necessary to fully validate the emissions data, the MDL (see Section 8.2.2 of this method) is used to establish the minimum amount that can be detected and reported. If the measured mass or concentration is below the lowest point in the calibration curve and above the MDL, flag the measured data as an estimate.

11.4 Sorbent Trap Blanks. The analysis of blanks is required, as this verifies the absence of, or an acceptable level of, HCl contamination. Blank concentrations should be taken into consideration when planning tests at low HCl sources. Concentrations in blanks should be low enough that they contribute no more than 10% of the collected sample mass, and that the sorbent trap Section 2 results do not exceed Section 1 breakthrough criterion. Correction of the sorbent trap results for the HCl content of the blank is not allowed. One blank sample should be collected with every three runs of paired traps. If the collected blanks do not meet these criteria, the sampling test runs should be repeated.

12.0 *Calculations and Data Analysis*
You must follow the procedures for calculation and data analysis listed in this section.

12.1 Nomenclature. The terms used in the equations are defined as follows:

B = Breakthrough (%).
B_{ws} = Moisture content of sample gas as measured by Method 4, percent/100.
C_a = Concentration of HCl for the sample collection period, for sorbent trap "a" (μg/dscm).
C_b = Concentration of HCl for the sample collection period, for sorbent trap "b" (μg/dscm).
C_d = Average of C_a and C_b HCl concentration, dry basis (μg/dscm).
C_{Rec} = HCl concentration of spiked compound measured (μg/dscm).
C_{ST1} = HCl concentration calculated from mass (m1) of HCl measured on sorbent trap Section 1 and sample volume (μg/dscm).
C_{SP1} = HCl concentration calculated from known spiked mass on sorbent trap Section 1 and sample volume (μg/dscm).
C_w = HCl concentration, wet basis (μg/scm).
m_1 = Mass measured on sorbent trap Section 1 (μg).
m_{1a} = Mass measured on sorbent trap Section 1 of trap "a" (μg).
m_{1b} = Mass measured on sorbent trap Section 1 of trap "b" (μg).
m_2 = Mass measured on sorbent trap Section 2 (μg).
m_a = Total mass of HCl measured on nonspiked trap, sorbent trap "a" (μg).
m_b = Total mass of HCl measured on spiked trap, sorbent trap "b" (μg).
m_u = Total mass of HCl measured on nonspiked trap in Field Recovery Test (μg).
$m_{recovered}$ = Mass of spiked HCl recovered in Analytical Bias or Field Recovery Test (μg).

m_s = Total mass of HCl measured on spiked trap in Field Recovery Test (µg).
m_{spiked} = Mass of HCl spiked in Analytical Bias or Field Recovery Test (µg).
m_{sp}= Mass of known amount of HCl spiked on first section of trap (µg).
O_{2d} = Concentration of dry oxygen (%).
R = Percentage of spiked mass recovered (%).
RD = Relative deviation between the HCl concentrations from traps "a" and b" (%).
V_t = Total volume of dry gas metered during the collection period (dscm); for the purposes of this method, standard temperature and pressure are defined as 20°C and 760 mm Hg, respectively. Normal and standard conditions are the same for purposes of this method.
V_a = Total volume of dry gas metered through trap "a" during the collection period (dscm, or dNm^3); for the purposes of this method, standard temperature and pressure are defined as 20°C and 760 mm Hg, respectively. Normal and standard conditions are the same for purposes of this method.
V_b = Total volume of dry gas metered through trap "b" during the collection period (dscm); for the purposes of this method, standard temperature and pressure are defined as 20°C and 760 mm Hg, respectively. Normal and standard conditions are the same for purposes of this method.
v_s = Volume of gas sampled, spiked trap in Field Recovery Test (dscm).
v_u = Volume of gas sampled, nonspiked trap in Field Recovery Test (dscm).

12.2 Calculation of Spike Recovery (Analytical Bias Test)
Calculate the percent recovery of HCl using Equation 12-1.

$$R = \frac{m_{recovered}}{m_{spiked}} \times 100 \qquad \text{[Eq. 12-1]}$$

12.3 Calculation of Breakthrough
Use Equation 12-2 to calculate the percent HCl breakthrough of the second section of the sorbent trap relative to the mass collected on first section.

$$B = \frac{m_2}{m_1} \times 100 \qquad \text{[Eq. 12-2]}$$

12.4 Calculation of HCl Concentration in Nonspiked Paired-Trap Set (sorbent trap "a")
Calculate the HCl concentration measured with sorbent trap "a" using Equation 12-3.

$$C_a = \frac{m_1+m_2}{V_a} = \frac{m_a}{V_a} \qquad \text{[Eq. 12-3]}$$

For nonspiked sorbent trap "b," replace "a" with "b" in Equation 12-3. Report the average concentration, C_d:

$$C_d = \frac{(C_a+C_b)}{2} \qquad \text{[Eq. 12-4]}$$

12.5 Calculation of HCl Concentration in a Nonspiked and Spiked Paired-Trap Set

For the nonspiked trap "a," use Equation 12-3. For the spiked trap "b," calculate the concentration using Equation 12-5.

$$C_b = \frac{m_b - m_{sp}}{V_b} \qquad \text{[Eq. 12-5]}$$

Report the average concentration, C_d, using Equation 12-4.

12.6 Calculation of Spike Recovery in a Nonspiked and Spiked Paired-Trap Set

First, calculate the concentration of HCl using the total mass measured in Section 1 of spiked trap "b" using Equation 12-6.

$$C_{ST1} = \frac{m_{1b}}{V_b} \qquad \text{[Eq. 12-6]}$$

Then calculate the concentration of HCl contributed by the known mass of the spike using Equation 12-7.

$$C_{SP1} = \frac{m_{sp}}{V_b} \qquad \text{[Eq. 12-7]}$$

Next calculate the spiked HCl recovery concentration using the spiked concentration and the mass measured in the first section of trap "a" divided by the volume sampled as shown in Equation 12-8.

$$C_{Rec} = C_{ST1} - \frac{m_{1a}}{V_a} \qquad \text{[Eq. 12-8]}$$

Finally, calculate percent recovery using Equation 12-9.

$$R = \frac{C_{Rec}}{C_{SP1}} \times 100 \qquad \text{[Eq. 12-9]}$$

12.7 Calculation of Paired-Trap Agreement
Calculate the relative deviation (RD) between the HCl concentrations measured with the paired sorbent traps using Equation 12-10.

$$RD = \frac{|C_a - C_b|}{C_a + C_b} \times 100 \qquad \text{[Eq. 12-10]}$$

12.8 Calculation of HCl Concentration from the Run
Assuming acceptable paired trap agreement and spike recovery are obtained (see Table 17-1), the reported HCl concentration is the average of the results from sorbent traps "a" and "b," as calculated by Equation 12-4.

12.9 Moisture Correction

If measurements need to be corrected to a wet basis, use Equation 12-11:

$$C_w = C_d \times (1 - B_{ws}) \qquad \text{[Eq. 12-11]}$$

12.10 Conversion to Parts per Million by Volume (ppmv)

If measurements need to be converted from µg/dscm to ppmv, use Equation 12-12:

$$C_{ppm} = C_{\text{µg/dscm}} \; x \; 0.000659 \qquad \text{[Eq. 12-12]}$$

13.0 *Method Performance*

Measurement data are validated using initial, one-time laboratory tests, coupled with test program-specific tests and procedures. The analytical matrix interference test and the HCl analytical bias test described in Section 8.2 are used to verify the appropriateness of the selected analytical approach(es), as well as to define the valid working ranges for sample analysis. Field test samples are validated by meeting the above requirements, the use of HCl spiked sorbent traps and blanks, as well as meeting specific sampling requirements (i.e., leak checks, paired-train agreement, and analytical requirements (i.e., valid calibration curve, continuing calibration performance, sample results within calibration curve and bounds of the HCl analytical bias test). Complete data validation requirements are summarized in Table 17-1.

14.0 *Pollution Prevention*

Reserved

15.0 *Waste Management*

Any wastes generated by this procedure must be disposed of according to a hazardous materials management plan that details and tracks various waste streams and disposal procedures.

16.0 *References*

1. Performance Specification 18—Performance Specifications and Test Procedures for Gaseous Hydrogen Chloride (HCl) Continuous Emission Monitoring Systems at Stationary Sources, 40 CFR 60, appendix B.

17.0 *Figures and Tables*

OTM-40

Table 17.1. Quality Assurance/Quality Control Criteria for OTM-40

QA/QC[1] Test or Specification	Acceptance Criteria	Frequency	Consequence If Not Met
Gas Flowmeter Calibration (at 3 settings or points)	Calibration factor (Y_i) at each flow rate must be within ±2% of the average value (Y)	Prior to initial use and when posttest check is not within ±5% of Y	Recalibrate at 3 points until the acceptance criteria are met
Gas Flowmeter Posttest Calibration Check (Single-Point)	Calibration factor (Y_i) must be within ±5% of the Y value from the most recent 3-point calibration	After each field test. For mass flowmeters, must be done on-site, using stack gas	Recalibrate gas flowmeter at 3 points to determine a new value of Y. For mass flowmeters, must be done on-site, using stack gas. Apply the new Y value to the field test data
Temperature Sensor Calibration	Absolute temperature measured by sensor within ±1.5% of a reference sensor	Prior to initial use and before each test thereafter	Recalibrate; sensor may not be used until specification is met
Barometer Calibration	Absolute pressure measured by instrument within ±10 mm Hg of reading with a NIST-traceable barometer	Prior to initial use and before each test thereafter	Recalibrate; instrument may not be used until specification is met
Pretest Leak Check	≤4% of target sampling rate	Prior to sampling	Sampling shall not commence until the leak check is passed
Posttest Leak Check	≤4% of target sampling rate	After sampling	Sample is not valid
Analytical Matrix Interference Test	Establish minimum dilution (if any) to eliminate sorbent matrix interferences	Prior to analyzing any field samples or blanks, must be done for each type of sorbent material used	Field sample results are not valid
Analytical Bias Test	Average recovery between 90%–110% at each of the 2 spike concentration levels	Prior to analyzing field samples and prior to use of new sorbent media	Field samples shall not be analyzed until the percent recovery criteria has been met
Multipoint Analyzer Calibration	Each analyzer reading within ±10% of true value and $R^2 \geq 0.99$	On the day of analysis, before analyzing any samples	Recalibrate until successful
Analysis of Independent Calibration Standard	Within + 10% of true value	Following daily calibration, prior to analyzing field samples	Recalibrate and repeat independent standard analysis until successful
ysis of Continuing Calibration Verification Standard (CCV)	Within + 10% of true value	Following daily calibration, after analyzing ≤10 field samples, and at end of each set of analyses	Invalidate all samples from the last successful CCV, recalibrate and repeat independent standard analysis, reanalyze samples until successful
Test Run Total Sample Volume	Within ±20% of total volume sampled during field recovery test (See Section 8.2.4)	Every sample	Sample not valid
Sorbent Trap Section 2 Breakthrough	≤ 20% of Section 1 mass	Every sample	Sample not valid[2]
Paired Sorbent Trap Agreement (1 Spiked / 1 Nonspiked)	≤10% RD	Every run	Run not valid[2]
Sample Analysis	Within valid calibration range (within calibration curve)	All samples	Samples invalidated if not within calibrated range
Sample Analysis	With the bounds of the HCl analytical bias test	All samples	Expand bounds of HCl analytical bias test; if not successful, samples are not valid
Field Recovery Test	Average recovery between 85% and 115%	Once per field test program	Field sample runs not validated without successful field recovery test

[1] Quality assurance/quality control.

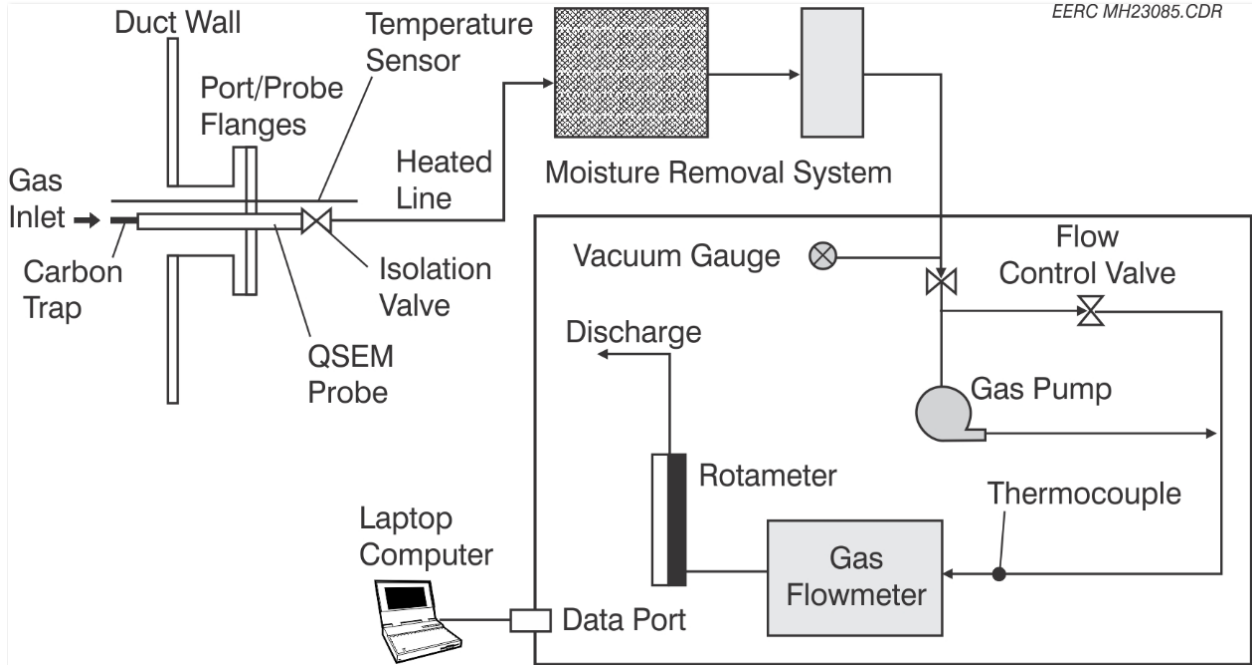[2] And data from the pair of sorbent traps are also not valid.

Figure 17-1. Sorbent trap sampling system.

APPENDIX

DETERMINATION OF LOD FOR OTM-40

DETERMINATION OF LOD FOR THE OTM-40

Determination of the Limit of Detection (LOD) for HCl Trap Analysis Using a Dionex ICS-2000 Ion Chromatograph

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Objective:

Determine the LOD for the method of HCl trap analysis by using the procedure defined by EPA Method 301 and by direct measurement. This experiment will also quantify the amount of background chloride which is present on the sorbent material.

Theory:

The Limit of Detection (LOD) defines the lowest level that quantitative results may be obtained for an analytical method with an acceptable degree of confidence. Method 301 defines the LOD as three times the standard deviation of the blank signal. Theoretically, the blank should have no signal; however, the sorbent material which is used contains trace amounts of chloride. The chemical supplier estimates that there are less than 10 μg of chloride in each one gram trap section. This amount can be significant when the traps are used to sample from low concentration stationary sources. (1, 2)

In order to determine the LOD for instrumental analysis according to Method 301, an estimate must first be made for the LOD and this is called LOD1. Seven standards are prepared at LOD1 and the standard deviation is determined for the measured concentrations at this level and is called S_1. (1)

The standard deviation S_x, can be extracted directly from run data as shown in equation 1. a_i is the standard response determined for each successive run, a_m is the mean of all of the standard responses, and n is the number of samples.

$$S_x = \frac{\sqrt{\Sigma_i^n (a_i - a_m)}}{n-1} \qquad (1)$$

LOD0 is temporarily defined as $3 \cdot S_1$, and if LOD_1 is less than two times LOD_0, then $S_0 = S_1$ and the LOD may be defined as LOD_1. If not, then two more sets of seven standards at concentrations lower than LOD_1 shall be produced. S_2 and S_3 shall be determined for these sets. S_1, S_2 and S_3 shall be plotted as a function of concentration and linear regression performed to extrapolate to the value at zero concentration, which then becomes S_0.(1)

Procedure:
Standard Preparation and Analysis
- g portions of sorbent were weighed and placed into test tubes.
- The sorbent was spiked with the appropriate mass of chloride by using a concentrated chloride standard.
  - A 10,000±46 μg/mL concentrated standard was diluted to 100±0.5 μg/mL by using a class A 100 mL volumetric flask. Calibrated Micropipettes were used to deliver the concentrated standard.
- 3.0 mL of Deionized (DI) water were added to the test tubes using a repeater pipette and the resulting mixture was aggressively mixed until the sorbent was fully dissolved.
- 7.0 mL of proprietary Ohio Lumex Chloride Extraction Solution were added to the test tubes and the resulting mixture was aggressively mixed for 10 seconds.
- The test tubes were place into a centrifuge to fully separate the aqueous and organic layers.
- The top (organic) layer was extracted, filtered, and analyzed for chloride concentration by the ICS-2000 ion chromatograph.

Determination of LOD_0 and S_0 by Method 301
The LOD for the HCl trap analysis was determined by using the procedure described in Method 301. Since each sample contained the same volume of solution, the ion chromatograph was calibrated by mass of chloride spiked in the sample rather than concentration.
- A mass of 10 μg was chosen as an approximate LOD, and this was called LOD_1.
- Seven blank samples were spiked at 10 μg of chloride.
- The chloride mass in each sample was measured by using ion chromatography.
- The standard deviation for the spiked samples was determined and assigned as S_1.
- LOD_0 was defined as $3S_1$.
- Since LOD_1 was less than $2LOD_0$, two additional sets of standards were prepared at masses lower than LOD_1 (10μg) and they were called LOD_2 and LOD_3.
- LOD_2 and LOD_3 were 8 μg and 5 μg, respectively.
- S_2 and S_3 were determined from each set of standards using the same method used to determine S_1.
- S_1,S_2, and S_3 were plotted as a function of chloride mass and a linear regression was performed.
- The zero concentration value was extrapolated from the line and assigned as S_0.
- The LOD_0 was the calculated LOD for the analysis and was equal to $3S_0$.

Data:
S₁ Determination for 10 μg Standards
Table 1. *The measured masses for seven 10 μg standards and the resulting average.*

Spike, μg	Measured mass, μg
10	10.49
10	10.42
10	9.39
10	10.17
10	8.91
10	8.50
10	8.60

Average = 9.5 μg
Std. Dev./S_1 = 0.86 μg
$3 \cdot S_1$ = 2.58 μg

S_2 and S_3 Determination for 8 μg and 5 μg Respectively

Table 2. *The measured masses for seven 8 μg standards and the resulting average and standard deviation.*

Spike, μg	Measured mass, μg
8	10.49
8	10.19
8	9.48
8	8.20
8	8.65
8	9.31
8	8.11

Average = 9.20 μg
Std. Dev./S_2 = 0.93 μg

Table 3. *The measured masses for seven 5 μg standards and the resulting average and standard deviation*
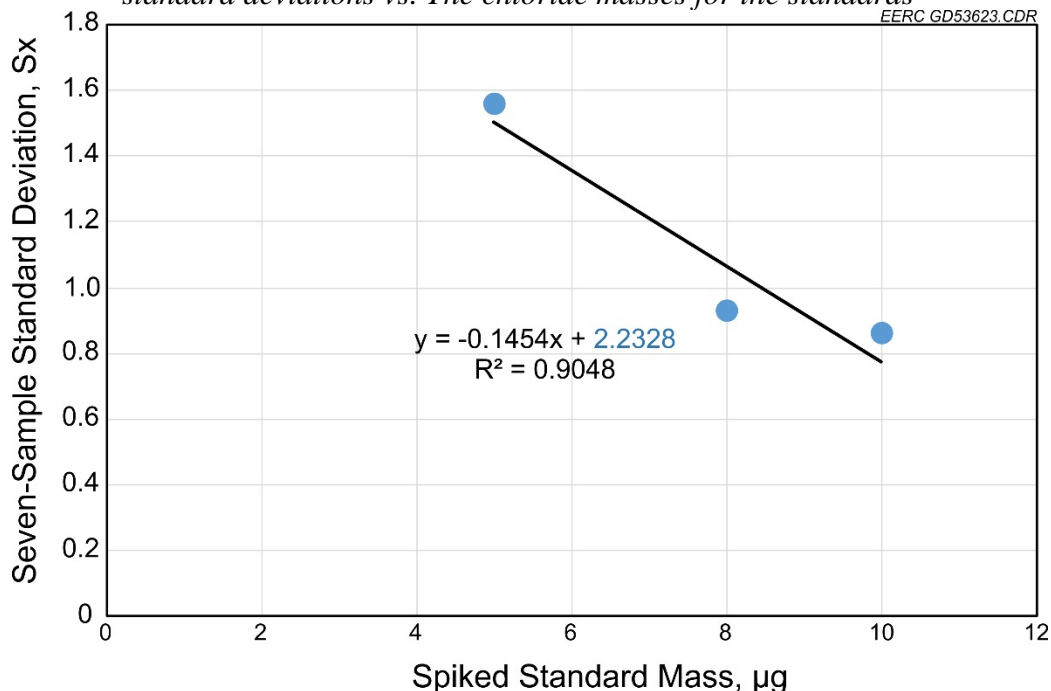
Spike, μg	Measured mass, μg
5	8.94
5	6.28
5	8.21
5	8.48
5	8.75
5	11.27
5	7.19

Average = 8.44 μg
Std. Dev./S_3 = 1.56 μg

Plot 1. *S0 was extracted (shown in blue) as the y-intercept of the standard deviations vs. The chloride masses for the standards*

Conclusion:

S_0 was extracted from Plot 1 as 2.23 and three times S_0 yields the **LOD_0 which is equal to 6.7 μg**. This value for the LOD depends only on the standard deviation for the samples and does not take into account the quantitation limitations associated with the amount of chloride background that is present on the sorbent in the trap section. Notice that the average measured masses for the 5 and 8 μg spikes are higher than the spike value which may be attributed to the background.

The Limit of Quantitation (LOQ) defines the lowest level for which chloride may be detected. The acceptable quantitation range for measurements shall be determined separately from what is contained in this experiment but will certainly utilize the data produced from it. (2)

References:

1. Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media. *40 CFR Part 63*. **2011**.
2. Mishalanie, E.A.; Lesnik, B.; Araki, R.; Segall R. *Validation and Peer Review of U.S. Environmental Protection Agency Chemical Methods of Analysis;* **2005**.