PERFORMANCE SPECIFICATION 18—PERFORMANCE SPECIFICATIONS AND TEST PROCEDURES FOR GASEOUS HYDROGEN CHLORIDE (HCl) CONTINUOUS EMISSION MONITORING SYSTEMS AT STATIONARY SOURCES

1.0 Scope and Application

1.1 Analyte. This performance specification (PS) is applicable for measuring gaseous concentrations of hydrogen chloride (HCl), CAS: 7647-01-0, on a continuous basis in the units of the applicable standard or in units that can be converted to units of the applicable standard(s).

1.2 Applicability.

1.2.1 This specification is used to evaluate the acceptability of HCl continuous emission monitoring systems (CEMS) at the time of installation or soon after and whenever specified in the regulations. The specification includes requirements for initial acceptance including instrument accuracy and stability assessments and use of audit samples if they are available.

1.2.2 The Administrator may require the operator, under section 114 of the Clean Air Act, to conduct CEMS performance evaluations at other times besides the initial test to evaluate the CEMS performance. See 40 CFR part 60, §§60.13(c) and 63.8(e)(1).

1.2.3 A source that demonstrates their CEMS meets the criteria of this PS may use the system to continuously monitor gaseous HCl under any regulation or permit that requires compliance with this PS. If your CEMS is capable of reporting the HCl concentration in the units of the applicable standard, no additional CEMS components are necessary. If your CEMS does not report concentrations in the units of the existing standard, then other CEMS components (*e.g.,*oxygen (O_2), temperature, stack gas flow, moisture and pressure) may be necessary to convert the units reported by your CEMS to the units of the standard.

1.2.4 These specification test results are intended to be valid for the life of the system. As a result, the HCl measurement system must be tested and operated in a configuration consistent with the configuration that will be used for ongoing continuous emissions monitoring.

1.2.5 Substantive changes to the system configuration require retesting according to this PS. Examples of such conditions include, but are not limited to: major changes in dilution ratio (for dilution based systems); changes in sample conditioning and transport, if used, such as filtering device design or materials; changes in probe design or configuration and changes in materials of construction. Changes consistent with instrument manufacturer upgrade that fall under manufacturer's certification do not require additional field verification. Manufacturer's upgrades require recertification by the manufacturer for those requirements allowed by this PS, including interference, level of detection (LOD), and light intensity qualification.

1.2.6 This specification is not designed to evaluate the ongoing CEMS performance nor does it identify specific calibration techniques and auxiliary procedures to assess CEMS performance over an extended period of time. The requirements in appendix F, Procedure 6 are designed to provide a way to assess CEMS performance over an extended period of time. The source owner or operator is responsible to calibrate, maintain, and operate the CEMS properly.

2.0 Summary of Performance Specification

2.1 This specification covers the procedures that each CEMS must meet during the performance evaluation test. Installation and measurement location specifications, data reduction procedures, and performance criteria are included.

2.2 The technology used to measure gaseous HCl must provide a distinct response and address any appropriate interference correction(s). It must accurately measure gaseous HCl in a representative sample (path or point sampling) of stack effluent.

2.3 The relative accuracy (RA) must be established against a reference method (RM) (e.g., Method 26A, Method 320, ASTM International (ASTM) D6348-12, including mandatory annexes, or Method 321 for Portland cement plants as specified by the applicable regulation, as appropriate for the source concentration and category). Method 26 may be approved as a RM by the Administrator on a case-by-case basis if not otherwise allowed or denied in an applicable regulation.

2.4 A standard addition (SA) procedure using a reference standard is included in appendix A to this performance specification for use in verifying LOD. For extractive CEMS, where the SA is done by dynamic spiking (DS), the appendix A procedure is allowed as an option for assessing calibration drift and is also referenced by Procedure 6 of appendix F to this part for ongoing quality control tests.

3.0 Definitions

3.1 *Beam attenuation* is the reduction in electromagnetic radiation (light) throughput from the maximum beam intensity experienced during site specific CEMS operation.

3.2 *Beam intensity* is the electromagnetic radiation (light) throughput for an IP-CEMS instrument measured following manufacturers specifications.

3.3 *Calibration cell* means a gas containment cell used with cross stack or integrated path (IP) CEMS for calibration and to perform many of the test procedures required by this performance specification. The cell may be a removable sealed cell or an evacuated and/or purged cell capable of exchanging reference and other calibration gases as well as zero gas standards. When charged, it contains a known concentration of HCl and/or interference gases. The calibration cell is filled with zero gas or removed from the optical path during stack gas measurement.

3.4 *Calibration drift* (CD) means the absolute value of the difference between the CEMS output response and an upscale reference gas or a zero-level gas, expressed as a percentage of the span value, when the CEMS is challenged after a stated period of operation during which no unscheduled adjustments, maintenance or repairs took place.

3.5 *Centroidal area* means a central area that is geometrically similar to the stack or duct cross section and is no greater than 10 percent of the stack or duct cross-sectional area.

3.6 *Continuous Emission Monitoring System* (CEMS) means the total equipment required to measure the pollutant concentration or emission rate continuously. The system generally consists of the following three major subsystems:

3.6.1 *Sample interface* means that portion of the CEMS used for one or more of the following: Sample acquisition, sample transport, sample conditioning, defining the optical measurement path, and protection of the monitor from the effects of the stack effluent.

3.6.2 *HCl analyzer* means that portion of the HCl CEMS that measures the total vapor phase HCl concentration and generates a proportional output.

3.6.3 *Data recorder* means that portion of the CEMS that provides a permanent electronic record of the analyzer output. The data recorder may record other pertinent data such as effluent flow rates, various instrument temperatures or abnormal CEMS operation. The data recorder may also include automatic data reduction capabilities and CEMS control capabilities.

3.7 *Diluent gas* means a major gaseous constituent in a gaseous pollutant mixture. For combustion sources, either carbon dioxide (CO_2) or oxygen (O_2) or a combination of these two gases are the major gaseous diluents of interest.

3.8 *Dynamic spiking* (DS) means the procedure where a known concentration of HCl gas is injected into the probe sample gas stream for extractive CEMS at a known flow rate to assess the performance of the measurement system in the presence of potential interference from the flue gas sample matrix.

3.9 *Independent measurement(s)* means the series of CEMS data values taken during sample gas analysis separated by two times the procedure specific response time (RT) of the CEMS.

3.10 *Integrated path CEMS* (IP-CEMS) means an in-situ CEMS that measures the gas concentration along an optical path in the stack or duct cross section.

3.11 *Interference* means a compound or material in the sample matrix other than HCl whose characteristics may bias the CEMS measurement (positively or negatively). The interference may not prevent the sample measurement, but could increase the analytical uncertainty in the measured HCl concentration through reaction with HCl or by changing the electronic signal generated during HCl measurement.

3.12 *Interference test* means the test to detect CEMS responses to interferences that are not adequately accounted for in the calibration procedure and may cause measurement bias.

3.13 *Level of detection* (LOD) means the lowest level of pollutant that the CEMS can detect in the presence of the source gas matrix interferents with 99 percent confidence.

3.14 *Liquid evaporative standard* means a reference gas produced by vaporizing National Institute of Standards and Technology (NIST) traceable liquid standards of known HCl concentration and quantitatively diluting the resultant vapor with a carrier gas.

3.15 *Measurement error* (ME) is the mean difference between the concentration measured by the CEMS and the known concentration of a reference gas standard, divided by the span, when the entire CEMS, including the sampling interface, is challenged.

3.16 *Optical path* means the route light travels from the light source to the receiver used to make sample measurements.

3.17 *Path length* means, for an extractive optical CEMS, the distance in meters of the optical path within a gas measurement cell. For an IP-CEMS, path length means the distance in meters of the optical path that passes through the source gas in the stack or duct.

3.18 *Point CEMS* means a CEMS that measures the source gas concentration, either at a single point at the sampling probe tip or over a path length for IP-CEMS less than 10 percent of the equivalent diameter of the stack or duct cross section.

3.19 *Stack pressure measurement device* means a NIST-traceable gauge or monitor that measures absolute pressure and conforms to the design requirements of ASME B40.100-2010, "Pressure Gauges and Gauge Attachments" (incorporated by reference—see §60.17).

3.20 *Reference gas standard* means a NIST-traceable gas standard containing a known concentration of HCl certified in accordance with an EPA traceability protocol in section 7.1 of this PS.

3.21 *Relative accuracy* (RA) means the absolute mean difference between the gas concentration or the emission rate determined by the CEMS and the value determined by the RM, plus the confidence coefficient of a series of nine test runs, divided by the average of the RM or the applicable emission standard.

3.22 *Response time* (RT) means the time it takes for the measurement system, while operating normally at its target sample flow rate, dilution ratio, or data collection rate to respond to a known step change in gas concentration, either from a low- or zero-level to a high-level gas concentration or from a high-level to a low or zero-level gas concentration, and to read 95 percent of the change to the stable instrument response. There may be several RTs for an instrument related to different functions or procedures (e.g., DS, LOD, and ME).

3.23 *Span value* means an HCl concentration approximately equal to two times the concentration equivalent to the emission standard unless otherwise specified in the applicable regulation, permit or other requirement. Unless otherwise specified, the span may be rounded up to the nearest multiple of 5.

3.24 *Standard addition* means the addition of known amounts of HCl gas (either statically or dynamically) to the actual measurement path or measured sample gas stream.

3.25 *Zero gas* means a gas or liquid with an HCl concentration that is below the LOD of the measurement system.

4.0 Interferences

Sample gas interferences will vary depending on the instrument or technology used to make the measurement. Interferences must be evaluated through the interference test in this PS. Several compounds including carbon dioxide (CO_2), carbon monoxide (CO), formaldehyde (CH_2O), methane (CH_4), and water (H_2O) are potential optical interferences with certain types of HCl monitoring technology. Ammonia is a potential chemical interference with HCl.

5.0 Safety

The procedures required under this PS may involve hazardous materials, operations, and equipment. This PS 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 determine the applicable regulatory limitations prior to performing these procedures. The CEMS user's manual and materials recommended by the RM should be consulted for specific precautions to be taken.

6.0 Equipment and Supplies

Equipment and supplies for CEMS will vary depending on the measurement technology and equipment vendors. This section provides a description of the equipment and supplies typically found in one or more types of CEMS.

6.1 Sample Extraction System. The portion of an extractive CEMS that collects and transports the sample to the pressure regulation and sample conditioning module. The extraction system must deliver a representative sample to the measurement instrument. The sample extraction system typically consists of a sample probe and a heated umbilical line.

6.2 Sample Conditioning Module. The portion of an extractive CEMS that removes particulate matter and moisture from the gas stream and provides a sample gas stream to the CEMS analysis module or analyzer. You must keep the particle-free gas sample above the dew point temperature of its components.

6.3 HCl Analyzer. The portion of the CEMS that detects, quantifies and generates an output proportional to the sample gas HCl concentration.

6.4 System Controller. The portion of the CEMS that provides control of the analyzer and other sub-systems (*e.g.,*sample extraction, sample conditioning, reference gas) as necessary for continuous operation and periodic maintenance/QC activities.

6.5 Data Recorder. The portion of the CEMS that provides a record of analyzer output. The data recorder may record other pertinent data such as effluent flow rates, various instrument temperatures or abnormal CEMS operation. The data recorder output range must include the full range of expected HCl concentration values in the gas stream to be sampled including zero and span value.

6.6 Reference Gas System(s). Gas handling system(s) needed to introduce reference and other gases into the measurement system. For extractive CEMS, the system must be able to introduce gas flow sufficient to flood the sampling probe and prevent entry of gas from the effluent stream. For IP-CEMS, the system must be able to introduce a known concentration of HCl, at known cell length, pressure and temperature, into the optical path used to measure HCl gas concentration.

6.7 Moisture Measurement System. If correction of the measured HCl emissions for moisture is required, you must install, operate, maintain, and quality assure a continuous moisture monitoring system for measuring and recording the moisture content of the flue gases. The following continuous moisture monitoring systems are acceptable: An FTIR system validated according to Method 301 or section 13.0 of Method 320 in appendix A to part 63 of this chapter; a continuous moisture sensor; an oxygen analyzer (or analyzers) capable of measuring O_2 both on a wet basis and on a dry basis; a stack temperature sensor and a moisture look-up table, *i.e.,* a psychrometric chart (for saturated gas streams following wet scrubbers or other demonstrably saturated gas streams, only); or other continuous moisture measurement methods approved by the Administrator. Alternatively, for any type of fuel, you may determine an appropriate site-specific default moisture value (or values), using measurements made with Method 4—Determination of Moisture Content In Stack Gases, in appendix A-3 to of this part. If this option is selected, the site-specific moisture default value(s) must represent the fuel(s) or fuel blends that are combusted in the unit during normal, stable operation, and must account for any distinct difference(s) in the stack gas moisture content associated with different process operating conditions. At least nine Method 4 runs are required for determining each site-specific default moisture percentage. Calculate each site-specific default moisture value by taking the arithmetic average of the Method 4 runs. Each site-specific moisture default value shall be updated whenever the current value is non-representative, due to changes in unit or process operation, but in any event no less frequently than annually.

7.0 Reagents and Standards

7.1 Reference Gases. Reference gases (*e.g.,* cylinder gases or liquid evaporative standards) used to meet the requirements of this PS must be NIST certified or NIST-traceable and vendor certified to ±5.0 percent accuracy. HCl cylinder gases must be certified according to Reference 5 in section 16 of this PS through a documented unbroken chain of comparisons each contributing to the reported uncertainty. Liquid evaporative standards must be certified using the gravimetrically-based procedures of the latest version of the EPA Traceability Protocol for Qualification and Certification of Evaporative HCl Gas

Standards and Humidification of HCl Gas Standards from Cylinders (*see* EPA-HQ-OAR-2013-0696-0026.pdf).

7.2 Cylinder gas and/or liquid evaporative standards must be used within their certification periods.

7.3 High concentration cylinder gas or liquid evaporative HCl standards may be diluted for use in this specification. You must document the quantitative introduction of HCl standards into the system using Method 205, found in 40 CFR part 51, appendix M, or other procedure approved by the Administrator.

8.0 CEMS Measurement Location Specifications and Pretest Preparation

8.1 Prior to the start of your initial PS tests, you must ensure that the CEMS is installed according to the manufacturer's specifications and the requirements in this section. You may use either point or IP sampling technology.

8.2 CEMS Installation. Install the CEMS at an accessible location where the pollutant concentration or emission rate measurements are directly representative of the HCl emissions or can be corrected so as to be representative of the total emissions from the affected facility. The CEMS need not be installed at the same location as the relative accuracy test location. If you fail the RA requirements in this specification due to the CEMS measurement location and a satisfactory correction technique cannot be established, the Administrator may require the CEMS to be relocated.

8.2.1 Single point sample gas extraction should be (1) no less than 1.0 m (3.3 ft.) from the stack or duct wall or (2) within the centroidal area of the stack or duct cross section.

8.2.2 IP-CEMS measurements should (1) be conducted totally within the inner area bounded by a line 1.0 m (3.3 ft.) from the stack or duct wall, (2) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross-sectional area, or (3) be located over any part of the centroidal area.

8.2.2.1 You must measure the IP-CEMS path length from the inner flange of the sampling ports or the inner end of the instrument insertion into the stack cavity using a laser tape measure, mechanical measurement tape, or similar device accurate to ±1.5 mm (0.059 in).

8.2.2.2 You must ensure that any purge flow used to protect IP-CEMS instrument windows from stack gas does not alter the measurement path length. Purge flow of less than or equal to 10 percent of the gas velocity in the duct meets this requirement.

8.2.3 CEMS and Data Recorder Scale Check. After CEMS installation, record and document the measurement range of the HCl CEMS. The CEMS operating range and the range of the data recording device must encompass all potential and expected HCl concentrations, including the concentration equivalent to the applicable emission limit and the span value.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Performance Specification Test Procedure

After completing the CEMS installation, setup and calibration, you must complete the PS test procedures in this section. You must perform the following procedures and meet the performance requirements for the initial demonstration of your CEMS:

a. Interference Test;

b. Beam Intensity Test (IP-CEMS only);

c. Temperature Verification Procedure (IP-CEMS only);

d. Pressure Verification Procedure (IP-CEMS only);

e. Level of Detection Determination;

f. Response Time Test;

g. Measurement Error Test;

h. Calibration Drift Test; and

i. Relative Accuracy Test.

11.1 Interference Test

11.1.1 Prior to its initial use in the field, you must demonstrate that your monitoring system meets the performance requirements of the interference test in section 13.5 to verify that the candidate system measures HCl accurately in the presence of common interferences in emission matrices.

11.1.2 Your interference test must be conducted in a controlled environment. The equipment you test for interference must include the combination of the analyzer, related analysis software, and any sample conditioning equipment (*e.g.,* dilution module, moisture removal equipment or other interferent scrubber) used to control interferents.

11.1.3 If you own multiple measurement systems with components of the same make and model numbers, you need only perform this interference test on one analyzer and associated interference conditioning equipment combination. You may also rely on an interference test conducted by the manufacturer or a continuous measurement system integrator on a system having components of the same make and model(s) of the system that you use.

11.1.4 Perform the interference check using an HCl reference gas concentration of approximately five times the LOD.

11.1.5 Introduce the interference test gases listed in Table 1 in section 17.0 of this PS to the analyzer/conditioning system separately or in any combination. The interference test gases need not be of reference gas quality.

11.1.5.1 For extractive CEMS, the interference test gases may be introduced directly into the inlet to the analyzer/conditioning system after the probe extension coupling.

11.1.5.2 For IP-CEMS, the interference test gases may be added with the HCl in a calibration cell or separately in a temperature-controlled cell. The effective concentration of the gas in the cell must meet the requirements in Table 1 corrected for absolute pressure, temperature and the nominal stack sampling path length of the CEMS.

11.1.6 The interference test must be performed by combining an HCl reference gas with each interference test gas (or gas mixture). You must measure the baseline HCl response, followed by the response after adding the interference test gas(es) while maintaining a constant HCl concentration. You must perform each interference gas injection and evaluation in triplicate.

NOTE: The baseline HCl gas may include interference gases at concentrations typical of ambient air (*e.g.,* 21 percent O_2, 400 parts per million (ppm) CO_2, 2 percent H_2O), but these concentrations must be brought to the concentrations listed in Table 1 when their interference effects are being evaluated.

11.1.7 You should document the gas volume/rate, temperature, and pressure used to conduct the interference test. A gas blending system or manifold may be used.

11.1.8 Ensure the duration of each interference test is sufficient to condition the HCl measurement system surfaces before a stable measurement is obtained.

11.1.9 Measure the HCl response of the analyzer/sample conditioning system combination to the test gases in ppmv. Record the responses and determine the overall interference response using Table 2 in section 17.0.

11.1.10 For each interference gas (or mixture), calculate the mean difference (ΔMC_{avg}) between the measurement system responses with and without the interference test gas(es) using Equation 1 in section 12.2. Summarize the results following the format contained in Table 2 in section 17.

11.1.11 Calculate the percent interference (I) for the gas runs using Equation 2 in section 12.2.

11.1.12 The total interference response (*i.e.,* the sum of the interference responses of all tested gaseous components) must not exceed the criteria set forth in section 13.5 of this PS.

11.2 Beam Intensity Test for IP-CEMS

11.2.1 For IP-CEMS, you must establish the tolerance of your system to beam intensity attenuation.

11.2.1.1 Your beam intensity test may be conducted in either a controlled environment or on-site during initial setup and demonstration of your CEMS.

11.2.1.2 If you have multiple measurement systems with components of the same make and model numbers, you need only perform this attenuation check on one system and you may also rely on an attenuation test conducted by the manufacturer on a system having components of the same make and model(s) of the system that you use.

11.2.2 Insert one or more neutral density filter(s) or otherwise attenuate the beam intensity by a known percentage (*e.g.,* 90 percent of the beam intensity).

11.2.3 Perform a high-level HCl reference gas measurement.

11.2.4 Record and report the attenuated beam intensity, the measured HCl calibration gas concentration at full beam intensity, the measured HCl gas concentration with attenuated beam intensity, and the percent difference between the two HCl measurements with and without attenuation of the beam intensity. The percent difference must not exceed the criteria set forth in section 13.6 of this PS.

11.2.5 In the future, you may not operate your IP-CEMS at a beam intensity lower than that established based on the attenuation used during this test. However, you may repeat the test to establish a lower beam intensity limit or level.

11.3 Temperature Measurement Verification Procedure for IP-CEMS

11.3.1 Any measurement instrument or device that is used as a reference in verification of temperature measurement must have an accuracy that is traceable to NIST.

11.3.2 You must verify the temperature sensor used in IP-CEMS measurements on-site as part of the initial installation and verification procedures.

11.3.3 Comparison to Calibrated Temperature Measurement Device.

11.3.3.1 Place the sensor of a calibrated temperature reference device adjacent to the sensor used to measure stack temperature for your IP-CEMS. The calibrated temperature reference device must satisfy the accuracy requirements specified in Table 3 of this PS. The calibrated temperature reference device must also have a range equal to or greater than the range of your IP-CEMS temperature sensor.

11.3.3.2 Allow sufficient time for the response of the calibrated temperature reference device to reach equilibrium. With the process and control device operating under normal conditions, concurrently record the temperatures measured by your IP-CEMS system (M_t) and the calibrated temperature reference device (V_t). You must meet the accuracy requirements specified in section 13.7 of this PS.

11.3.3.3 If your IP-CEMS temperature sensor does not satisfy the accuracy requirement of this PS, check all system components and take any corrective action that is necessary to achieve the required minimum accuracy. Repeat this verification procedure until the accuracy requirement of this specification is satisfied.

11.4 Pressure Measurement Verification Procedure for IP-CEMS

11.4.1 For stack pressure measurement verification, you must select a NIST-traceable gauge or monitor that conforms to the design requirements of ASME B40.100-2010, “Pressure Gauges and Gauge Attachments,” (incorporated by reference—see §60.17) as a reference device.

11.4.2 As an alternative for a calibrated pressure reference device with NIST-traceable accuracy, you may use a water-in-glass U-tube manometer to verify your IP-CEMS pressure measurement equipment, provided there is also an accurate measurement of absolute atmospheric pressure at the manometer location.

11.4.3 Allow sufficient time for the response of the reference pressure measurement device to reach equilibrium. With the process and control device operating under normal conditions, concurrently record the pressures measured by your IP-CEMS system (M_P) and the pressure reference device (V_p). You must meet the accuracy requirements specified in section 13.8 of this PS.

11.4.4 If your IP-CEMS pressure sensor does not satisfy the accuracy requirement of this PS, check all system components and take any corrective action that is necessary to achieve the required minimum accuracy. Repeat this verification procedure until the accuracy requirement of this specification is satisfied.

11.5 Level of Detection Determination

11.5.1 You must determine the minimum amount of HCl that can be detected above the background in a representative gas matrix.

11.5.2 You must perform the LOD determination in a controlled environment such as a laboratory or manufacturer's facility.

11.5.3 You must add interference gases listed in Table 1 of this PS to a constant concentration of HCl reference gas.

11.5.3.1 You may not use an effective reference HCl gas concentration greater than five times the estimated instrument LOD.

11.5.3.2 For extractive CEMS, inject the HCl and interferents described in section 11.1.5 directly into the inlet to the analyzer.

11.5.3.3 For IP-CEMS, the HCl and interference test gases may be added to a calibration cell or separately in a temperature-controlled cell that is part of the measurement path. The effective concentration of the gas in the cell must meet the requirements in Table 1 corrected for absolute pressure, temperature and the nominal stack sampling path length of the CEMS.

11.5.4 Collect seven or more consecutive measurements separated by twice the RT (described in section 11.6) to determine the LOD.

11.5.5 Calculate the standard deviation of the measured values and define the LOD as three times the standard deviation of these measurements.

11.5.5.1 The LOD for extractive units must be determined and reported in ppmv.

11.5.5.2 The LOD for IP units must be determined and reported on a ppm-meter basis and the site- or installation-specific LOD must be calculated based on the actual measurement path length and gas density of the emissions at the specific site installation in ppmv.

11.5.6 You must verify the controlled environment LOD of section 11.5.2 of this PS for your CEMS during initial setup and field certification testing. You must use the SA procedure in appendix A of this PS with the following exceptions:

11.5.6.1 For the LOD verification in the field, you must make three independent SA measurements spiking the native source concentration by no more than three times the controlled environment LOD concentration determined in section 11.5.5.

11.5.6.2 For extractive CEMS, you must perform the SA as a dynamic spike by passing the spiked source gas sample through all filters, scrubbers, conditioners and other monitoring system components used during normal sampling, and as much of the sampling probe as practical. For IP-CEMS, you must perform the SA procedure by adding or passing a known concentration reference gas into a calibration cell in the optical path of the CEMS; you must also include the source measurement optical path while performing the SA measurement.

11.5.6.3 The amount detected, or standard addition response (SAR), is based on the average difference of the native HCl concentration in the stack or duct relative to the native stack concentration plus the SA. You must be able to detect the effective spike addition (ESA) above the native HCI present in the stack gas matrix. For extractive CEMS, the ESA is calculated using Equation A7 in appendix A of this PS. For IP-CEMS, the ESA is calculated as $C_{i,eff}$ using Equation 4 of this PS.

11.5.6.4 For extractive CEMS, calculate the SAR using Equation A4 in appendix A of this PS. For IP-CEMS, calculate the SAR using Equation A8.

11.5.6.5 If your system LOD field verification does not demonstrate a SAR greater than or equal to your initial controlled environment LOD, you must increase the SA concentration incrementally and repeat the field verification procedure until the SAR is equal to or greater than LOD. The site-specific standard addition detection level (SADL) is equal to the standard addition needed to achieve the acceptable SAR, and SADL replaces the controlled environment LOD. For extractive CEMS, the SADL is calculated as the ESA using Equation A7 in appendix A of this PS. For IP-CEMS, the SADL is the SA calculated using Equation A8 in appendix A of this PS. As described in section 13.1 of this PS, the LOD or the SADL that replaces an LOD must be less than 20 percent of the applicable emission limit.

11.6 Response Time Determination. You must determine ME-, LOD- and SA-RT

11.6.1 For ME- or LOD-RT, start the upscale RT determination by injecting zero gas into the measurement system as required by the procedures in section 11.7 or 11.5, respectively. You may use humidified zero gas. For standard addition RT, start the upscale RT determination by measuring the native stack gas concentration of HCl.

11.6.1.1 For extractive CEMS measuring ME- or LOD-RT, the output has stabilized when there is no change greater than 1.0 percent of full scale for 30 seconds.

11.6.1.2 For standard addition RT that includes the stack gas matrix the final stable response may continue to vary by more than 1 percent, but may be considered stable if the variability is random and not continuously rising or falling.

11.6.2 When the CEMS output has stabilized, record the response in ppmv and introduce an upscale (high level) or spike reference gas as required by the relevant procedure.

11.6.3 Record the time (upscale RT) required to reach 95 percent of the change to the final stable value.

11.6.4 Next, for ME or LOD RT, reintroduce the zero gas and record the time required to reach 95 percent of the change to the stable instrument response at the zero gas reading. For SA RT, introduce zero gas to the IP-CEMS cell or stop the spike gas flow to the extractive CEMS as required by the specified procedure and record the time required to reach 95 percent of the change to the stable instrument response of the native gas reading. This time is the downscale RT.

(NOTE: For CEMS that perform a series of operations (purge, blow back, sample integration, analyze, etc.), you must start adding reference or zero gas immediately after these procedures are complete.)

11.6.5 Repeat the entire procedure until you have three sets of data, then determine the mean upscale and mean downscale RTs for each relevant procedure. Report the greater of the average upscale or average downscale RTs as the RT for the system.

11.7 Measurement Error (ME) Test

11.7.1 On the same day and as close in time as practicable to when the ME test is conducted, perform and meet requirements for a calibration drift (CD) test using a zero gas as used in the Seven-Day Drift Test (see section 11.8) and document and report the results. To meet this requirement, the ME test may be conducted during the Seven-Day CD Test.

11.7.2 Extractive CEMS ME Test.

11.7.2.1 Introduce reference gases to the CEMS probe, prior to the sample conditioning and filtration system.

11.7.2.2 Measure three upscale HCl reference gas concentrations in the range shown in Table 4 of this PS.

11.7.2.3 Introduce the gases into the sampling probe with sufficient flow rate to replace the entire source gas sample.

11.7.2.4 Continue to add the reference gas until the response is stable as evidenced when the difference between two consecutive measurements is less than the LOD or within five percent of each other.

11.7.2.5 Make triplicate measurements for each reference gas for a total of nine measurements. Introduce different reference gas concentrations in any order but do not introduce the same gas concentration twice in succession.

11.7.2.6 At each reference gas concentration, determine the average of the three CEMS responses (MC_i). Calculate the ME using Equation 3A in section 12.3.

11.7.2.7 If you desire to determine the system RT during this test, you must inject zero gas immediately before and after each injection of the high-level gas standard.

11.7.2.8 For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system ME checks, and you may make only the adjustments necessary to maintain the proper ratio.

11.7.3 IP-CEMS ME Test.

11.7.3.1 Conduct a 3-level system ME test by individually adding the known concentrations of HCl reference gases into a calibration cell of known volume, temperature, pressure and path length.

Note: The optical path used for IP-CEMS ME checks must include the native HCl measurement path. You must also collect native stack concentration HCl measurements before and after each HCl standard measurement. Bracketing HCl reference gas measurements with native stack HCl measurements must be used in the calculations in Equation 5 in section 12.4.2 to correct the upscale measurements for stack gas HCl concentration changes.

11.7.3.2 Introduce HCl reference gas into your calibration cell in a range of concentrations that produce responses equivalent to the source concentrations shown in Table 4 of this PS for your path length.

11.7.3.3 Make triplicate measurements for each reference gas standard for a total of nine measurements. Introduce different calibration concentrations in any order but do not introduce the same reference gas concentration twice in succession.

11.7.3.4 You must calculate the effective concentration ($C_{i,eff}$) of the HCl reference gas equivalent to the stack concentration by correcting for calibration cell temperature, pressure, path length, line strength factor (LSF) and, if necessary, the native stack gas HCl concentration using Equation 4 in section 12.0.

11.7.3.5 You may use the LSF provided by your instrument manufacturer or determine an instrument-specific LSF as a function of temperature using a heated gas cell and equivalent concentrations ($C_{i,eff}$) between 50 and 150 percent of the emission limit.

11.7.3.6 At each reference gas concentration, average the three independent CEMS measurement responses corrected for native HCl stack concentration. Calculate the ME using Equation 6A in section 12.4.3.

11.7.4 You may use Figure 1 in section 17.0 to record and report your ME test results.

11.7.5 If the ME specification in section 13.3 is not met for all three reference gas concentrations, take corrective action and repeat the test until an acceptable 3-level ME test is achieved.

11.8 Seven-Day Calibration Drift (CD) Test

11.8.1 The CD Test Period. Prior to the start of the RA tests, you must perform a seven-day CD test. The purpose of the seven-day CD test is to verify the ability of the CEMS to maintain calibration for each of seven consecutive unit operating days as specified in section 11.8.5 of this PS.

11.8.2 The CD tests must be performed using the zero gas and mid-level reference gas standards as defined in Table 4 of this PS.

11.8.3 Conduct the CD test on each day during continuous operation of the CEMS and normal facility operations following the procedures in section 11.7 of this PS, except that the zero gas and mid-level gas need only be introduced to the measurement system once each.

11.8.4 If periodic automatic or manual adjustments are made to the CEMS zero and upscale response factor settings, conduct the CD test immediately before these adjustments.

NOTE: Automatic signal or mathematical processing of all measurement data to determine emission results may be performed throughout the entire CD process.

11.8.5 Determine the magnitude of the CD at approximately 24-hour intervals, for 7 consecutive unit operating days. The 7 consecutive unit operating days need not be 7 consecutive calendar days.

11.8.6 Record the CEMS response for single measurements of zero gas and mid-level reference gas. You may use Figure 2 in section 17 of this PS to record and report the results of your 7-day CD test.

11.8.6.1 For extractive CEMS, calculate the CD using Equation 3B in section 12.3. Report the absolute value of the differences as a percentage of the span value.

11.8.6.2 For IP-CEMS, you must include the source measurement optical path while performing the upscale CD measurement; you may exclude the source measurement optical path when determining the zero gas concentration. Calculate the CD for IP CEMS using equations 4, 5, 6B, and 7 in section 12.4.

11.8.7 The zero-level and mid-level CD for each day must be less than 5.0 percent of the span value as specified in section 13.2 of this PS. You must meet this criterion for 7 consecutive operating days past the 7-day CD test.

11.8.8 Dynamic Spiking Option for Seven-Day CD Test. For extractive CEMS, you have the option to conduct a mid-level dynamic spiking procedure for each of the 7 days in lieu of the mid-level reference gas injection described in sections 11.8.2 and 11.8.3. If this option is selected, the daily zero CD check is still required.

11.8.8.1 To conduct each of the seven daily mid-level dynamic spikes, you must use the DS procedure described in appendix A of this PS using a single spike of the mid-level reference gas (*see* Table 4).

11.8.8.2 You must perform the dynamic spike procedure by passing the spiked source gas sample through all filters, scrubbers, conditioners and other monitoring system components used during normal sampling, and as much of the sampling probe as practical.

11.8.8.3 Calculate the mid-level CD as a percent of span using Equation A6 of appendix A to this PS and calculate the zero drift using Equation 3B in section 12.3. Record and report the results as described in sections 11.8.6 and 11.8.7.

11.9 Relative Accuracy Test

11.9.1 Unless otherwise specified in an applicable regulation, use Method 26A in 40 CFR part 60, appendix A-8, Method 320 in 40 CFR part 63, appendix A, or ASTM D6348-12 including all annexes, as applicable, as the RMs for HCl measurement. Obtain and analyze RM audit samples, if they are available, concurrently with RM test samples according to the same procedure specified for performance tests in the general provisions of the applicable part. If Method 26 is not specified in an applicable subpart of the regulations, you may request approval to use Method 26 in appendix A-8 to this part as the RM on a site-specific basis under §§63.7(f) or 60.8(b). Other RMs for moisture, O_2, etc., may be necessary. Conduct the RM tests in such a way that they will yield results representative of the emissions from the source and can be compared to the CEMS data.

11.9.1.1 When Method 26A is used as the RM, you must sample sufficient gas to reach three times your method detection limit for Method 26A in 40 CFR part 60, appendix A-8, or for a minimum of one hour, whichever is greater.

11.9.1.2 When Method 320 or Method 321, both found in 40 CFR part 63, appendix A, or ASTM D6348-12, are used as the RM, you must collect gas samples that are at stack conditions (hot and wet) and you must traverse as required in section 11.9.3.

11.9.2 Conduct the diluent (if applicable), moisture (if needed), and pollutant measurements simultaneously. However, diluent and moisture measurements that are taken within an hour of the pollutant measurements may be used to calculate dry pollutant concentration and emission rates.

11.9.3 Reference Method Measurement Location and Traverse Point(s) Selection.

11.9.3.1 Measurement Location. Select, as appropriate, an accessible RM measurement location at least two equivalent diameters downstream from the nearest control device, point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate may occur, and at least one half equivalent diameter upstream from the effluent exhaust or a control device. When pollutant concentration changes are due solely to diluent leakage (*e.g.,* air heater leakages) and pollutants and diluents are simultaneously measured at the same location, a half diameter may be used in lieu of two equivalent diameters. The equivalent duct diameter is calculated according to Method 1 in appendix A-1 to this part. The CEMS and RM sampling locations need not be the same.

11.9.3.2 Traverse Point Selection. Select traverse points that assure acquisition of representative RM samples over the stack or duct cross section according to one of the following options: (a) sample at twelve traverse points located according to section 11.3 of Method 1 in appendix A-1 to this part, (b) sample at 6 Method 1 traverse points according to section 6.5.6(b)(1) of appendix A to part 75 of this chapter, or (c) sample at three points on a measurement line (“3-point long line”) that passes through the centroidal area of the duct in the direction of any potential stratification. If this line interferes with the CEMS measurements, you may displace the line up to 20 cm (12 in.) or 5.0 percent of the equivalent diameter of the cross section, whichever is less, from the centroidal area. Locate the three traverse points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, you may conduct a stratification test following the procedures in sections 11.9.3.2.1 through 11.9.3.2.4 to justify sampling at a single point or three points located on the measurement line at 0.4, 1.2, and 2.0 m from the stack wall (“3-point short line”). Stratification testing must be conducted at the sampling location to be used for the RM measurements during the RA test and must be made during normal facility operating conditions. You must evaluate the stratification by measuring the gas on the same moisture basis as the HCl CEMS (wet or dry). Stratification testing must be repeated for each RA test program to justify single point or “3-point short line” sampling.

11.9.3.2.1 Use a probe of appropriate length to measure the HCl concentration or an alternative analyte, as described in this section, using 12 traverse points located according to section 11.3 of Method 1 in appendix A-1 to 40 CFR part 60 for a circular stack or nine points at the centroids of similarly-shaped, equal area divisions of the cross section of a rectangular stack.

11.9.3.2.2 You may substitute a stratification test for SO_2 for the HCl stratification test. If you select this option, you must follow the test procedures in Method 6C of appendix A-4 to 40 CFR part 60 or Method 320 of appendix A of 40 CFR part 63.

11.9.3.2.3 Calculate the mean measured concentration for all sampling points (MN_{avg}).

11.9.3.2.4 Calculate the percent stratification (S_t) of each traverse point using Equation 8 in section 12.5.

11.9.3.2.5 The gas stream is considered to be unstratified and you may perform the RA testing at a single point that most closely matches the mean if the concentration at each traverse point differs from the mean concentration for all traverse points by: (a) No more than 5.0 percent of the mean concentration; or (b) 0.2 ppm (for HCl) or 3 ppm (for SO_2) absolute, whichever is less restrictive.

11.9.3.2.6 If the criterion for single point sampling (5.0 percent, 0.2 ppm for HCl or 3 ppm for SO_2 are not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by no more than 10.0 percent of the mean, the gas stream is considered to be minimally stratified, and you may take RA samples using the “3-point short line”. Alternatively, you may use the 3-point short line if each traverse point differs from the mean value by no more than 0.4 ppm (for HCl) or 5 ppm (for SO_2).

11.9.3.2.7 If the concentration at any traverse point differs from the mean concentration by more than 10 percent, the gas stream is considered stratified and you must sample using one of the options in section 11.9.3.2 above.

11.9.3.3 Conduct all necessary RM tests within 3 cm (1.2 in.) of the traverse points, but no closer than 3 cm (1.2 in.) to the stack or duct wall.

11.9.4 In order to correlate the CEMS and RM data properly, record the beginning and end of each RM run (including the time of day in hours, minutes, and seconds) using a clock synchronized with the CEM clock used to create a permanent time record with the CEMS output.

11.9.5 You must conduct the RATA during representative process and control operating conditions or as specified in an applicable regulation, permit or subpart.

11.9.6 Conduct a minimum of nine RM test runs. *NOTE:* More than nine RM test runs may be performed. If this option is chosen, up to three test run results may be excluded so long as the total number of test run results used to determine the CEMS RA is greater than or equal to nine. However, all data must be reported including the excluded test runs.

11.9.7 Analyze the results from the RM test runs using Equations 9-14 in section 12.6. Calculate the RA between the CEMS results and the RM.

11.10 Record Keeping and Reporting

11.10.1 For systems that use a liquid evaporative standard generator to deliver HCl reference gas standards, record supporting data for these devices, including liquid feed calibrations, liquid standard concentration(s) and NIST-traceability, feed rate and gas flow calibrations for all diluent and HCl gas flows. All calibrations must include a stated uncertainty, and the combined uncertainty of the delivered HCl reference gas concentration must be calculated and reported.

11.10.2 Record the results of the CD test, the RT test, the ME test, the RA test, and for IP-CEMS, the results of the beam intensity, temperature and pressure verification procedures. Also keep records of the RM and CEMS field data, calculations, and reference gas certifications necessary to confirm that the performance of the CEMS met the performance specifications.

11.10.3 For systems that use Method 205 to prepare HCl reference gas standards, record results of Method 205 performance test field evaluation, reference gas certifications, and gas dilution system calibration.

11.10.4 Record the LOD for the CEMS. For extractive CEMS, record the LOD in ppmv. For IP-CEMS, record the LOD on a ppm-meter basis along with a calculation of the installation specific LOD in ppmv. For both CEMS types, you must also record the field verified SADL.

11.10.5 Record the results of the interference test.

11.10.6 Report the results of all certification tests to the appropriate regulatory agency (or agencies), in hardcopy and/or electronic format, as required by the applicable regulation or permit.

12.0 Calculations and Data Analysis

12.1 Nomenclature

C_i = Zero or HCl reference gas concentration used for test i (ppmv);

$C_{i,eff}$ = Equivalent concentration of the reference gas value, C_i, at the specified conditions (ppmv);

CC = Confidence coefficient (ppmv);

$CD_{extractive}$ = Calibration drift for extractive CEMS (percent);

CD_{IP} = Calibration drift for IP-CEMS (percent);

CD_0 = Calibration drift at zero HCl concentrations for an IP-CEMS (percent);

d_{avg} = Mean difference between CEMS response and the reference gas (ppmv);

d_i = Difference of CEMS response and the RM value (ppmv);

I = Total interference from major matrix stack gases, (percent);

LSF = Line strength factor for IP-CEMS instrument specific correction for temperature and gas matrix effects derived from the HITRAN and/or manufacturer specific database (unitless);

ΔMC_{avg} = Average of the 3 absolute values of the difference between the measured HCl calibration gas concentrations with and without interference from selected stack gases (ppmv);

MC_i = Measured HCl reference gas concentration i (ppmv);

MC_i = Average of the measured HCl reference gas concentration i (ppmv);

MC_{int} = Measured HCl concentration of the HCl reference gas plus the individual or combined interference gases (ppmv);

$ME_{extractive}$ = Measurement error for extractive CEMS (percent);

ME_{IP} = Measurement error for IP-CEMS (percent);

MN_{avg} = Average concentration at all sampling points (ppmv);

MN_{bi} = Measured native concentration bracketing each calibration check measurement (ppmv);

MN_i = Measured native concentration for test or run I (ppmv);

n = Number of measurements in an average value;

P_{stack} = Absolute stack pressure (mm Hg)

$P_{reference}$ = Absolute pressure of the calibration cell for IP-CEMS (mm Hg)

PL_{Cell} = Path length of IP-CEMS calibration cell (m);

PL_{Stack} = Path length of IP-CEMS stack optical path (m);

RA = Relative accuracy of CEMS compared to a RM (percent);

RM_i = RM concentration for test run i (ppmv);

RM_{avg} = Mean measured RM value (ppmv);

S = Span value (ppmv);

S_d = Standard deviation of the differences (ppmv);

S_{ti} = Stratification at traverse point i (percent);

SADL = Standard addition detection level (ppmv);

$t_{0.975}$ = One-sided t-value at the 97.5th percentile obtained from Table 5 in section 17.0 for n-1 measurements;

$T_{reference}$ = Temperature of the calibration cell for IP-CEMS (degrees Kelvin);

T_{stack} = Temperature of the stack at the monitoring location for IP-CEM (degrees Kelvin).

12.2 *Calculate the difference between the measured HCl concentration with and without interferents for each interference gas (or mixture) for your CEMS as:*

$$\Delta MC_{avg} = \frac{\sum_{i=1}^{3} |MC_i - MC_{int}|}{3} \qquad \text{Eq. 1}$$

Calculate the total percent interference as:

$$I = \sum_{i=1}^{n} \frac{\Delta MC_{avg}}{MC_i} * 100 \qquad \text{Eq. 2}$$

12.2.1 Calculate the equivalent concentration $C_{i,eff}$ using Equation 4:

$$C_{i,eff} = \left[C_i \times \frac{PL_{cell}}{PL_{Stack}} \times \frac{T_{stack}}{T_{reference}} \times \frac{P_{reference}}{P_{stack}} LSF \right] \qquad \text{Eq. 4}$$

12.3 Calculate the ME or CD at Concentration i for an Extractive CEMS as:

$$ME_{extractive} = \frac{|C_i - MC_i|}{S} * 100 \qquad \text{Eq. 3A}$$

$$CD_{extractive} = \frac{|C_i - MC_i|}{S} * 100 \qquad \text{Eq. 3B}$$

12.4 Calculate the ME or CD at Concentration i for IP-CEMS That Use a Calibration Cell as Follows:

12.4.1 Calculate the equivalent concentration $C_{i,eff}$ using Equation 4:

$$C_{i,eff} = \left[C_i \times \frac{PL_{cell}}{PL_{Stack}} \times \frac{T_{stack}}{T_{reference}} \times LSF \right] \qquad \text{Eq. 4}$$

12.4.2 Calculate the average native concentration before and after each calibration check measurement as:

$$MN_{bi} = \frac{MN_i + MN_{i+1}}{2} \qquad \text{Eq. 5}$$

12.4.3 Calculate the ME or CD at concentration i for an IP-CEM as:

$$ME_{IP} = \frac{\sum_1^3 |(MC_i - MN_{bi}) - C_{ieff}|}{3S} * 100 \qquad \text{Eq. 6A}$$

$$CD_{IP} = \frac{|MC_i - MN_{bi} - C_{i,eff}|}{S} * 100 \qquad \text{Eq. 6B}$$

12.4.4 Calculate the zero CD as a percent of span for an IP-CEMS as:

$$CD_0 = \frac{(|(MC_i - MN_b) - (MC_{i+1} - MN_b)|)}{S} * 100 \qquad \text{Eq. 7}$$

12.5 Calculate the Percent Stratification at Each Traverse Point as:

$$S_{ti} = \frac{|MN_i - \mathrm{MN}_{avg}|}{MN_{avg}} * 100 \qquad \text{Eq. 8}$$

12.6 Calculate the RA Using RM and CEMS Data

12.6.1 Determine the CEMS final integrated minute average pollutant concentration or emission rate for each RM test period. Consider system RT, if important, and confirm that the results have been corrected to the same moisture, temperature and diluent concentration basis.

12.6.2 When Method 26A (or if approved for use, Method 26), found in 40 CFR part 60, appendix A-8 of this part, is used as the RM, compare each CEMS integrated average value against the corresponding RM value for identical test periods. Make these comparisons on the same basis (*e.g.,* wet, dry, ppmv, or units of the standard). To convert results generate by Method 26A or 26 in mg/DSCM to ppmv, use the conversion factor 0.662 ppm/(mg/DSCM).

12.6.3 If the RM is Method 320 or Method 321, found in 40 CFR part 63, appendix A, or ASTM D6348-12, make a direct comparison of the average RM results and CEMS average value for identical test periods.

12.6.4 For each test run, calculate the arithmetic difference of the RM and CEMS results using Equation 9.

$$d_i = RM_i - MN_i \qquad \text{Eq. 9}$$

12.6.5 Calculate the standard deviation of the differences (S_d) of the CEMS measured and RM results using Equation 10.

$$S_d = \sqrt{\frac{\sum_i^n \left(d_i - \left(\frac{\sum_{i=1}^n d_i}{n}\right)\right)^2}{n-1}} \qquad \text{Eq. 10}$$

12.6.6 Calculate the confidence coefficient (CC) for the RATA using Equation 11.

$$CC = t_{0.975} * \left(\frac{S_d}{(n^{1/2})}\right) \qquad \text{Eq. 11}$$

12.6.7 Calculate the mean difference (d_{avg}) between the RM and CEMS values in the units of ppmv or the emission standard using Equation 12.

$$d_{avg} = \frac{1}{n}\sum_{i=1}^n d_i \qquad \text{Eq. 12}$$

12.6.8 Calculate the average RM value using Equation 13.

$$RM_{avg} = \frac{1}{n}\sum_{i=1}^n RM_i \qquad \text{Eq. 13}$$

12.6.9 Calculate RA of the CEMS using Equation 14.

$$RA = \left[\left(\left|d_{avg}\right| + CC\right)/RM_{avg}\right] * 100 \qquad \text{Eq. 14}$$

13.0 Method Performance

13.1 Level of Detection. You may not use a CEMS whose LOD or SADL is greater than 20 percent of the applicable regulatory limit or other action level for the intended use of the data.

13.2 Calibration Drift. The zero- and mid-level calibration drift for the CEMS must not exceed 5.0 percent of the span value for 7 consecutive operating days.

13.3 Measurement Error. The ME must be less than or equal to 5.0 percent of the span value at the low-, mid-, and high-level reference gas concentrations.

13.4 Relative Accuracy. Unless otherwise specified in an applicable regulation or permit, the RA of the CEMS, whether calculated in units of HCl concentration or in units of the emission standard, must be less than or equal to 20.0 percent of the RM when RM_{avg} is used in the denominator of Equation 14.

13.4.1 In cases where the RA is calculated on a concentration (ppmv) basis, if the average RM emission level for the test is less than 75 percent of the HCl concentration equivalent to the emission standard, you may substitute the HCl concentration equivalent to the standard in the denominator of Equation 14 in place of RM_{avg}.

13.4.2 Similarly, if the RA is calculated in units of the emission standard and the HCl emission level measured by the RMs is less than 75 percent of the emission standard, you may substitute the emission standard in the denominator of Equation 14 in place of RM_{avg}.

13.4.3 The alternative calculated RA in paragraph 13.4.1 or 13.4.2 must be less than or equal to 15.0 percent.

13.5 Interference Test.

13.5.1 The sum of the interference response(s) from Equation 2 must not be greater than 2.5 percent of the calibration span or ±3.0 percent of the equivalent HCl concentration used for the interference test, whichever is less restrictive. The results are also acceptable if the sum of the interference response(s) does not exceed six times the LOD or 0.5 ppmv for a calibration span of 5 to 10 ppm, or 0.2 ppmv for a calibration span of less than 5 ppmv.

13.6 IP-CEMS Beam Intensity Test. For IP-CEMS, the percent difference between the measured concentration with and without attenuation of the light source must not exceed ±3.0 percent.

13.7 IP-CEMS Temperature Measurement Verification. Your temperature sensor satisfies the accuracy required if the absolute relative difference between measured value of stack temperature (M_t) and the temperature value from the calibrated temperature reference device (V_t) is ≤1.0 percent or if the absolute difference between M_t and V_t is ≤2.8 °C (5.0 °F), whichever is less restrictive.

13.8 IP-CEMS Pressure Sensor Measurement Verification. Your pressure sensor satisfies the accuracy required if the absolute relative difference between the measured value of stack pressure (M_P) and the pressure value from the calibrated pressure reference device (V_P) is ≤5.0 percent or if the absolute difference between M_p and V_P is ≤0.12 kilopascals (0.5 inches of water column), whichever is less restrictive.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Bibliography

1. Method 318—Extractive FTIR Method for the Measurement of Emissions From the Mineral Wool and Wool Fiberglass Industries, 40 CFR, part 63, subpart HHHHHHH, appendix A.

2. “EPA Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions from Stationary Industrial Sources,” February, 1995.

3. “Measurement of Gaseous Organic and Inorganic Emissions by Extractive FTIR Spectroscopy,” EPA Contract No. 68-D2-0165, Work Assignment 3-08.

4. “Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media,” 40 CFR part 63, appendix A.

5. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, U.S. Environmental Protection Agency office of Research and Development, EPA/600/R-12/531, May 2012.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 1—INTERFERENCE TEST GAS CONCENTRATIONS

Potential interferent gas[1]	**Approximate concentration (balance N_2)**
CO_2	15% ±1% CO_2.[2]
CO	100 ±20 ppm.
CH_2O	20 ±5 ppm.
CH_4	100 ±20 ppm.
NH_3	10 ±5 ppm (extractive CEMS only).
NO_2	250 ±50 ppm.
SO_2	200 ±20 ppm.
O_2	3% ±1% O_2.[2]
H_2O	10% ±1% H_2O.[2]
N_2	Balance.[2]

[1] Any of these specific gases can be tested at a lower level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level in CEMS field installations.

[2] Gases for short path IP cell interference tests cannot be added above 100 percent stack equivalent concentration. Add these gases at the indicated percentages to make up the remaining cell volume.

Table 2. Example Interference Test Data Sheet

Date of Test: ____
Analyzer Type: ____
Model No.: ____
Serial No.: ____
Span: ____
Test Organization: _______________________________________
Test Personnel: ____

Interference Gas or Gas Combination	HCl Concentration (ppmv)	HCl Concentration (ppmv) w/Interference	Absolute Difference (ppmv)	Average Absolute Difference (ppmv)
Sum of Interference Responses				
Percent of Baseline Concentration				
Percent of Span				

TABLE 3—DESIGN STANDARDS FOR TEMPERATURE SENSORS

If the sensor is a . . .	**You can use the following design standards as guidance in selecting a sensor for your IP-CEMS**
1. Thermocouple	a. ASTM E235-88 (1996), "Specification for Thermocouples, Sheathed, Type K, for Nuclear or Other High-Reliability Applications."
	b. ASTM E585/E585M-04, "Specification for Compacted Mineral-Insulated, Metal-Sheathed, Base Metal Thermocouple Cable."
	c. ASTM E608/E608M-06, "Specification for Mineral-Insulated, Metal-Sheathed Base Metal Thermocouples."
	d. ASTM E696-07, "Specification for Tungsten-Rhenium Alloy Thermocouple Wire."
	e. ASTM E1129/E1129M-98 (2002), "Standard Specification for Thermocouple Connectors."
	f. ASTM E1159-98 (2003), "Specification for Thermocouple Materials, Platinum-Rhodium Alloys, and Platinum."
	g. ISA-MC96.1-1982, "Temperature Measurement Thermocouples."
2. Resistance temperature detector	ASTM E1137/E1137M-04, "Standard Specification for Industrial Platinum Resistance Thermometers."

TABLE 4—PERFORMANCE SPECIFICATION TEST ZERO AND REFERENCE GAS RANGES

Test	**Units**	**HCl Zero and Reference Gas Concentrations in Terms of Percent of Span**[a]				**Section**
		Zero	**Low Level**	**Mid Level**	**High Level**	
Calibration Drift	% of Span	<LOD	NA	50-60[b]	NA	11.8
Measurement Error	% of Span	NA	20-30	50-60	80-100	11.7

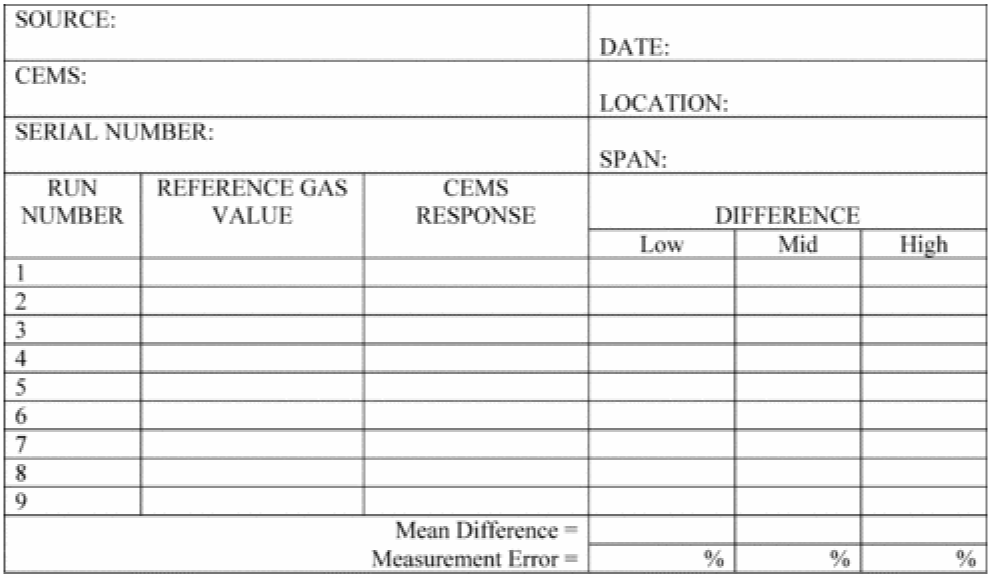
[a] Reference gas concentration must be NIST traceable. (see section 7.1)

[b] Mid-level is required. For DS calibration drift option, choose a concentration that yields a value in this range at the analyzer.

TABLE 5—STUDENT'S T-VALUES

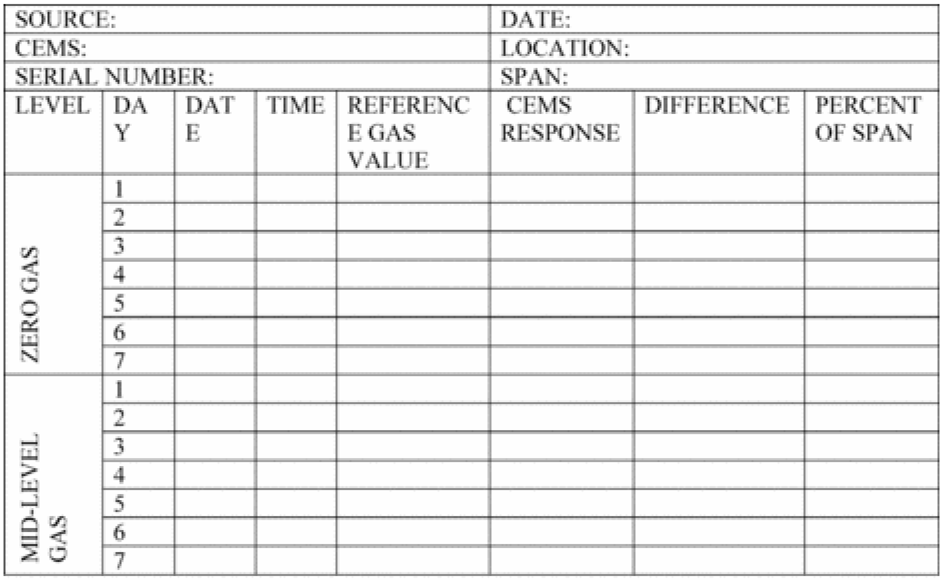
n-1[a]	t-value	n-1[a]	t-value	n-1[a]	t-value
1	12.71	11	2.201	21	2.080
2	4.303	12	2.179	22	2.074
3	3.182	13	2.160	23	2.069
4	2.776	14	2.145	24	2.064
5	2.571	15	2.131	25	2.060
6	2.447	16	2.120	26	2.056
7	2.365	17	2.110	27	2.052
8	2.306	18	2.101	28	2.048
9	2.262	19	2.093	29	2.045
10	2.228	20	2.086	30	2.042

[a] The value n is the number of independent pairs of measurements. Either discrete (independent) measurements in a single run, or run averages can be used.



SOURCE:			DATE:		
CEMS:			LOCATION:		
SERIAL NUMBER:			SPAN:		
RUN NUMBER	REFERENCE GAS VALUE	CEMS RESPONSE	DIFFERENCE		
			Low	Mid	High
1					
2					
3					
4					
5					
6					
7					
8					
9					
		Mean Difference =			
		Measurement Error =	%	%	%

Figure 1. Measurement Error Determination



SOURCE:					DATE:		
CEMS:					LOCATION:		
SERIAL NUMBER:					SPAN:		
LEVEL	DAY	DATE	TIME	REFERENCE GAS VALUE	CEMS RESPONSE	DIFFERENCE	PERCENT OF SPAN
ZERO GAS	1						
	2						
	3						
	4						
	5						
	6						
	7						
MID-LEVEL GAS	1						
	2						
	3						
	4						
	5						
	6						
	7						

Figure 2. Calibration Drift Determination

PS-18 Appendix A Standard Addition Procedures

1.0 Scope and Application

1.1 This appendix to Performance Specification (PS) 18 describes the procedure and performance requirements for standard addition (SA) as a quality check for hydrogen chloride (HCl) continuous emission monitoring systems (CEMS).

1.2 This appendix is applicable to quality checks of both extractive and integrated path (IP) technologies used to measure HCl emissions.

1.3 For extractive CEMS, this procedure must be used, as a level of detection (LOD) verification of all field-installed CEMS. Additionally, it is allowed by Procedure 6 in appendix F to this part as an alternative to upscale calibration drift (CD) tests, cylinder gas audits and relative accuracy audits (RAAs), and may be used for quality assurance purposes under other applicable regulations or permits that require HCl monitoring.

1.4 For IP-CEMS, this procedure must be used as a LOD verification of all field-installed CEMS.

2.0 Summary of the Appendix for Standard Addition

As used here, SA is a gas phase method of standard additions (either static or dynamic) used to verify the accuracy of CEMS measurements in the presence of the sample matrix. For extractive CEMS, it consists of spiking a known quantity of HCl dynamically into the measurement system as an addition to the native HCl and the native source gas matrix. For IP-CEMS, this procedure consists of introducing a known quantity of HCl into the optical path that also includes the native source gas.

3.0 Definitions. (See PS-18 and Procedure 6 of Appendix F to Part 60 for the Definitions Used in This Appendix.)

4.0 Interferences. Interferences are discussed in PS-18, section 4.0

5.0 *Safety.* The procedures required under this appendix may involve hazardous materials, operations and equipment. This procedure may not address all of the safety problems associated with these procedures. You as the facility or operator must establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. As the CEMS user, you should consult instrument operation manuals, material safety data sheets, compressed gas safety requirements, and other Occupational Safety and Health Administration regulations for specific precautions to be taken.

6.0 *Equipment and Supplies.* An example of equipment and supplies is described in section 6 of PS-18.

7.0 *Reagents and Standards.* SA materials must meet the requirements defined for reference gases in section 7 of PS-18 to perform this procedure with the following exception. You may use gases certified by the gas vendor to ±5 percent to perform the daily calibration drift assessment in section 4.1 of Procedure 6 in appendix F of this part.

NOTE: For extractive CEMS the concentrations of reference gases required for SA are likely to be significantly higher than the concentration of reference gases associated with PS-18 requirements.

8.0 *Standard Addition and Dynamic Spiking Procedure.* The standard addition procedure consists of measuring the native source gas concentration, addition of reference gas, and measurement of the resulting SA elevated source gas concentration. For extractive CEMS, HCl is spiked dynamically and thus, one must account for the dilution of sample gas from the addition of the HCl reference gas. For IP-CEMS, standard addition of an HCl reference gas is made by either adding an HCl reference gas to a flow through cell or inserting a sealed reference gas cell into the measurement path of the CEMS. The enclosed cell or a fixed cell must contain an HCl concentration that accounts for the difference in path length of the cell used for SA relative to the measurement path.

8.1 SA Concentration and Measurement Replicates.

8.1.1 You must inject HCl gas to create a measured concentration based on the requirements of the particular performance test (*e.g.,* LOD verification, CD, DSA).

8.1.2 Each dynamic spike (DS) or standard addition (SA) replicate consists of a measurement of the source emissions concentration of HCl (native stack concentration) with and without the addition of HCl. With a single CEMS, you must alternate the measurement of the native and SA-elevated source gas so that each measurement of SA-elevated source gas is immediately preceded and followed by a measurement of native stack gas. Introduce the SA gases in such a manner that the entire CEMS is challenged. Alternatively, you may use an independent continuous HCl monitor to measure the native source concentration before and after each standard addition as described in section 8.1.4.

8.1.3 Unless specified otherwise by an applicable rule, your SA-elevated concentration may not exceed 100 percent of span when the SA and native HCl concentration are combined.

8.1.4 As an alternative to making background measurements pre- and post-SA, you may use an independent continuous HCl monitor as a temporary unit to measure native stack HCl concentration while simultaneously using the CEMS to measure the SA-elevated source concentration. If you use an independent continuous HCl monitor you must make one concurrent background or native HCl measurement using both the installed CEMS and the independent continuous HCl monitor, immediately before the SA procedure in section 8.2 or 8.3 begins, to confirm that the independent monitoring system measures the same background concentration as the CEMS being qualified with this PS.

8.2 SA Procedure for Extractive CEMS (Dynamic Spiking)

8.2.1 Your HCl spike addition must not alter the total volumetric sample system flow rate or basic dilution ratio of your CEMS (if applicable).

8.2.2 Your spike gas flow rate must not contribute more than 10 percent of the total volumetric flow rate through the CEMS.

8.2.3 You must determine a dilution factor (DF) or relative concentration of HCl for each dynamic spike. Calibrated, NIST-traceable flow meters accurate to within 2.0 percent or highly accurate tracer gas measurements are required to make the necessary DF determinations at the accuracy required for this PS. Calibrated, NIST-traceable flow meters (*e.g.,*venturi, orifice) accurate to within 2.0 percent should be recertified against an NIST-traceable flow meter annually. NOTE:Since the spiking mass balance calculation is directly dependent on the accuracy of the DF determination, the accuracy of measurements required to determine the total volumetric gas flow rate, spike gas flow rate, or tracer gas standard addition concentration is critical to your ability to accurately perform the DS procedure and calculate the results.

8.2.4 You must monitor and record the total sampling system flow rate and sample dilution factor (DF) for the spiking and stack gas sampling systems to ensure they are known and do not change during the spiking procedure. Record all data on a data sheet similar to Table A1 in section 13 of this appendix.

8.2.4.1 You may either measure the spike gas flow and the total flow with calibrated flow meters capable of NIST traceable accuracy to ±2.0 percent or calculate the flow using a stable tracer gas included in your spike gas standard.

8.2.4.2 If you use flow measurements to determine the spike dilution, then use Equation A1 in section 11.2.1 of this appendix to calculate the DF. Determination of the spike dilution requires measurement of HCl spike flow (Q_{spike}) and total flow through the CEM sampling system (Q_{probe}).

8.2.4.3 If your CEMS is capable of measuring an independent stable tracer gas, you may use a spike gas that includes the tracer to determine the DF using Equation A2 or A3 (sections 11.2.2 and 11.2.3 of this appendix) depending on whether the tracer gas is also present in the native source emissions.

8.2.4.4 For extractive CEMS, you must correct the background measurements of HCl for the dilution caused by the addition of the spike gas standard. For spiking systems that alternate between addition of HCl and zero gas at a constant DF, the background measurements between spikes will not be equal to the native source concentration.

8.2.5 Begin by collecting unspiked sample measurements of HCl. You must use the average of two unspiked sample measurements as your pre-spike background.

NOTE: Measurements should agree within 5.0 percent or three times the level of detection to avoid biasing the spike results.

8.2.5.1 Introduce the HCl gas spike into the permanent CEMS probe, upstream of the particulate filter or sample conditioning system and as close to the sampling inlet as practical.

8.2.5.2 Maintain the HCl gas spike for at least twice the DS response time of your CEMS or until the consecutive measurements agree within 5.0 percent. Collect two independent measurements of the native plus spiked HCl concentration.

8.2.5.3 Stop the flow of spike gas for at least twice the DS response time of your CEMS or until the consecutive measurements agree within 5.0 percent. Collect two independent measurements of the native HCl concentration.

8.2.6 Repeat the collection of sample measurements in section 8.2.5 until you have data for each spike concentration including a final set of unspiked sample measurements according to section 8.2.5.3.

8.2.7 Verify that the CEMS responded as expected for each spike gas injection, and that the data quality is not impacted by large shifts in the native source concentration. Discard and repeat any spike injections as necessary to generate a complete set of the required replicate spike measurements.

8.2.8 Calculate the standard addition response (SAR) for extractive CEMS, using Equation A4 in section 11.2, of this appendix.

8.2.9 If the DS results do not meet the specifications for the appropriate performance test in PS-18 or Procedure 6 of appendix F of this part, you must take corrective action and repeat the DS procedure.

8.3 SA Procedure for IP-CEMS (Static Spiking).

8.3.1 For IP-CEMS, you must make measurements of native source gas HCl concentration and an HCl standard addition using a calibration cell added to the optical measurement path.

8.3.2 Introduce zero gas into a calibration cell located in the optical measurement path of the instrument. Continue to flush the zero gas into the cell for at least the SA response time of your CEMS or until two consecutive measurements taken are within 5.0 percent, then collect two independent measurements. Alternatively you may measure native concentrations without the calibration cell in the optical path.

8.3.3 Introduce the HCl spike gas into the calibration cell. Continue to flush the spike gas into the cell for at least the SA response time of your CEMS or until two consecutive measurements taken are within 5.0 percent of one another. Then collect two independent measurements of the SA addition to the native concentration. Alternatively you may insert a sealed calibration cell, containing HCl at the appropriate concentration, into the optical path to measure the SA addition to the native concentration.

8.3.4 Repeat the collection of SA-elevated and native HCl measurements in sections 8.3.2 and 8.3.3 until you have data for each SA concentration. Then, make a final native HCl measurement. The measured concentrations must be corrected for calibration cell and stack temperature, pressure and stack measurement path length.

8.3.5 Calculate the standard addition response (SAR) for an IP-CEMS, using Equation A8 in section 11.3 of this appendix.

8.3.6 If the SA results do not meet the specifications for the appropriate performance test in PS-18 or Procedure 6 of appendix F of this part, you must take corrective action and repeat the SA procedure.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 *Calculations and Data Analysis.* Calculate the SA response for each measurement and its associated native HCl measurement(s), using equations in this section. (NOTE: For cases where the emission standard is expressed in units of lb/MMBtu or corrected to a specified O_2 or CO_2 concentration, an absolute accuracy specification based on a span at stack conditions may be calculated using the average concentration and applicable conversion factors. The appropriate procedures for use in cases where a percent removal standard is more restrictive than the emission standard are the same as in 40 CFR part 60, PS-2, sections 12 and 13.)

11.1 Nomenclature.

C_{spike} = Actual HCl reference gas concentration spiked (*e.g.,* bottle or reference gas concentration) ppmv;

$C_{tracer\ spiked}$ = Tracer gas concentration injected with spike gas (“reference concentration”) ppmv;

DF = Spiked gas dilution factor;

DSCD = Calibration drift determined using DS procedure (percent);

DSE = Dynamic spike error (ppmv);

ESA = Effective spike addition (ppmv);

MC_{SA} = Measured SA-elevated source gas concentration (ppmv);

MC_{spiked} = Measured HCl reference gas concentration i (ppmv);

MC_{native} = Average measured concentration of the native HCl (ppmv);

$M_{native\ tracer}$ = Measured tracer gas concentration present in native effluent gas (ppmv);

$M_{spiked\ tracer}$ = Measured diluted tracer gas concentration in a spiked sample (ppmv);

Q_{spike} = Flow rate of the dynamic spike gas (Lpm);

Q_{probe} = Average total stack sample flow through the system (Lpm);

S = Span (ppmv);

SAR = Standard addition response (ppmv)

11.2 Calculating Dynamic Spike Response and Error for Extractive CEMS.

11.2.1 If you determine your spike DF using spike gas and stack sample flow measurements, calculate the DF using equation A1:

$$DF = \frac{Q_{spike}}{Q_{probe}} \qquad \text{Eq. A1}$$

11.2.2 If you determine your spike DF using an independent stable tracer gas that is not present in the native source emissions, calculate the DF for DS using equation A2:

$$DF = \frac{M_{spiked\ tracer}}{C_{tracer\ spiked}} \qquad \text{Eq. A2}$$

11.2.3 If you determine your spike dilution factor using an independent stable tracer that is present in the native source emissions, calculate the dilution factor for dynamic spiking using equation A3:

$$DF = \frac{M_{spiked\ tracer} - M_{native\ tracer}}{C_{tracer\ spiked} - M_{native\ tracer}} \qquad \text{Eq. A3}$$

11.2.4 Calculate the SA response using Equation A4:

$$SAR = MC_{spiked} - (1 - DF) * MC_{native} \qquad \text{Eq. A4}$$

11.2.5 Calculate the DS error using Equation A5.

$$DSE = MC_{spiked} - MC_{native} - DF * (C_{spike} - MC_{native}) \qquad \text{Eq. A5}$$

11.2.6 Calculating CD using DS. When using the DS option for determining mid-level CD, calculate the CD as a percent of span using equation A6:

$$DSCD = \frac{|DSE|}{S} \qquad \text{Eq. A6}$$

11.2.7 The effective spike addition (ESA) is the expected increase in the measured concentration as a result of injecting a spike. Calculate ESA using Equation A7:

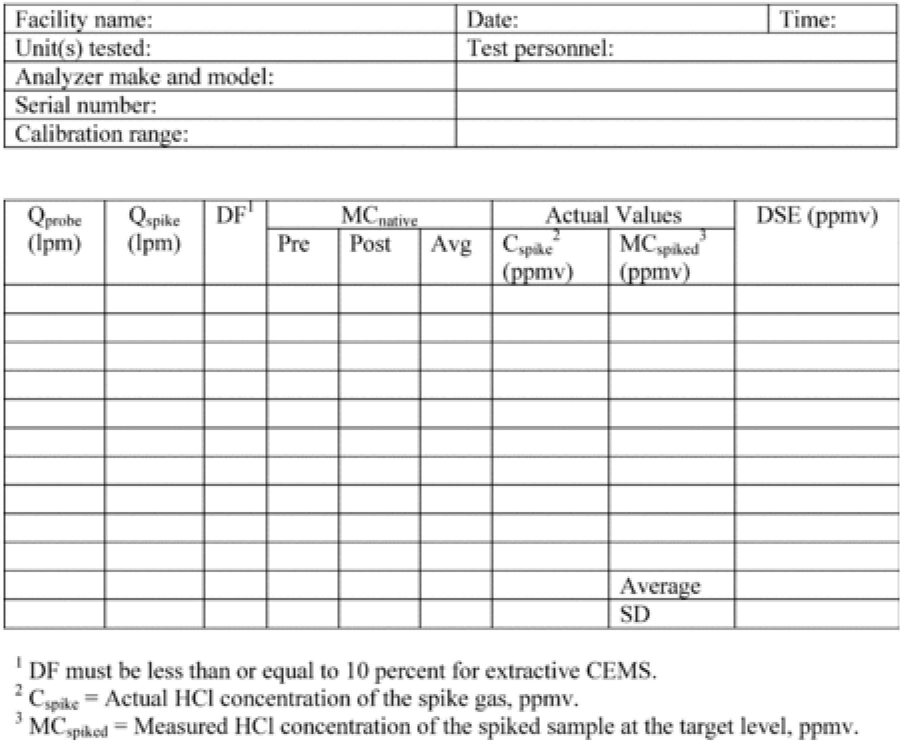
$$ESA = DF * (C_{spike} - MC_{native}) \qquad \text{Eq. A7}$$

11.3 Standard Addition Response for IP-CEMS. If you use an IP-CEMS and a calibration cell, calculate the SA response using Equation A8.

$$SAR = MC_{SA} - MC_{native} \qquad \text{Eq. A8}$$

13. Tables and Figures.

Table A1. Spike Data Sheet



Facility name:	Date:	Time:
Unit(s) tested:	Test personnel:	
Analyzer make and model:		
Serial number:		
Calibration range:		

Q_{probe} (lpm)	Q_{spike} (lpm)	DF[1]	MC_{native}			Actual Values		DSE (ppmv)
			Pre	Post	Avg	C_{spike}[2] (ppmv)	MC_{spiked}[3] (ppmv)	
							Average	
							SD	

[1] DF must be less than or equal to 10 percent for extractive CEMS.
[2] C_{spike} = Actual HCl concentration of the spike gas, ppmv.
[3] MC_{spiked} = Measured HCl concentration of the spiked sample at the target level, ppmv.