PERFORMANCE SPECIFICATION Z: SPECIFICATIONS AND TEST PROCEDURES FOR HCl CONTINUOUS EMISSION MONITORING SYSTEMS AT STATIONARY SOURCES

Revision 2.0
October, 2006

EXECUTIVE SUMMARY

This performance specification describes the criteria that a hydrochloric acid (HCl) continuous emission monitoring system (CEMS) must meet to be considered valid for EPA compliance and/or other regulatory applications. Each HCl CEMS must meet the criteria for accuracy, stability, and instrumental response laid out in this document. In addition, each HCl CEMS must meet the installation requirements in PS-Z.

REVISION HISTORY

1.1 REVISION 1.0

This document was part of the T149 Alternative Monitoring Petition, and was approved by the Office of Air Quality and Standards in January of 2006

1.2 REVISION 2.0

This revision is an update of the original Procedure Z document, October 2006. The following are key updates in revision 2.0:

1. Recommendation that all HCL QA gases be certified with a minimum tolerance of 5%
2. Recommendation that a site specific dynamic spiking protocol be used and, the dynamic spiking protocol would contain the detailed test procedure(s).
3. Discussion for the use of quantitative introduction of the HCL calibration gas and subsequent total flow measurement as method for determining the reference HCL concentration during each test run.
4. Updated the dynamic spiking overview section for easier flow of information
5. Updated the equations to include percent relative standard deviation and the calculation for the reference HCL concentration when using quantitative introduction of the HCL calibration gas with subsequent total flow measurement.

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2.0 USING PERFORMANCE SPECIFICATION Z

2.1 WHAT IS THE PURPOSE AND APPLICABILITY OF PERFORMANCE SPECIFICATION Z?

The purpose of Performance Specification Z (PS-Z) is to establish the initial performance requirements for evaluating the acceptability of a HCl CEMS. Such applications may include, (1) instrument, method or procedure calibration, and (2) evaluation or certification for initial acceptance.

2.1.1 Application

This specification is for evaluating the acceptability of a HCl CEMS at the time of installation and during periodic quality assurance checks. PS-Z applies to you if you will be using a HCl CEMS to demonstrate compliance with a regulatory HCl or HCl/Cl_2 emission standard.

2.1.2 Measurement Capabilities

The HCl CEMS must be capable of measuring HCl concentrations in the units of the applicable standard or in units that can be converted to units of the applicable standard.

2.1.3 Other Monitoring

If your HCl CEMS is capable of reporting the HCl concentration in the units of the existing regulation, no additional monitoring is necessary. If your HCl CEMS does not report concentrations, in the units of the existing standard, then other monitoring (e.g., oxygen, temperature, and pressure) are necessary to convert the units reported by your CEMS to the units of the standard.

2.2 WHAT WILL BE DISCUSSED IN PS-Z?

PS-Z covers two basic topics: (1) the instrument requirements for an HCl CEMS and (2) the requirements that each HCl CEMS must meet during the performance specification test.

2.2.1 Instrument Requirements

The HCl CEMS must be able to accurately report concentrations of HCl in stack effluent. It may do so by extracting a representative sample (path or point sampling may be used if the sample is representative) of stack effluent and analyzing the effluent to provide an output proportional to the HCl concentration. The CEMS operating range (zero to span) should encompass the response of the HCl CEMS for all expected HCl concentrations, including the applicable emission limit. The CEMS must have a system response time that is less than or equal to two minutes. Finally, the instrument or operator must be able to perform daily calibration drift tests, quarterly calibration error tests, and annual accuracy tests.

2.2.2 Performance Specification Test

The purpose of the performance specification test is to establish the accuracy, precision, bias, and system response time of the HCl CEMS. Specifically, the following will be either tested or documented as part of the performance specification test requirements listed in Sections 3.0 and 4.0 of this document: (1) data recorder scale, (2) daily calibration drift, (3) installation and measurement location, (4) calibration drift test, (5) calibration error test, (6) system response time, (7) stratification test, (8) accuracy determination.

2.3 WHAT ARE THE INSTALLATION AND PRE-PERFORMANCE SPECIFICATION TEST REQUIREMENTS?

2.3.1 Installation Requirements

The sampling location of the HCl CEMS should be downstream of all pollution control equipment at a position where the HCl concentration is directly representative or can be corrected so as to be representative of total emissions from the stationary source. It is recommended that the sampling location be at least two equivalent diameters downstream of the nearest control devices, point of pollution generation, bend, or other point at which a change in pollutant concentration or flow disturbance may occur. The sampling location is also recommended to be at least a half equivalent diameter upstream from the exhaust or control device. The equivalent diameter is calculated according 40 CFR Part 60, Appendix A, Method 1, Section 2.1[I].

Either point or path sampling may be used. For point sampling the measurement point should be no less than 1.0 meter from the stack or duct wall or located over the centroidal area of the stack or duct cross section. For a path sampling CEMS the effective measurement path should be (1) totally within the inner area bounded by a line 1.0 meter from the stack or duct wall, or (2) have at least 70 percent of the path within the inner 50 percent of the stack diameter or duct cross section, or (3) be centrally located over any part of the centroidal area.

The sample collection and instrumental analyzer portions of your HCl CEMS may be located any distance from the sampling point provided the transmission efficiency from the sampling point to the sample collection point can be determined and meets the criteria outlined later in this performance specification. It is also recommended that the sampling probe for the HCl CEMS be located at point without stratification (section 3.1.5).

2.3.2 Reference Method Measurement Location

You must select, as appropriate, an accessible reference method (RM) measurement point at least two equivalent diameters downstream from the nearest control device, the point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate may occur, and at least a half equivalent diameter upstream from the effluent exhaust or 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 CEMS and RM locations need not be the same. If dynamic spiking is employed to determine the system accuracy, bias, and precision, the spiking of the calibration gas must encompass the sampling system of the HCL CEMS.

2.3.2.1 Reference Method Traverse Points

Select traverse points that assure acquisition of representative samples over the stack or duct cross-section. The minimum requirements are as follows: Establish a "measurement line" that passes through the centroidal area and in the direction of any expected stratification. If this line interferes with the CEMS measurements, displace the line up to 30 cm (12 in.) (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area. Locate three traverse points at 16.7, 50.0, and 83.3 percent of the measurement line. If the measurement line is longer than 2.4 meters (7.8 ft) and pollutant stratification is not expected, the three traverse points may be located on the line at 0.4, 1.2, and 2.0 meters from the stack or duct wall. This option must not be used after wet scrubbers or at points where two streams with different pollutant concentrations are combined.

Other traverse points may be selected, provided that they can be shown to the satisfaction of the Administrator to provide a representative sample over the stack or duct cross section. 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.

2.4 WHAT SPECIAL DEFINITIONS APPLY TO PS-Z?

Calibration Drift: The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance or adjustment took place.

Calibration Error: The mean difference between the concentration indicated by the CEMS and the known concentration generated by a calibration source at three levels when the entire CEMS, including the sampling interface is challenged. A CE test is performed to document the accuracy and linearity of the CEMS over the entire measurement range.

Centroidal Area: means a concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross-sectional area.

Continuous Emission Monitoring System: means the total equipment required for the determination of a gas concentration or emission rate. The sample interface, pollutant analyzer, diluent analyzer, and data recorder are the major subsystems of the CEMS.

Correlation Coefficient: determines the extent of a linear relationship between two fields over a given period of time.

Data Recorder: The portion of the CEMS that provides a record of analyzer output, flags which indicate normal operation, and flags indicating abnormal operation. The data recorder may record other pertinent data such as effluent flow rates, and various instrument temperatures.

Diluent Analyzer: means that portion of the CEMS that senses the diluent gas (i.e. O_2) and generates an output proportional to the gas concentration.

Dynamic Spiking: a procedure used to document the accuracy, precision, and bias of the monitoring system by quantitatively spiking a certified gas into the pollutant gas stream.

High-level drift: means the absolute difference between a high-level calibration gas and the monitor response, in units of the applicable standard.

Instrument Measurement Range: The range of HCl concentrations the instrument can reliably measure from the lowest concentration to the highest.

Intercept: value of the Y variable when the X variable is equal to zero.

Linear Regression: a methodology used to find a formula that can be used to relate two variables that are linearly related.

Path Sampling CEMS: A CEMS that samples the source effluent along a path greater than 10 percent of the equivalent diameter of the stack or duct cross section.

Point Sampling CEMS: A CEMS that samples the source effluent at a single point.

Pollutant Analyzer: means that portion of the CEMS that senses the pollutant gas and generates an output proportional to the gas concentration.

Relative Accuracy (RA): means the absolute mean difference between the gas concentration or emission rate determined by the CEMS and the value determined by the Reference Method (RM), plus the 2.5 percent error confidence coefficient of a series of tests, divided by the mean of the RM tests or the applicable emission limit.

Response Time: The time interval between the start of a step change in the system input and when the pollutant analyzer output reached 95% of the final value.

Sample Interface: The portion of the CEMS used for one or more of the following: sample acquisition, sample transport, sample conditioning, or protection of the monitor from the effects of stack gas.

Slope: The rate of change of Y relative to the change in X.

Stratification: means the change in effluent concentration in a duct, over time when comparing a reference measurement (centroid of duct) to traversed sampling concentrations.

Zero drift: means the absolute difference between a high-level calibration gas and the monitor response, in units of the applicable standard.

3.0 INTERFERENCES, SAFETY, AND EQUIPMENT REQUIREMENTS

3.1 WHAT DO I NEED TO KNOW TO ENSURE THE SAFETY OF PERSONS USING PS-Z?

People using PS-Z may be exposed to hazardous material, operational hazards, and hazardous site conditions. PS-Z does not address all the safety issues associated with its use. It is your responsibility to ensure the safety of persons using PS-Z. Some helpful references may include the CEMS manual, the CEMS manufacturer, other reference methods, and on-site safety regulations.

3.2 WHAT EQUIPMENT AND SUPPLIES DO I NEED?

3.2.1 Equipment for the CEMS

1. **Sample Extraction System:** This portion of the CEMS must present a sample of source effluent to the sampling module that is directly representative or can be corrected so as to be representative of source. The sample extraction system typically consists of a sample probe and a heated umbilical line.

2. **Pressure Regulation Module:** The pressure regulation module is designed to remove both free particulates and water-soluble aerosols from the gas stream prior to analysis by the sampling module. This module also provides a sample gas to the analyzer at a constant pressure (optional).

3. **Analysis module:** The portion of the CEMS that quantitates stack gas concentrations of HCl.

4. **Diluent Module:** This portion of the CEMS quantifies stack gas concentrations of oxygen or CO_2. For systems with a multi-component analyzer, the same analyzer quantifies the concentration of all measured analytes.

5. **System Controller:** This portion of the CEMS provides control of the analyzer, sample probe, pressure regulation module and the sample interface.

6. **Data recorder**: Your HCl CEMS must be able to record HCl concentrations and instrument status signals (flags).

3.2.2 Equipment Specifications

The CEMS data recorder output range must include zero and a high-level value. The range of the data recorder and the measurement range of the HCl CEMS will be documented. The high-level value is chosen by the source owner or operator and is defined as follows:

For an HCl CEMS installed to measure controlled emissions or emissions that are in compliance with an applicable regulation, the high-level value should be at least 1.5 times the emission standard level and encompass the HCl concentration levels expected by the process.

The CEMS design should also allow the determination of calibration drift at the zero and high-level values. In special cases, the Administrator may approve a single-point calibration-drift determination.

3.3 WHAT REGENTS AND STANDARDS DO I NEED?

3.3.1 Reference Gases, Gas Cells, or Optical Filters

See Table 1 for reference gas concentration ranges.

4.0 PERFORMANCE EVALUATION PROCEDURES AND REPORTING

4.1 WHAT IS THE PURPOSE OF THE PERFORMANCE SPECIFICATION TESTS AND WHAT IS REQUIRED TO PERFORM THE TESTS?

The purpose of the performance specification tests is to determine the accuracy, precision, bias, and system response time of the HCl CEMS.

4.1.1 Pretest Preparation

Prior to the start of your initial performance specification tests, you must be sure that the HCl CEMS is installed according to the specifications laid out in this document. After installing the HCl CEMS, it is recommended you use the CEMS for a period of time to familiarize yourself with its operation. It is also recommend that you conduct daily checks of the zero and high-level drift, conduct a calibration error test, and conduct a calibration drift check to verify that the instrument is functioning properly. When you are confident that the instrument is performing satisfactorily it is time to prepare for the performance specification tests.

4.1.2 Data Recorder Scale Check

The range of the data recorder and the measurement range of the HCl CEMS will be documented. The CEMS operating range (zero to span) and the range of the data recorder should encompass both the response of the HCl CEMS for all expected HCl concentrations and the applicable emission limit.

4.1.3 Calibration Drift Check

The HCL CEMS must perform a calibration check at least once per day. Certified gases must be used to perform the zero and high-level drift checks. All data will be recorded.

4.1.4 Installation and Measurement Location Check

The installation location of the HCL CEMS must adhere to section 1.3.1 of this document. In addition, the location of any reference method testing must adhere to section 1.3.2 of this document.

4.1.5 Stratification Test

The stratification test must be conducted when the facility is operating during normal operation. The purpose of this test is to verify that excess stratification of the target pollutant does not exist at the sampling point of the monitoring system.

To determine whether effluent stratification exists, a dual probe system should be used to determine the average effluent concentration while measurements at each traverse point are being made. One probe, located at the stack or duct centroid, is used as a stationary reference point to indicate change in the effluent concentration over time. The second probe is used for sampling at the traverse points specified in Method 1. The traverse points are sampled for five minutes at each point. You may test for stratification at the HCl CEMS sampling point by using either velocity tests as described in Method 2[ii], HCl concentrations using Methods 26 or 26A, or an acceptable alternative (i.e. CO or Nox) A minimum of 12 sampling points will be used, with 6 sampling points along each of the two traverses.

4.1.6 Seven-day Calibration Drift Test

The seven-day calibration drift test must be conducted when the facility is operating during normal operation. The purpose of this test is to verify that the instrument operation is stable. During the calibration drift test period you must determine the magnitude of the zero calibration drift and the high-level calibration drift at least once each day. During the stability tests no adjustments or calibrations may be made to the CEMS. If periodic automatic or manual adjustments are made to the CEMS zero and high-level calibration settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the CD may also be determined.

The calibration drift will be determined at the zero and high-level value of the HCl CEMS. Introduce to the CEMS the reference gases, gas cells, or optical filters (these need not be certified) for the zero and high level values. Record the CEMS response and subtract this value from the reference value. The calibration gas concentrations are provided in Table 1.

4.1.7 Calibration Error

The HCL CEMS will be challenged three non-consecutive times with zero, mid-level, and high-level certified HCL gases (Table 1). The cylinder gases need not be EPA Protocol 1 gases. The calibration gases will be injected into the sample system as close to the sampling probe outlet as practical and will pass through all CEMS components used during normal monitoring. The difference between the instrument response and the reference value (certified gas) will be calculated after each injection and the resulting three differences will be averaged to determine the CE at each measurement point.

4.1.8 System Response Time

Introduce zero gas into the analyzer. When the system output has stabilized (no change greater than 1 percent of full scale for 30 sec), introduce an upscale calibration gas and wait for a stable value. Record the time (upscale response time) required to reach 95 percent of the final stable value. Next, reintroduce the zero gas and wait for a stable reading before recording the response time (downscale response time). Repeat the entire procedure three times and determine the mean upscale and downscale response times. The slower or longer of the two means is the system response time.

Calibration gas ranges for the response time test are provided in Table 1. If using a multi-component analyzer, the response time can be based on any analyte measured by the CEMS.

4.1.9 CEMS Accuracy

The accuracy of the HCl CEMS shall be determined by performing either a relative accuracy determination or by dynamic spiking.

4.1.9.1 Relative Accuracy (RA)

Conduct the RA test while the affected facility is operating during normal operation, or as specified in an applicable subpart. The RA test may be conducted during the CD test period.

Reference Methods (RM). Unless otherwise specified in an applicable subpart of the regulations, Methods 26 or 26A, or their approved alternatives, are the reference methods for HCl. Other reference methods for moisture, oxygen, etc. may be necessary.

Sampling Strategy for RM Tests. Conduct the RM tests in such a way that they will yield results representative of the emissions from the source and can be correlated to the CEMS data. It is preferable to 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. In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period of each run (including the exact time of day) on the CEMS chart recordings or other permanent record of output. For integrated samples make a sample traverse of at least 21 minutes, sampling for an equal time at each traverse point.

Number of RM Tests. Conduct a minimum of nine sets of all necessary RM test runs.

NOTE: More than nine sets of RM tests may be performed. If this option is chosen, a maximum of three sets of the test results may be rejected so long as the total number of test results used to determine the RA is greater than or equal to nine. However, all data must be reported, including the rejected data.

Correlation of RM and CEMS Data. Correlate the CEMS and the RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration or emission rate for each pollutant RM test period. Consider system response time, if important, and confirm that the pair of results are on a consistent moisture, temperature, and diluent concentration basis. Then, compare each integrated CEMS value against the corresponding average RM value. If the RM has an integrated sampling technique, make a direct comparison of the RM results and CEMS integrated average value.

Calculate the mean difference between the RM and CEMS values in the units of the emission standard, the standard deviation, the confidence coefficient, and the relative accuracy according to the procedures in Section 4.0.

4.1.9.2 Dynamic Spiking

Dynamic spiking can be used in lieu of the Relative Accuracy Determination as an alternative method for documenting the accuracy, precision, and bias of the HCl CEMS. This section provides an overview of a typical dynamic spiking procedure. A site specific dynamic spiking protocol, which provides detailed steps of the actual procedure, is required. Figure 1 provides an overview of a typical dynamic spiking arrangement.

While the HCl CEMS is sampling flue gas, HCl reference gas is introduced into the CEMS sample interface by using a mass flow controller (or equivalent). The target ratio of actual flue gas to the HCl reference gas is 9:1, but must be kept at a minimum ratio of 1:1. The HCl concentration is quantitated by the HCl CEMS.

Certified HCL calibration gas is spiked at a minimum of three levels (low, mid, high) through the HCL CEMS measurement range. For each test level, a minimum of 30, one minute averaged HCL values are collected. The percent relative standard deviation, for each data set, should not exceed 20%. Table 1 provides guidance on the HCL concentrations for the low, mid, and high test runs.

Several methods exist to calculate the dynamically spiked HCL concentration (represents the reference HCL concentration). Two common methods are: (1) Use of an element of opportunity and (2) Quantitative introduction of the HCL calibration gas with total flow measurement. Other methods may be used; however, a site specific protocol should document the procedure(s) used.

An element of opportunity can be used to calculate the dynamically spiked HCl concentration (represents the reference HCl concentration). The element of opportunity can either be be an analyte, which would normally be present in the flue gas at steady concentrations, or total flow through the system. Examples of prospective analytes which could be used as elements of opportunity are O_2, NOx, SO_2, CO_2, or moisture. The analyte(s) is measured using a certified reference CEMS, separate from the HCL CEMS.

Total flow through the system may also be used as an element of opportunity to calculate the dynamically spiked HCL concentration. Examples the total flow measurement are the use of a calibrated laminar flow element, or use of a tracer gas with subsequent downstream measurement (for example: hydrocarbon tracer gas with subsequent calibrated GC measurement downstream).

Regardless of the element of opportunity, It is recommended that the element of opportunity data set, for each test level (low, mid, high) have a relative percent standard deviation less than or equal to 20%.

Quantitatively introducing the HCL calibration gas, and, measuring the total flow is another method for documenting the dilution, and subsequent theoretical value of the HCL concentration spiked for each test run. Use of this method requires documenting the quantitative introduction of HCL gas into the system; such as a method 205 procedure or similar protocol.

It is important to compensate the HCl reference concentration(s) for any background HCL present in the flue gas. The HCl concentration of the flue gas (baseline HCL) shall be determined prior to each spiking trial. The baseline HCl concentration is based upon a series of at least 10, one-minute averaged data points. Baseline data must be collected immediately prior to each test run. The data points must include the HCl concentration, element of opportunity concentration(s) and/or the total flow. A site-specific standard operating procedure for the HCL dynamic spiking is required.

Linear regression is used to establish the accuracy, precision, and bias of the HCl CEMS. The criteria for the HCl dynamic spiking are:

1. The correlation coefficient (r) must be greater than or equal to 0.90
2. The slope must be 1.0, +/- 0.15
3. The Intercept must be equal to or less than 15% of the instrument span

4.2 HOW DO I REPORT THE RESULTS OF THE INITIAL PERFORMANCE SPECIFICATION TEST?

Summarize the results of the calibration drift, calibration error, response time, stratification, and accuracy tests in tabular form. Include all data sheets, calculations, and records of CEMS measurements necessary to substantiate the performance of the CEMS and any other devices or methods (e.g., method 26A). The CEMS measurements shall be reported to the agency in units of ppmv, on a dry basis.

5.0 PERFORMANCE CRITERIA AND CALCULATIONS

5.1 WHAT ARE THE PERFORMANCE CRITERIA FOR MY HCL CEMS?

You must demonstrate that your HCl CEMS has adequate precision, accuracy, system response time and data reporting capabilities to determine if your facility is in compliance with HCl emission standards or operating permit limits as specified in applicable regulations or permits. You will demonstrate this capacity by showing that your HCl CEMS meets the following performance criteria.

5.1.1 Data Recorder Scale

The measurement range of the HCL CEMS, and the data recorder scale, must encompass the expected HCL concentrations as well as the applicable emission limit.

5.1.2 Calibration Drift

The daily zero and high-level calibration drift is 5% of the instrument span. Zero and high-level calibration drifts shall be adjusted, at a minimum, whenever the 24-hour zero drift exceeds the limits of the calibration drift specification. The amount of excess zero and high-level drift measured at the 24-hour interval checks will be recorded. Section 4.2 provides the equations for calculating the zero and high-level calibration drifts.

5.1.3 Installation and Measurement Location

The installation requirements and measurement location of the HCL CEMS will meet the specifications outlined in section 3.1.1 and 3.1.2 of this document.

5.1.4 Stratification Test

The stratification in the stack or duct, at the measurement location, must be less than or equal to a 10 percent between the average concentration in the duct or stack and the concentration at any point more than 1.0 meter form the duct or stack wall. Section 4.2.2 provides the equation for calculating the stratification of the stack or duct.

5.1.5 Seven-day Calibration Drift Test Criteria

The daily zero and high-level drift each must be less than 5% of the instrument span for seven consecutive days. See Section 4.2.2 for the equations used to determine the zero and high-level drift.

5.1.6 Calibration Error Test

The mean difference between the CEMS and the reference values, at all three test levels, must be no greater than 5% of span. See Section 4.2.3 for the equation used to determine the calibration error.

5.1.7 Response Time Test

The CEMS response time shall not exceed 2.0 min to achieve 95 percent of the final stable value. If using a multi-component analyzer, the response time can be based on any analyte measured by the CEMS.

5.1.8 Relative Accuracy

The RA of the CEMS must not be greater than 20% of the mean value of the reference method (RM) test data, or not greater than 10% in terms of the emission standard (ppmv, dry), or have an absolute difference of less than 5 ppmv between the mean reference value and the mean CEMS value. See Section 4.2.5 for the equations used to determine the relative accuracy of your CEMS.

5.1.9 Dynamic Spiking

Dynamically spiking may be used in lieu of a relative accuracy test as a means to document the accuracy, precision, and bias of the HCl CEMS.

The criteria for the HCl dynamic spiking is:

- The correlation coefficient, r, must be greater than or equal to 0.90
- The slope must be 1.0, +/- 0.15
- The Intercept must be equal to or less than 15% of the instrument span.

See Section 4.2.8 for equations to determine the linear correlation coefficient, the slope and the intercept.

At a minimum, the data set must meet the correlation coefficient. If this is not met, the dynamic spiking procedure must be repeated until the correlation coefficient criteria is met. If the HCl CEMS has met the correlation coefficient requirement, but does not meet either the slope, or intercept criteria, a bias exists and a correction factor must be applied to the HCl CEMS for data collection. The equations to determine the corrected value are provided in Section 4.2.8.1. The correction factor must be applied to the HCl CEMS one-minute average data until a new dynamic spiking procedure indicates the specific bias no longer exists, or, a different correction factor (bias) is indicated.

5.2 WHAT CALCULATIONS, EQUATIONS, AND DATA ANALYSES ARE NEEDED?

5.2.1 Daily Upscale and Zero Drift

$$CD = (|R - A| / S) * 100 \qquad \textbf{(Equation 1)}$$

where:

CD = Percent calibration drift (%),

R = Reference value of zero or high level calibration gas introduced into the monitoring system (ppmv),

A = Actual monitor response to calibration gas (ppmv),

S = Span of the instrument (ppmv).

5.2.2 Calibration Error

$$CE = |d_{avg} / S| * 100 \qquad \textbf{(Equation 2)}$$

where:

CE = Percent calibration error (%),

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

S = Span of the monitor (ppmv).

5.2.3 Mean Difference

Calculate the arithmetic mean difference as follows:

$$d_{avg} = \frac{1}{n} \sum d_i \qquad \textbf{(Equation 3)}$$

where :

d_{avg} = Arithmetic mean of differences

n = Number of data sets

di = difference of each data set

And

$$d_i = x_i - y_i$$ **(Equation 4)**

where:

x_i = Value at data set x

yi = Value at data set y

5.2.4 Relative Accuracy

The RA for the monitors will be calculated using the least restrictive of equation 6 or equation 7:

$$RA = (|d_{avg}| + |CC|)$$ **(Equation 5)**

or

$$RA = ((|d_{avg}| + |CC|) / TM_{avg}) * 100$$ **(Equation 6)**

where:

RA = Relative accuracy, either percent or ppmv or % absolute,

d_{avg} = Arithmetic mean of differences between value measured by the installed CEMS and the reference method,

CC = Confidence coefficient,

TM_{avg} = Average value measured by the reference test method monitors.

5.2.5 Confidence Coefficient

The confidence coefficient will be calculated using equation 8:

$$CC = t_{0.975} * (S_d / (n^{½}))$$ **(Equation 7)**

where:

CC = Confidence coefficient,

$t_{0.975}$ = t-value obtained from Table 2.1 in Performance Specification 2, 40 CFR Part 60 Appendix B

5.2.6 Standard Deviation (of Differences)

S_d = Standard deviation of differences measured between the installed CEMS and the reference methods calculated using equation 8:

$$S_d = \left[\frac{\sum_{i=1}^{n} d_i^2 - \left(\frac{\sum_{i=1}^{n} d_i}{n} \right)^2}{n-1} \right]^{1/2}$$ **(Equation 8)**

where: n = Number of values in this data set.

5.2.7 Stratification

The value, at each traverse point, is compared to the average value for all sampling points to determine the percent stratification using the following equation:

$$S = \left| C_i - C_{ave} \right| * 100\%$$ **(Equation 9)**

where:

S = percent stratification

C_i = concentration or velocity at sampling point i

C_{ave} = average concentration or velocity at all sampling points

5.2.8 Baseline data

5.2.8.1 HCL CEMS data

The baseline HCL concentration is measured prior to each dynamic spiking run. For each baseline HCL data set, calculate the average, in ppm, using equation 10.

Calculate the arithmetic mean of a data set as follows:

$$\bar{x} = \frac{1}{n} \sum x_i$$ **(Equation 10)**

where **:**

$\bar{x}$ = Arithmetic mean

n = Number of data points

x_i = Value of each data point

5.2.8.2 Element of Opportunity Data

The element of opportunity data set is acquired prior to each dynamic spiking test run, simultaneous to the baseline HCL concentration data set. For each element of opportunity, calculate the average value using equation 10.

5.2.8.3 Flow via dilution

When using dilution of a measured analyte (such as a hydrocarbon with subsequent GC measurement) as an indicator of total flow, calculate the total flow, in liters per minute using equation 11.

Calculate the total flow as follows:

$$\text{Tflow} = \frac{(Analtye - spike\ )*Tflow}{(Analyte - measured)}$$ **(Equation 11)**

Tflow = Total flow through the system in lpm

Analyte-Spike = Concentration of Spiked Analyte (ppm)

Analyte-measured = Measurement, downstream, of spiked Analyte (ppm)

Calculate the average flow value, for the data set, using equation 10.

5.2.9 Dynamic Spiking Test run data

5.2.9.1 HCL CEMS data

For each dynamic spiking test run, calculate the average and percent relative standard deviation of the data set using equations 10 and 12, respectively.

Calculate the percent standard deviation as follows:

$$PRS_d = \frac{\left[\dfrac{\sum_{i=1}^{n} d_i^2 - \left(\dfrac{\sum_{i=1}^{n} d_i}{n} \right)^2}{n-1} \right]^{1/2}}{\bar{x}} \qquad \textbf{(Equation 12)}$$

Where:

PRS_d = Percent Relative Standard Deviation of the data set

$\bar{x}$ = Arithmetic mean

5.2.9.2 Element of Opportunity data

For each dynamic spiking test run, calculate the average and percent relative standard deviation of the data set using equations 10 and 12, respectively. If using total flow as a means to determine the reference HCL calibration gas concentration, use equation 11 to calculate the total flow prior to determining the average and percent relative standard deviation of the data set.

5.2.10 Reference HCL concentration calculations

5.2.10.1 Element of opportunity to calculate reference HCL concentration

Equation 13 is used to calculate the reference HCL concentration for a given dynamic spiking test run.

HCl $_{\text{ref}}$ = $$1-\frac{Opp-post_{avg}}{Opp-pre_{avg}}*CalGas+BaselineHCl$$ **(Equation 13)**

where:

Opp-post $_{\text{avg}}$ = average reference element of opportunity value during dynamic spiking test run

Opp-pre $_{\text{avg}}$ = average reference element of opportunity value during baseline test run

CalGas = HCl calibration gas concentration

Baseline HCl = CEMS HCl average baseline value

5.2.10.2 Quantitative HCL calibration gas introduction and total flow to calculate reference HCL concentration

When using the quantitative introduction of calibration gas and total system flow to calculation the reference HCL concentration for a given dynamic spiking test run, use equation 14. Equation 11 is used to calculate the total system flow.

HCl $_{\text{ref}}$ = $$\frac{Cflow_{avg}}{Tflow_{avg}}*CalGas+BaselineHCl$$ **(Equation 14)**

Where:

HCl $_{\text{ref}}$ = Reference HCl value for run “X”

Cflow = Average calibration HCL gas flow rate into system (lpm)

Tflow = Average Total System Flow during run (lpm)

CalGas = HCl calibration gas concentration

Baseline HCl = CEMS HCl average baseline value

5.2.11 Linear Regression

Linear regression is used to calculate the accuracy, precision, and bias of the HCL CEMS. For each dynamic spiking test run, plot the HCL CEMS reference value, Xaxis, versus the HCL measured value, Y axis. Determine the correlation coefficient (r), the slope, and the intercept using equations 15-18.

$$\hat{y} = b_o + b_1 x$$ **(Equation 15)**

where:

b_o = The y intercept

b_1 = The slope

The intercept is calculated according to the following equation:

$$b_o = \bar{y} - b_1 \bar{x}$$ **(Equation 16)**

where:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

$$\bar{y} = \frac{1}{n} \sum_{i=1}^{n} y_i$$

The slope of the line is calculated according to equation below:

$$b_1 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{n} (x_i - \bar{x})^2}$$ **(Equation 17)**

The linear correlation coefficient is calculated according to the following equation.

$$r^2 = \frac{\left(\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})\right)^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}$$

(Equation 18)

5.3 CRITERIA FOR ACCEPTANCE

The criteria for the HCl dynamic spiking is:

- The correlation coefficient, r, must be greater than or equal to 0.90
- The slope must be 1.0, +/- 0.15
- The Intercept must be equal to or less than 15% of the instrument span.

At a minimum, the data set must meet the correlation coefficient. If this is not met, the dynamic spiking procedure must be repeated until the correlation coefficient criteria are met. If the HCl CEMS has met the correlation coefficient requirement, but does not meet either the slope, or intercept criteria, a bias exists and a correction factor must be applied to the HCl CEMS for data collection. The equations to determine the corrected value are provided in Section 5.4. The correction factor must be applied to the HCl CEMS one-minute average data until a new dynamic spiking procedure indicates the specific bias no longer exists, or, a different correction factor (bias) is indicated.

5.4 BIAS CORRECTION

If the HCl CEMS fails to meet both the slope and intercept criteria, the following correction factor must be applied to the one-minute average HCl data:

$$C^C = \frac{y_i - b_0}{b_1}$$

(Equation 19)

Where:

C^C = corrected CEMS HCL concentration

y_i = CEMS reported HCL concentration

b_0 = the intercept of the least squares linear regression line

b_1 = the slope of the least squares linear regression line

b). If the HCl CEMS fails to meet the slope criteria, but meets the intercept criteria, the following correction factor must be applied to the one-minute average HCl data:

$$C^C = \frac{y_i}{b_1} \qquad \textbf{(Equation 20)}$$

c). If the HCl CEMS fails to meet the intercept criteria, but meets the slope criteria, the following correction factor must be applied to the one-minute average HCl data:

$$C^C = y_i - b_0 \qquad \textbf{(Equation 21)}$$

6.0 OTHER REQUIREMENTS AND INFORMATION

6.1 WHAT QUALITY CONTROL MEASURES ARE REQUIRED?

Ongoing quality control will include daily calibration drift tests, quarterly calibration error audits (absolute calibration audit), and annual accuracy test audits. Specific procedures and performance criteria are included in Procedure DD: Quality Control and Quality Assurance Requirements for Hydrochloric Acid Continuous Emission Monitoring Systems at Stationary Sources.

6.2 WHAT CALIBRATION AND STANDARDIZATION PROCEDURES MUST I PERFORM?

Refer to your CEMS owner’s manual and manufacturer to determine what calibration and standardization procedures are required for your HCl CEMS.

6.3 WHAT POLLUTION PREVENTION PROCEDURES MUST I FOLLOW? [RESERVED]

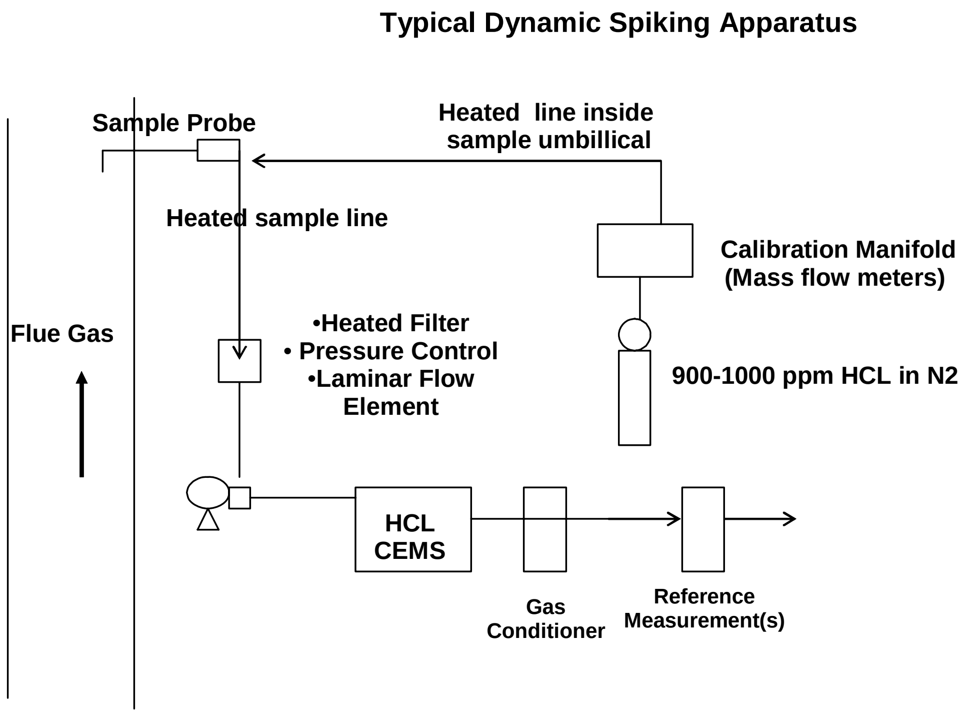
Table 1. Performance Specification Test Calibration Gas Ranges

		HCl Calibration Gas Concentrations [a]		
Test	**Units**	**Zero**	**Mid-Level**	**High-Level**
Calibration Drift and Response Time Test [b]	% of Span	0-30	NA	50-100
Calibration Error Test	% of Span	0-30	30-50	50-100
Dynamic Spiking	% of Span	0-50	25-75	50-100

[a] A copy of the supplier's certificate of analysis must be provided for each gas cylinder. Calibration gases do not need to be Protocol 1 gases. It is recommended that the calibration gases, for all QA, have a minimum tolerance of 5%.

[b] If conducting the response time using a multi-component analyzer, the response time test can be based on any measured analyte.

Figure 1. Typical Dynamic Spiking Apparatus



7.0 RELEVANT REFERENCES

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