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**PROCEDURE DD: QUALITY CONTROL AND  
QUALITY ASSURANCE REQUIREMENTS FOR  
HYDROCHLORIC ACID CONTINUOUS EMISSION  
MONITORING SYSTEMS AT STATIONARY  
SOURCES**

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## **EXECUTIVE SUMMARY**

Procedure DD outlines the continuing quality control and quality assurance requirements for a hydrochloric acid (HCl) continuous emission monitoring system (CEMS). Procedure DD provides the procedures and performance criteria for daily checks of the high-level and zero-level drift. This procedure also provides the procedures and performance criteria for quarterly absolute calibration audits as well as annual accuracy audits.

## REVISION HISTORY

### 1.1 REVISION 1.0

This revision 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 DD 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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Table 1. Ongoing Quality Assurance/Quality Control Calibration Gas Ranges

Figure 1. Dynamic Spiking Overview

## 2.0 USING PROCEDURE DD

### 2.1 WHAT IS THE PURPOSE AND APPLICABILITY OF PROCEDURE DD?

The purpose of Procedure DD is to establish the minimum requirements for quality control (QC) and quality assurance (QA) procedures for the HCl CEMS. These quality control and quality assurance procedures are in place to ensure the accuracy and validity of the data reported by the HCl CEMS for emission compliance purposes. Any HCl CEMS used for reporting purposes to the Environmental Protection Agency (EPA), state, or local environmental agencies must comply with Procedure DD immediately after the completion of the performance specification test outlined in Performance Specification Z<sup>1</sup>.

### 2.2 WHAT ARE THE BASIC REQUIREMENTS OF PROCEDURE DD?

Procedure DD includes procedures and performance criteria for conducting daily calibration drift tests,, quarterly absolute calibration audits, and annual accuracy determinations. Procedure DD also covers the requirements and timelines associated with periods when the HCl is out of control.

### 2.3 WHAT SPECIAL DEFINITIONS APPLY TO PROCEDURE DD?

**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<sub>2</sub>) 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-level.

**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.

**Zero-level-level 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 PROCEDURE DD?

People using Procedure DD may be exposed to hazardous material, operational hazards, and hazardous site conditions. Procedure DD does not address all the safety issues associated with its use. It is your responsibility to ensure the safety of persons using Procedure DD. 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. **Analyzer 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<sub>2</sub>. 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).

#### 3.3 WHAT REAGENTS AND STANDARDS DO I NEED?



### **3.3.1 Reference Gases, Gas Cells, or Optical Filters**

See Table 1 for calibration gas concentration ranges.

## **4.0 QUALITY CONTROL, CALIBRATION AND STANDARDIZATION**

### **4.1 WHAT QUALITY CONTROL MEASURES ARE REQUIRED BY PROCEDURE DD?**

You must develop and implement a quality control program that, at a minimum includes detailed written procedures for all of the following activities.

1. Procedures for performing drift checks on a daily basis, including but not limited to, zero-level drift, high-level drift, and sample volume measurement drift (when applicable).
2. Procedures and methods of adjusting the HCl CEMS in response to the results of the drift checks.
3. Preventative maintenance of the HCl CEMS.
4. Data recording, calculations, and reporting.
5. Procedures for required audits, including absolute calibration audits and accuracy audits.
6. Procedures for adjusting your CEMS based on audit results.
7. A program of corrective action and stack operation procedures in case of a CEMS malfunction and an out of control period.

You are required to keep written documentation of your QA/QC procedures on record and available for inspection for the life of the CEMS or until you are no longer subject to the requirements of this procedure. If you fail two consecutive audits you must revise your QA/QC procedures.

### **4.2 WHAT CALIBRATION CHECKS AND AUDIT PROCEDURES MUST I PERFORM FOR MY HCL CEMS?**

Ongoing quality control will include daily calibration drift tests, quarterly absolute calibration audits, and annual accuracy test audits, which are discussed below:

#### **4.2.1 Daily Calibration Drift Checks**

The zero-level and high-level drift shall be checked once daily. The calibration gas concentration (certified gas) ranges are provided in Table 1. To determine the zero-level drift or calibration drift, introduce to the CEMS the reference gases, gas cells, or optical filters (these need not be certified) for the zero-level and high-level values. Record the CEMS response and subtract this value from the reference value. The calibration drift shall not exceed 5% of the instrument span. Zero-level and high-level calibration drifts shall be adjusted, at a minimum, whenever the 24-hour zero-level drift exceeds the limits of the calibration

drift specification. The amount of excess zero-level and high-level drift measured at the 24-hour interval checks will be recorded.

#### **4.2.2 Quarterly Absolute Calibration Audit (Calibration Error Test)**

The quarterly Absolute Calibration Audit will follow the Calibration Error procedure outlined in Performance Specification Z. The HCl CEMS shall be challenged three non-consecutive times with zero-level, mid-level, and high-level certified gases. The cylinder gases will be certified gases (EPA Protocol 1 gases are not available for HCl). The calibration gases will be injected into the sample system as close to the sampling probe as practical and will pass through all CEMS components used during normal monitoring. The absolute 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 calibration error at each measurement point. The calibration error for each of the three levels will not exceed 5% of span.

An absolute calibration audit will be performed quarterly, except during the quarter the annual accuracy is performed.

#### **4.2.3 Annual Accuracy Test Audit**

The annual accuracy audit of the HCl CEMS will consist of a calibration drift test (seven day drift) and an accuracy determination by performing either a relative accuracy determination, or by dynamic spiking.

##### **4.2.3.1 Seven-Day Drift Test (seven day drift)**

Prior to the start of the accuracy test (either the Relative Accuracy or Dynamic Spiking) you must perform a calibration drift test for a period of seven consecutive days. The seven-day calibration drift test must be conducted when the facility is under normal operations. During the calibration drift test period you must determine the magnitude of the zero-level 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-level and calibration settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the CD can be determined. The zero-level and high-level drift each must be less than 5% of the instrument span for each of seven consecutive days.

##### **4.2.3.2 Relative Accuracy Determination**

The relative accuracy determination will be conducted while the affected facility is operating during normal operation, or as specified in an applicable subpart.

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 calculations in Section 4.0. 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.

#### **4.2.3.3 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 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<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, CO<sub>2</sub>, 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 similiar protocol.

It is important to compensate the HCl reference concentration 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,  $\pm 0.15$
3. The Intercept must be equal to or less than 15% of the instrument span

## 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 stability, precision, accuracy, 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 Daily Calibration Check Criteria

The daily zero-level drift or calibration drift each shall not exceed 5% of span. The calculations are provided in Section 4.2.2.

#### 5.1.2 Quarterly Absolute Audit

The absolute mean difference between the CEMS and the reference values, at all three test points, must be no greater than 5% of span. The calculations are provided in Section 4.2.3.

#### 5.1.3 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. The calculations are provided in Sections 4.2.5 - 4.2.7.

#### 5.1.4 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 (1) The correlation coefficient,  $r$ , must be greater than or equal to 0.90 (2) The slope must be 1.0,  $\pm 0.15$  (3) The Intercept must be equal to or less than 15% of the instrument span.

The calculations are provided in Section 4.2.8.

##### 5.1.4.1 Out of Control

The HCl CEMS will be considered out of control if the zero-level (low-level) or high level calibration drift exceeds two times the applicable calibration drift specification (i.e. the calibration drift is greater than  $\pm 10$

% of span.) In addition, the HCI CEMS will also be considered out of control if the CEMS fails the quarterly absolute calibration audit or the annual accuracy test audit.

When the CEMS is out of control, the owner or operator shall take the necessary corrective action and shall repeat all necessary tests, which indicate that the system is out of control. The owner or operator shall take corrective action and conduct retesting until the performance requirements are below the applicable criteria.

The out of control period begins immediately after the failed drift test or audit. The out of control period ends immediately following the successful completion of required procedures associated with the failure of the audit test. During the out of control period you may not use the data generated by the HCI CEMS for compliance purposes.

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

### 5.2.1 Daily Upscale and Zero Drift

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

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

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

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:

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

where :

$d_{avg}$  = Arithmetic mean of differences

$n$  = Number of data sets

$d_i$  = difference of each data set

And

$$d_i = x_i - y_i \quad \text{(Equation 4)}$$

where:

$x_i$  = Value at data set x

$y_i$  = 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:

$$RA = (|d_{avg}| + |CC|) \quad \text{(Equation 5)}$$

or

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

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<sub>avg</sub> = Average value measured by the reference test method monitors.

### 5.2.5 Confidence Coefficient

The confidence coefficient will be calculated using equation 8:

$$CC = t_{0.975} * (S_d / (n^{1/2})) \quad \text{(Equation 7)}$$

where:

CC = Confidence coefficient,

t<sub>0.975</sub> = 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<sub>d</sub> = Standard deviation of differences measured between the installed CEMS and the reference methods calculated using equation 8:

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

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:

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

where:

S = percent stratification

C<sub>i</sub> = 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:

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

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:

$$T_{flow} = \frac{(Analyte - spike) * T_{flow}}{(Analyte - measured)} \quad \text{(Equation 11)}$$

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:

$$PRSD = \frac{\left[ \frac{\sum_{i=1}^n d_i^2 - \left( \frac{\sum_{i=1}^n d_i}{n} \right)^2}{n - 1} \right]^{1/2}}{\bar{x}} \quad \text{(Equation 12)}$$

Where:

$PRSD$  = 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.

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

where:

Opp-post<sub>avg</sub> = average reference element of opportunity value during dynamic spiking test run

Opp-pre<sub>avg</sub> = 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 calculate the reference HCL concentration for a given dynamic spiking test run, use equation 14. Equation 11 is used to calculate the total system flow.

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

Where:

$HCl_{ref}$  = 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, X axis, versus the HCL measured value, Y axis. Determine the correlation coefficient (r), the slope, and the intercept using equations 15-18.

$$\hat{y} = b_o + b_1x \quad \text{(Equation 15)}$$

where:

$b_o$  = The y intercept

$b_1$  = The slope

The intercept is calculated according to the following equation:

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

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:

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

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

$$r^2 = \frac{\left( \sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y}) \right)^2}{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2} \quad \text{(Equation 18)}$$

### 5.3 CRITERIA FOR ACCEPTANCE

The criteria for the HCI 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 HCI 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 HCI 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 HCI 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:

$$C^C = \frac{y_i - b_0}{b_1} \quad \text{(Equation 19)}$$

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:

$$C^C = \frac{y_i}{b_1} \quad \text{(Equation 20)}$$

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:

$$C^C = y_i - b_0 \quad \text{(Equation 21)}$$





## **6.0 OTHER REQUIREMENTS AND INFORMATION**

### **6.1 DATA RECORDING AND REPORTING**

In general, all data and records associated with the HCl CEMS must be retained for 5 years. At a minimum, at least 2 years of data and records must be readily available at the site. The balance of the records may be retained offsite.

HCl CEMS calibration drift tests and audit results shall be reported at intervals specified in the applicable regulation.

### **6.2 WHAT POLLUTION PREVENTION PROCEDURES MUST I FOLLOW? [RESERVED]**

### **6.3 WHAT REFERENCE TABLES AND FIGURES ARE RELEVANT TO PROCEDURE DD?**

Table 1. Ongoing Quality Assurance/Quality Control Calibration Gas Ranges

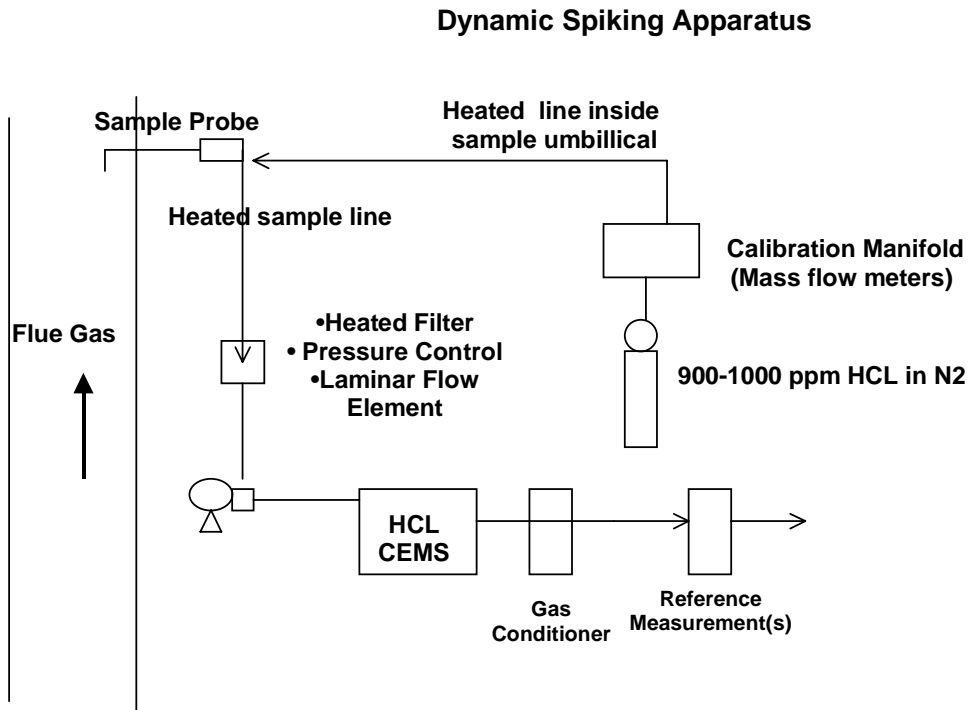
Figure 1. Dynamic Spiking Overview

**Table 1. Ongoing Quality Assurance/Quality Control Calibration Gas Ranges**

|                            |              | <b>HCl Calibration Gas Concentrations <sup>a</sup></b> |                  |                   |
|----------------------------|--------------|--------------------------------------------------------|------------------|-------------------|
| <b>Test</b>                | <b>Units</b> | <b>Zero-level</b>                                      | <b>Mid-Level</b> | <b>High-Level</b> |
| Daily Calibration Drift    | % of Span    | 0-30                                                   | NA               | 50-100            |
| Absolute Calibration Audit | % of Span    | 0-29                                                   | 30-49            | 50-100            |
| Dynamic Spiking            | % of Span    | 0-50                                                   | 25-75            | 50-100            |

<sup>a</sup>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%.

Figure 1. Typical Dynamic Spiking Apparatus



## 7.0 RELEVANT REFERENCES

- I. Performance Specification Z: Specifications and Test Procedures for Hydrochloric Acid Continuous Emission Monitoring Systems at Stationary Sources. 2005.
- II. Dynamic Spiking Protocol: Test procedure for dynamic spiking of the Eli Lilly Ecochem HCL CEMS, 2006.