

**(PROPOSED) TEST METHOD 322 - MEASUREMENT OF HYDROGEN CHLORIDE EMISSIONS FROM PORTLAND CEMENT KILNS BY GFCIR**

1.0 Applicability and Principle

1.1 Applicability. This method is applicable to the determination of hydrogen chloride (HCl) concentrations in emissions from portland cement kilns. This is an instrumental method for the measurement of HCl using an extractive sampling system and an infrared (IR) gas-filter correlation (GFC) analyzer. This method is intended to provide the cement industry with a direct interface instrumental method. A procedure for analyte spiking is included for quality assurance. This method is considered to be self-validating provided that the requirements in section 9 of this method are followed.

1.2 Principle. A gas sample is continuously extracted from a stack or duct over the test period using either a source-level hot/wet extractive subsystem or a dilution extractive subsystem. A nondispersive infrared gas filter correlation (NDIR-GFC) analyzer is specified for the measurement of HCl in the sample. The total measurement system is comprised of the extractive subsystem, the analyzer, and the data acquisition subsystem. Test system performance specifications are included in this method to provide for the collection of accurate, reproducible data.

1.3 Test System Operating Range. The measurement range (span) of the test system shall include the anticipated HCl concentrations of the effluent and spiked samples. The range should be selected so that the average of the effluent measurements is between 25 and 75 percent of span. If at any time during a test run, the effluent concentration exceeds the span value of the test system, the run shall be considered invalid.

2.0 Summary of Method

2.1 Sampling and Analysis. Kiln gas is continuously extracted from the stack or duct using either a source level, hot/wet extractive system, or an in-situ dilution probe or heated out-of-stack dilution system. The sample is then directed by a heated sample line maintained above 350°F to a GFC analyzer having a range appropriate to the type of sampling system. The gas filter correlation analyzer incorporates a gas cell filled with HCl. This gas cell is periodically moved into the path of an infrared measurement beam of the instrument to filter out essentially all of the HCl absorption wavelengths. Spectral filtering provides a reference from which the HCl concentration of the sample can be determined. Interferences are minimized in the analyzer by choosing a spectral band over which compounds such as CO<sub>2</sub> and H<sub>2</sub>O either do not absorb significantly or do not match the spectral pattern of the HCl infrared absorption.

2.2 Operator Requirements. The analyst must be familiar with the specifications and test procedures of this method and follow them in order to obtain reproducible and accurate data.

### 3.0 Definitions

3.1 Measurement System. The total equipment required for the determination of gas concentration. The measurement system consists of the following major subsystems:

3.1.1 Sample Interface. That portion of a system used for one or more of the following: sample acquisition, sample transport, sample conditioning, or protection of the analyzers from the effects of the stack gas.

3.1.2 Gas Analyzer. That portion of the system that senses the gas to be measured and generates an output proportional to its concentration.

3.1.3 Data Recorder. A strip chart recorder, analog computer, or digital recorder for recording measurement data from the analyzer output.

3.2 Span. The upper limit of the gas concentration measurement range displayed on the data recorder.

3.3 Calibration Gas. A known concentration of a gas in an appropriate diluent gas (i.e.,  $N_2$ ).

3.4 Analyzer Calibration Error. The difference between the gas concentration exhibited by the gas analyzer and the known concentration of the calibration gas when the calibration gas is introduced directly to the analyzer.

3.5 Sampling System Bias. The sampling system bias is the difference between the gas concentrations exhibited by the measurement system when a known concentration gas is introduced at the outlet of the sampling probe and the known value of the calibration gas.

3.6 Response Time. The amount of time required for the measurement system to display 95 percent of a step change in gas concentration on the data recorder.

3.7 Calibration Curve. A graph or other systematic method of establishing the relationship between the analyzer response and the actual gas concentration introduced to the analyzer.

3.8 Linearity. The linear response of the analyzer or test system to known calibration inputs covering the concentration range of the system.

3.9 Interference Rejection. The ability of the system to reject the effect of interferences in the analytical measurement processes of the test system.

### 4.0 Interferences

4.1 Sampling System Interferences. An important consideration in measuring HCl using an extractive measurement system is to ensure that a representative kiln gas sample is delivered to the gas analyzer. A sampling system interferant is a factor that inhibits an analyte from reaching the analytical instrumentation. Condensed water vapor is a strong sampling system interferant for HCl and other water soluble compounds.

"Cold spots" in the sampling system can allow water vapor in the sample to condense resulting in removal of HCl from the sample stream. The extent of HCl sampling system bias depends on concentrations of potential interferants, moisture content of the gas stream, temperature of the gas stream, temperature of sampling system components, sample flow rate, and reactivity of HCl with other species in the gas stream. For measuring HCl in a wet gas stream, the temperatures of the gas stream and sampling system components and the sample flow rate are of primary importance. In order to prevent problems with condensation in the sampling system, these parameters must be closely monitored.

4.1.1 System Calibration Checks. Performing these calibration checks where HCl calibration gas is injected through the entire system both before and after each test run demonstrates the integrity of the sampling system and capability of the analyzer for measuring this water soluble and otherwise unstable compound under ideal conditions (i.e., HCl in N<sub>2</sub>).

4.1.2 Analyte Spiking Checks. For analyte spiking checks, HCl calibration gas is quantitatively added to the sample stream at a point upstream of the particulate filter and all other sample handling components both before and after each test run. The volume of HCl spike gas should not exceed 10 percent of the total sample volume so that the sample matrix is relatively unaffected. Successfully performing these checks demonstrates the integrity of the sampling system for measuring this water soluble and reactive compound under actual sample matrix conditions. Successfully performing these checks also demonstrates the adequacy of the interference rejection capability of the analyzer. (See section 9.3 of this method.)

4.2 Analytical Interferences. Analytical interferences are reduced by the GFC spectroscopic technique required by the method. The accuracy of HCl measurements provided by some GFC analyzers is known to be sensitive to the moisture content of the sample. This must be taken into account in order to acquire accurate results. These analyzers must be calibrated for the specific moisture content of the samples.

## 5.0 Safety

This method may involve sampling at locations having high positive or negative pressures, or high concentrations of hazardous or toxic pollutants, and cannot address all safety problems encountered under these diverse sampling conditions. It is the responsibility of the tester(s) to ensure proper safety and health practices, and to determine the applicability of regulatory limitations before performing this test method. Because HCl is a respiratory irritant, it is advisable to limit exposure to this compound.

## 6.0 Equipment and Supplies

Note: Mention of company or product names does not constitute endorsement by the U. S. Environmental Protection Agency.

6.1 Measurement System. Use any GFC measurement system for HCl that meets the specifications of this method. All sampling system components must be maintained above the kiln gas temperature, when possible, or at least 350°F. The length of sample transport line should be minimized and sampling rate should be as high as possible to minimize adsorption of HCl. The essential components of the measurement system are described in sections 6.1.1 through 6.1.12.

6.1.1 Sample Probe. Glass, stainless steel, Hastalloy™, or equivalent, of sufficient length to traverse the sample points. The sampling probe shall be heated to a minimum of 350°F to prevent condensation. Dilution extractive systems must use a dilution ratio such that the average diluted concentrations are between 25 to 75 percent of the selected measurement range of the analyzer.

6.1.2 Calibration Valve Assembly. Use a heated, three-way valve assembly, or equivalent, for selecting either sample gas or introducing calibration gases to the measurement system or introducing analyte spikes into the measurement system at the outlet of the sampling probe before the primary particulate filter.

6.1.3 Particulate Filter. A coarse filter or other device may be placed at the inlet of the probe for removal of large particulate (10 microns or greater). A heated (Balston® or equivalent) filter rated at 1 micron is necessary for primary particulate removal, and shall be placed immediately after the heated probe. The filter/filter holder shall be maintained at 350°F or a higher temperature. Additional filters at the inlet of the gas analyzer may be used to prevent accumulation of particulate material in the measurement system and extend the useful life of components. All filters shall be fabricated of materials that are nonreactive with HCl. Some types of glass filters are known to react with HCl.

6.1.4 Sample Transport Lines. Stainless steel or polytetrafluoroethylene (PTFE) tubing shall be heated to a minimum temperature of 350°F (sufficient to prevent condensation and to prevent HCl and NH<sub>3</sub> from combining into ammonium chloride in the sampling system) to transport the sample gas to the gas analyzer.

6.1.5 Sample Pump. Use a leak-free pump to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump components that contact the sample must be heated to a temperature greater than 350°F and must be constructed of a material that is nonreactive to HCl.

6.1.6 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, must be used to maintain a constant sampling rate within ±10 percent. These components must be heated to a temperature greater than 350°F. (Note: The tester may elect to install a back-pressure regulator to maintain

the sample gas manifold at a constant pressure in order to protect the analyzer(s) from over-pressurization, and to minimize the need for flow rate adjustments.)

6.1.7 Sample Gas Manifold. A sample gas manifold, heated to a minimum of 350°F, is used to divert a portion of the sample gas stream to the analyzer and the remainder to the by-pass discharge vent. The sample gas manifold should also include provisions for introducing calibration gases directly to the analyzer. The manifold must be constructed of material that is nonreactive to the gas being sampled.

6.1.8 Gas Analyzer. Use a nondispersive infrared analyzer utilizing the gas filter correlation technique to determine HCl concentrations. The analyzer shall meet the applicable performance specifications of section 8.0 of this method. (Note: Housing the analyzer in a clean, thermally-stable, vibration free environment will minimize drift in the analyzer calibration.) The analyzer (system) shall be designed so that the response of a known calibration input shall not deviate by more than ±3 percent from the expected value. The analyzer or measurement system manufacturer may provide documentation that the instrument meets this design requirement. Alternatively, a known concentration gas standard and calibration dilution system meeting the requirements of Method 205 of appendix M to part 51 of this chapter, "Verification of Gas Dilution Systems for Field Calibrations" (or equivalent procedure), may be used to develop a multi-point calibration curve over the measurement range of the analyzer.

6.1.9 Gas Regulators. Single stage regulator with cross purge assembly that is used to purge the CGA fitting and regulator before and after use. (This purge is necessary to clear the calibration gas delivery system of ambient water vapor after the initial connection is made, or after cylinder changeover, and will extend the life of the regulator.) Wetted parts are 316 stainless steel to handle corrosive gases.

6.1.10 Data Recorder. A strip chart recorder, analog computer, or digital recorder, for recording measurement data. The data recorder resolution (i.e., readability) shall be 0.5 percent of span. Alternatively, a digital or analog meter having a resolution of 0.5 percent of span may be used to obtain the analyzer responses and the readings may be recorded manually. If this alternative is used, the readings shall be obtained at equally-spaced intervals over the duration of the sampling run. For sampling run durations of less than 1 hour, measurements at 1-minute intervals or a minimum of 30 measurements, whichever is less restrictive, shall be obtained. For sampling run durations greater than 1 hour, measurements at 2-minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be obtained.

6.1.11 Mass Flow Meters/Controllers. A mass flow meter having the appropriate calibrated range and a stated accuracy of

±2 percent of the measurement range is used to measure the HCl spike flow rate. This device must be calibrated with the major component of the calibration spike gas (e.g., nitrogen) using an NIST traceable bubble meter or equivalent. When spiking HCl, the mass flow meter/controller should be thoroughly purged before and after introduction of the gas to prevent corrosion of the interior parts.

6.1.12 System Flow Measurement. A measurement device or procedure to determine the total flow rate of sample gas within the measurement system. A rotameter, or mass flow meter calibrated relative to a laboratory standard to within ±2 percent of the measurement value at the actual operating temperature, moisture content, and sample composition (molecular weight) is acceptable. A system which ensures that the total sample flow rate is constant within ±2 percent and which relies on an intermittent measurement of the actual flow rate (e.g., calibrated gas meter) is also acceptable.

6.2 HCl Calibration Gases. The calibration gases for the gas analyzer shall be HCl in N<sub>2</sub>. Use at least three calibration gases as specified below:

6.2.1 High-Range Gas. Concentration equivalent to 80 to 100 percent of the span.

6.2.2 Mid-Range Gas. Concentration equivalent to 40 to 60 percent of the span.

6.2.3 Zero Gas. Concentration of less than 0.25 percent of the span. Purified ambient air may be used for the zero gas by passing air through a charcoal filter or through one or more impingers containing a solution of 3 percent H<sub>2</sub>O<sub>2</sub>.

6.2.4 Spike Gas. A calibration gas of known concentration (typically 100 to 200 ppm) used for analyte spikes in accordance with the requirements of section 9.3 of this method.

## 7.0 Reagents and Standards

7.1 Hydrogen Chloride. Hydrogen Chloride is a reactive gas and is available in steel cylinders from various commercial gas vendors. The stability is such that it is not possible to purchase a cylinder mixture whose HCl concentration can be certified at better than ±5 percent. The stability of the cylinder may be monitored over time by periodically analyzing cylinder samples. The cylinder gas concentration must be verified within 1 month prior to the use of the calibration gas. Due to the relatively high uncertainty of HCl calibration gas values, difficulties may develop in meeting the performance specifications if the mid-range and high-range calibration gases are not consistent with each other. Where problems are encountered, the consistency of the test gas standards may be determined: (1) by comparing analyzer responses for the test gases with the responses to additional certified calibration gas standards, (2) by reanalysis of the calibration gases in accordance with sections 7.2.1 or 7.2.2 of this method, or (3) by other procedures subject to the approval of EPA.

7.2 Calibration Gas Concentration Verification. There are two alternatives for establishing the concentrations of calibration gases. Alternative No. 1 is preferred.

7.2.1 Alternative No. 1. The value of the calibration gases may be obtained from the vendor's certified analysis within 1 month prior to the test. Obtain a certification from the gas manufacturer that identifies the analytical procedures and date of certification.

7.2.2 Alternative No. 2. Perform triplicate analyses of the gases using Method 26 of appendix A to part 60 of this chapter. Obtain gas mixtures with a manufacturer's tolerance not to exceed  $\pm 5$  percent of the tag value. Within 1 month of the field test, analyze each of the calibration gases in triplicate using Method 26 of appendix A to part 60 of this chapter. The tester must follow all of the procedures in Method 26 (e.g., use midget impingers, heated Pallflex TX40H175 filter (TFE-glass mat), etc. if this analysis is performed. Citation 3 in section 13 of this method describes procedures and techniques that may be used for this analysis. Record the results on a data sheet. Each of the individual HCl analytical results for each calibration gas shall be within 5 percent (or 5 ppm, whichever is greater) of the triplicate set average; otherwise, discard the entire set and repeat the triplicate analyses. If the average of the triplicate analyses is within 5 percent of the calibration gas manufacturer's cylinder tag value, use the tag value; otherwise, conduct at least three additional analyses until the results of six consecutive runs agree within 5 percent (or 5 ppm, whichever is greater) of the average. Then use this average for the cylinder value.

7.3 Calibration Gas Dilution Systems. Sample flow rates of approximately 15 L/min are typical for extractive HCl measurement systems. These flow rates coupled with response times of 15 to 30 minutes will result in consumption of large quantities of calibration gases. The number of cylinders and amount of calibration gas can be reduced by the use of a calibration gas dilution system in accordance with Method 205 of appendix M to part 51 of this chapter, "Verification of Gas Dilution Systems for Field Instrument Calibrations." If this option is used, the tester shall also introduce an undiluted calibration gas approximating the effluent HCl concentration during the initial calibration error test of the measurement system as a quality assurance check.

#### 8.0 Test System Performance Specifications

8.1 Analyzer Calibration Error. This error shall be less than  $\pm 5$  percent of the emission standard concentration or  $\pm 1$  ppm, (whichever is greater) for zero, mid-, and high-range gases.

8.2 Sampling System Bias. This bias shall be less than  $\pm 7.5$  percent of the emission standard concentration or  $\pm 1.5$  ppm (whichever is greater) for zero and mid-range gases.

8.3 Analyte Spike Recovery. This recovery shall be between

70 to 130 percent of the expected concentration of spiked samples calculated with the average of the before and after run spikes.

## 9.0 Sample Collection, Preservation, and Storage

9.1 Pretest. Perform the procedures of sections 9.1.1 through 9.1.3.3 of this method before measurement of emissions (procedures in section 9.2 of this method). It is important to note that after a regulator is placed on an HCl gas cylinder valve, the regulator should be purged with dry N<sub>2</sub> or dry compressed air for approximately 10 minutes before initiating any HCl gas flow through the system. This purge is necessary to remove any ambient water vapor from within the regulator and calibration gas transport lines; the HCl in the calibration gas may react with this water vapor and increase system response time. A purge of the system should also be performed at the conclusion of a test day prior to removing the regulator from the gas cylinder. Although the regulator wetted parts are corrosion resistant, this will reduce the possibility of corrosion developing within the regulator and extend the life of the equipment.

9.1.1 Measurement System Preparation. Assemble the measurement system by following the manufacturer's written instructions for preparing and preconditioning the gas analyzer and, as applicable, the other system components. Introduce the calibration gases in any sequence, and make all necessary adjustments to calibrate the analyzer and the data recorder. If necessary, adjust the instrument for the specific moisture content of the samples. Adjust system components to achieve correct sampling rates.

9.1.2 Analyzer Calibration Error. Conduct the analyzer calibration error check in the field by introducing calibration gases to the measurement system at any point upstream of the gas analyzer in accordance with sections 9.1.2.1 and 9.1.2.2 of this method.

9.1.2.1 After the measurement system has been prepared for use, introduce the zero, mid-range, and high-range gases to the analyzer. During this check, make no adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Record the analyzer responses to each calibration gas. Note: A calibration curve established prior to the analyzer calibration error check may be used to convert the analyzer response to the equivalent gas concentration introduced to the analyzer. However, the same correction procedure shall be used for all effluent and calibration measurements obtained during the test.

9.1.2.2 The analyzer calibration error check shall be considered invalid if the difference in gas concentration displayed by the analyzer and the concentration of the calibration gas exceeds  $\pm 5$  percent of the emission standard concentration or  $\pm 1$  ppm, (whichever is greater) for the zero, mid-, or high-range calibration gases. If an invalid calibration



is exhibited, cross-check or recertify the calibration gases, take corrective action, and repeat the analyzer calibration error check until acceptable performance is achieved.

9.1.3 Sampling System Bias Check. For nondilution extractive systems, perform the sampling system bias check by introducing calibration gases either at the probe inlet or at a calibration valve installed at the outlet of the sampling probe. For dilution systems, calibration gases for both the analyzer calibration error check and the sampling system bias check must be introduced prior to the point of sample dilution. For dilution and nondilution systems, a zero gas and either a mid-range or high-range gas (whichever more closely approximates the effluent concentration) shall be used for the sampling system bias check.

9.1.3.1 Introduce the upscale calibration gas, and record the gas concentration displayed by the analyzer. Then introduce zero gas, and record the gas concentration displayed by the analyzer. During the sampling system bias check, operate the system at the normal sampling rate, and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rates at the analyzer. Alternately introduce the zero and upscale gases until a stable response is achieved. The tester shall determine the measurement system response time by observing the times required to achieve a stable response for both the zero and upscale gases. Note the longer of the two times and note the time required for the measurement system to reach 95 percent of the step change in the effluent concentration as the response time.

9.1.3.2 For nondilution systems, where the analyzer calibration error test is performed by introducing gases directly to the analyzer, the sampling system bias check shall be considered invalid if the difference between the gas concentrations displayed by the measurement system for the sampling system bias check and the known gas concentration standard exceeds  $\pm 7.5$  percent of the emission standard or  $\pm 1.5$  ppm, (whichever is greater) for either the zero or the upscale calibration gases. If an invalid calibration is exhibited, take corrective action, and repeat the sampling system bias check until acceptable performance is achieved. If adjustment to the analyzer is required, first repeat the analyzer calibration error check, then repeat the sampling system bias check.

9.1.3.3 For dilution systems (and nondilution systems where all calibration gases are introduced at the probe), the comparison of the analyzer calibration error results and sampling system bias check results is not meaningful. For these systems, the sampling system bias check shall be considered invalid if the difference between the gas concentrations displayed by the analyzer and the actual gas concentrations exceed  $\pm 7.5$  percent of the emission standard or  $\pm 1.5$  ppm, (whichever is greater) for either the zero or the upscale calibration gases. If an invalid

calibration is exhibited, take corrective action, and repeat the sampling system bias check until acceptable performance is achieved. If adjustment to the analyzer is required, first repeat the analyzer calibration error check.

## 9.2 Emission Test Procedures

9.2.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to Method 26 of appendix A to part 60 of this chapter.

9.2.2 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check. Maintain constant rate sampling (i.e.,  $\pm 10$  percent) during the entire run. Field test experience has shown that conditioning of the sample system is necessary for approximately 1-hour prior to conducting the first sample run. This conditioning period should be repeated after particulate filters are replaced and at the beginning of each new day or following any period when the sampling system is inoperative. Experience has also shown that prior to adequate conditioning of the system, the response to analyte spikes and/or the change from an upscale calibration gas to a representative effluent measurement may be delayed by more than twice the normal measurement system response time. It is recommended that the analyte spikes (see section 9.3 of this method) be performed to determine if the system is adequately conditioned. The sampling system is ready for use when the time required for the measurement system to equilibrate after a change from a representative effluent measurement to a representative spiked sample measurement approximates the calibration gas response time observed in section 9.1.3.1 of this method.

9.2.3 Sample Duration. After completing the sampling system bias checks and analyte spikes prior to a test run, constant rate sampling of the effluent should begin. For each run, use only those measurements obtained after all residual response to calibration standards or spikes are eliminated and representative effluent measurements are displayed to determine the average effluent concentration. At a minimum, this requires that the response time of the measurement system has elapsed before data are recorded for calculation of the average effluent concentration. Sampling should be continuous for the duration of the test run. The length of data collection should be at least as long as required for sample collection by Method 26 of part 60 of this chapter. One hour sampling runs using this method have provided reliable data for cement kilns.

9.2.4 Validation of Runs. Before and after each run, or if adjustments are necessary for the measurement system during the run, repeat the sampling system bias check procedure described in section 9.1.3 of this method. (Make no adjustments to the measurement system until after the drift checks are completed.)

Record the analyzer's responses.

9.2.4.1 If the post-run sampling system bias for either the zero or upscale calibration gas exceeds the sampling system bias specification, then the run is considered invalid. Take corrective action, and repeat both the analyzer calibration error check procedure (section 9.1.2 of this method) and the sampling system bias check procedure (section 9.1.3 of this method) before repeating the run.

9.2.4.2 If the post-run sampling system bias for both the zero and upscale calibration gas are within the sampling system bias specification, then construct two 2-point straight lines, one using the pre-run zero and upscale check values and the other using the post-run zero and upscale check values. Use the slopes and y-intercepts of the two lines to calculate the gas concentration for the run in accordance with equation 1 of this method.

9.3 Analyte Spiking—Self-Validating Procedure. Use analyte spiking to verify the effectiveness of the sampling system for the target compounds in the actual kiln gas matrix. Quality assurance (QA) spiking should be performed before and after each sample run. The spikes may be performed following the sampling system bias checks (zero and mid-range system calibrations) before each run in a series and also after the last run. The HCl spike recovery should be within  $\pm 30$  percent as calculated using equations 1 and 2 of this method. Two general approaches are applicable for the use of analyte spiking to validate a GFC HCl measurement system: (1) two independent measurement systems can be operated concurrently with analyte spikes introduced to one of the systems, or (2) a single measurement system can be used to analyze consecutively, spiked and unspiked samples in an alternating fashion. The two-system approach is similar to Method 301 of this appendix and the measurement bias is determined from the difference in the paired concurrent measurements relative to the amount of HCl spike added to the spiked system. The two-system approach must employ identical sampling systems and analyzers and both measurement systems should be calibrated using the same mid- and high-range calibration standards. The two-system approach should be largely unaffected by temporal variations in the effluent concentrations if both measurement systems achieve the same calibration responses and both systems have the same response times. (See Method 301 of this appendix for appropriate calculation procedures.) The single measurement system approach is applicable when the concentration of HCl in the source does not vary substantially during the period of the test. Since the approach depends on the comparison of consecutive spiked and unspiked samples, temporal variations in the effluent HCl concentrations will introduce errors in determining the expected concentration of the spiked samples. If the effluent HCl concentrations vary by more than  $\pm 10$  percent (or  $\pm 5$  ppm,

whichever is greater) during the time required to obtain and equilibrate a new sample (system response time), it may be necessary to: (1) use a dual sampling system approach, (2) postpone testing until stable emission concentrations are achieved, (3) switch to the two-system approach [if possible] or, (4) rely on alternative QA/QC procedures. The dual-sampling system alternative uses two sampling lines to convey sample to the gas distribution manifold. One of the sample lines is used to continuously extract unspiked kiln gas from the source. The other sample line serves as the analyte spike line. One GFC analyzer can be used to alternately measure the HCl concentration from the two sampling systems with the need to purge only the components between the common manifold and the analyzer. This minimizes the time required to acquire an equilibrated sample of spiked or unspiked kiln gas. If the source varies by more than  $\pm 10$  percent or  $\pm 5$  ppm, (whichever is greater) during the time it takes to switch from the unspiked sample line to the spiked sample line, then the dual-sampling system alternative approach is not applicable. As a last option, (where no other alternatives can be used) a humidified nitrogen stream may be generated in the field which approximates the moisture content of the kiln gas. Analyte spiking into this humidified stream can be employed to assure that the sampling system is adequate for transporting the HCl to the GFC analyzer and that the analyzer's water interference rejection is adequate.

9.3.1 Spike Gas Concentration and Spike Ratio. The volume of HCl spike gas should not exceed 10 percent of the total sample volume (i.e., spike to total sample ratio of 1:10) to ensure that the sample matrix is relatively unaffected. An ideal spike concentration should approximate the native effluent concentration, thus the spiked sample concentrations would represent approximately twice the native effluent concentrations. The ideal spike concentration may not be achieved because the native HCl concentration cannot be accurately predicted prior to the field test, and limited calibration gas standards will be available during the field test. Some flexibility is available by varying the spike ratio over the range from 1:10 to 1:20. Practical constraints must be applied to allow the tester to spike at an anticipated concentration. Thus, the tester may use a 100 ppm calibration gas and a spike ratio of 1:10 as default values where information regarding the expected HCl effluent concentration is not available prior to the tests. Alternatively, the tester may select another calibration gas standard and/or lower spike ratio (e.g., 1:20) to more closely approximate the effluent HCl concentration.

9.3.2 Spike Procedure. Introduce the HCl spike gas mixture at a constant flow rate ( $\pm 2$  percent) at less than 10 percent of the total sample flow rate. (For example, introduce the HCl spike gas at 1 L/min ( $\pm 20$  cc/min) into a total sample flow rate of 10 L/min). The spike gas must be preheated before

introduction into the sample matrix to prevent a localized condensation of the gas stream at the spike introduction point. A heated sample transport line(s) containing multiple transport tubes within the heated bundle may be used to spike gas up through the sampling system to the spike introduction point. Use a calibrated flow device (e.g., mass flow meter/controller) to monitor the spike flow rate. Use a calibrated flow device (e.g., rotameter, mass flow meter, orifice meter, or other method) to monitor the total sample flow rate. Calculate the spike ratio from the measurements of spike flow and total flow. (See equation 2 and 3 in section 10.2 of this method.)

9.3.3 Analyte Spiking. Determine the approximate effluent HCl concentrations by examination of preliminary samples. For single-system approaches, determine whether the HCl concentration varies significantly with time by comparing consecutive samples for the period of time corresponding to at least twice the system response time. (For analyzers without sample averaging, estimate average values for two to five minute periods by observing the instrument display or data recorder output.) If the concentration of the individual samples varies by more than  $\pm 10$  percent relative to the mean value or  $\pm 5$  ppm, (whichever is greater), an alternate approach may be needed.

9.3.3.1 Adjust the spike flow rate to the appropriate level relative to the total flow by metering spike gas through a calibrated mass flow meter or controller. Allow spike flow to equilibrate within the sampling system for at least the measurement system response time and a steady response to the spike gas is observed before recording response to the spiked gas sample. Next, terminate the spike gas flow and allow the measurement system to sample only the effluent. After the measurement system response time has elapsed and representative effluent measurements are obtained, record the effluent unspiked concentration. Immediately calculate the spike recovery.

9.3.3.2 If the spike recovery is not within acceptable limits and a change in the effluent concentration is suspected as the cause for exceeding the recovery limit, repeat the analyte spike procedure without making any adjustments to the analyzer or sampling system. If the second spike recovery falls within the recovery limits, disregard the first attempt and record the results of the second spike.

9.3.3.3 Analyte spikes must be performed before and after each test run. Sampling system bias checks must also be performed before and after each test run. Depending on the particular sampling strategy and other constraints, it may be necessary to compare effluent data either immediately before or immediately after the spike sample to determine the spike recovery. Either method is acceptable provided a consistent approach is used for the test program. The average spike recovery for the pre- and post-run spikes shall be used to determine if spike recovery is between 70 and 130 percent.

## 10.0 Data Analysis and Emission Calculations

The average gas effluent concentration is determined from the average gas concentration displayed by the gas analyzer and is adjusted for the zero and upscale sampling system bias checks, as determined in accordance with section 9.2.3 of this method. The average gas concentration displayed by the analyzer may be determined by integration of the area under the curve for chart recorders, or by averaging all of the effluent measurements. Alternatively, the average may be calculated from measurements recorded at equally spaced intervals over the entire duration of the run. For sampling run durations of less than 1-hour, average measurements at 2-minute intervals or less, shall be used. For sampling run durations greater than 1-hour, measurements at 2-minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be used. Calculate the effluent gas concentration using equation 1.

$$C_{\text{gas}} = \frac{(m_i + m_f) \left[ \frac{(C_{\text{avg}} - b_c)}{m_c} \right] + (b_i + b_f)}{2} \quad (\text{Eq. 1})$$

where:  
 $b_c$  = Y-intercept of the calibration least-squares line.

$b_f$  = Y-intercept of the final bias check 2-point line.

$b_i$  = Y-intercept of the initial bias check 2-point line.

$C_{\text{gas}}$  = Effluent gas concentration, as measured, ppm.

$C_{\text{avg}}$  = Average gas concentration indicated by gas analyzer, as measured, ppm.

$m_c$  = Slope of the calibration least-squares line.

$m_f$  = Slope of the final bias check 2-point line.

$m_i$  = Slope of the initial bias check 2-point line.

The following equations are used to determine the percent recovery (%R) for analyte spiking:

$$\%R = (S_M / C_E) \times 100 \quad (\text{Eq. 2})$$

where:

$S_M$  = Mean concentration of duplicate analyte spiked samples (observed).

$C_E$  = Expected concentration of analyte spiked samples (theoretical).

$$C_E = C_S(Q_S / Q_T) + S_U(1 - Q_S / Q_T) \quad (\text{Eq. 3})$$

where:

$C_S$  = Concentration of HCl spike gas (cylinder tag value).

$Q_S$  = Spike gas flow rate.

$Q_T$  = Total sample flow rate (effluent sample flow plus spike flow).

$S_U$  = Native concentration of HCl in unspiked effluent samples.

Acceptable recoveries for analyte spiking are  $\pm 30$  percent.

#### 11.0 Pollution Prevention

Gas extracted from the source and analyzed or vented from the system manifold shall be either scrubbed, exhausted back into the stack, or discharged into the atmosphere where suitable dilution can occur to prevent harm to personnel health and welfare or plant or personal property.

#### 12.0 Waste Management

Gas standards of HCl are handled as according to the instructions enclosed with the materials safety data sheets.

#### 13.0 References

1. Peeler, J.W., Summary Letter Report to Ann Dougherty, Portland Cement Association, June 20, 1996.

2. Test Protocol, Determination of Hydrogen Chloride Emissions from Cement Kilns (Instrumental Analyzer Procedure) Revision 4; June 20, 1996.

3. Westlin, Peter R. and John W. Brown. Methods for Collecting and Analyzing Gas Cylinder Samples. Source Evaluation Society Newsletter. 3(3):5-15. September 1978.