

Hydrogen Chloride Cylinder Gas Concentration Analysis Using U.S. EPA Method 26

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ABSTRACT

The EPA's Maximum Achievable Control Technology (MACT) standards will require the measurement of hydrogen chloride (HCl) at sources. Continuous Emission Monitoring Systems (CEMS) are expected to be used to ensure compliance with MACT standards. In the fall of 1995, the EPA Office of Air Quality Planning and Standards (OAQPS) and the EPA National Risk Management Research Laboratory conducted combustion emission measurement tests to evaluate proposed performance specifications for a typical HCl CEMS. To evaluate the relative accuracy of a CEMS versus the current compliance method (EPA Method 26), the CEMS was first calibrated using HCl from compressed gas cylinders and then used to sample HCl-spiked emissions from a natural-gas-fired rotary kiln incinerator. Although at present there is no National Institute of Science and Technology (NIST) certified reference material for HCl gas, specialty gas companies produce and certify compressed gas cylinders of HCl for use in calibration and span checks of CEMS.

As part of the quality assurance program for the CEMS study, Research Triangle Institute (RTI) carried out an independent determination of the concentrations of HCl in commercial compressed gas cylinders used for calibration of the CEMS. A study of the potential for losses of HCl in calibration or sample delivery lines was also conducted. Results are reported in this paper.

INTRODUCTION

In the fall of 1995, the EPA Office of Air Quality Planning and Standards and the EPA National Risk Management Research Laboratory conducted combustion emission measurement tests to evaluate proposed performance specifications for a typical HCl CEMS. Emissions were produced by operating the EPA Rotary Kiln Incinerator Simulator (RKIS) and spiking its emissions with anhydrous HCl to give target HCl levels from zero to approximately 100 ppm¹. The CEMS sampled the RKIS continuously; several Method 26² trains sampled emissions periodically. HCl concentration values from the CEMS and the wet chemistry Method 26 are to be compared to assess relative accuracy. A schematic diagram of the RKIS is given in Figure 1. Sampling points for the CEMS and Method 26 sampling trains are identified. Acurex, Inc. operated the RKIS and the CEMS. Energy and Environmental Research Corporation operated the Method 26 sampling trains and arranged for Method 26 impinger sample analysis for chloride by ion chromatography (IC).

RTI provided quality assurance services for these tests. Goals of the quality assurance program were: (1) carry out a systems audit of the sample collection/handling and documentation activities for CEMS and Method 26 analyses; (2) provide performance audit test solutions to the study's analytical laboratory for IC analysis of chloride ions; (3) devise and apply a wet chemistry method to independently determine the concentration of HCl in the compressed gas cylinders used for calibration of the CEMS; (4) determine if line losses occur during delivery of the calibration gases to the CEMS; and (5) compare the results of the cylinder gas analyses to the manufacturer's stated concentrations.

This paper discusses the methodology used to determine the HCl concentration in the compressed gas cylinders and to assess the potential for HCl losses in the gas calibration and sample delivery lines. The differences between the cylinder gas manufacturer's stated values and the values found by analysis of impinger samples for chloride ions are compared in terms of individual cylinder concentration levels and in terms of regression relationships for the entire set of cylinders.

METHODOLOGY

Sampling from Cylinders

An abbreviated version of the Method 26 sampling train was selected to capture gases from the calibration cylinders for an assay. The sampling train arrangement is shown in Figure 2. The first and second midjet impingers contained 15 mL of 0.1 N sulfuric acid (H_2SO_4) absorbing solution; the third and fourth impingers contained 0.1 N sodium hydroxide (NaOH) in water, and the fifth impinger contained silica gel to dry the air prior to volume measurement by the dry gas meter. The bases of the impingers were immersed in an ice bath during sampling. A stainless steel needle valve, in line between the cylinder regulator and the impingers, was used to adjust the flow rate. The flow rate of cylinder gas was determined with a NIST-traceable soap film flowmeter and set to a known flow rate between 1 and 2 liters per minute. The total volume sampled was indicated by the displacement indicated by the calibrated dry gas meter.

The calibration cylinder gases were sampled at two locations. The first sampling point was within 2 feet (0.6 meter) of the cylinder regulator. The second sampling point was at the end of the approximately 75-foot (23-meter) long Teflon supply line which connected the cylinder to the CEMS inlet. Stainless steel regulators (high purity gas type) were attached to the cylinders. These regulators were dedicated and not removed from the cylinders. The regulators were first purged with cylinder gas to flush out any air or moisture. Then, while a low flow of gas was maintained, a stainless steel needle valve was connected to the outlet of the regulator. Teflon lines and connections were used throughout; open lines were capped to prevent entrance of moisture. The needle valve was purged for several minutes, and the flow through the valve was adjusted to approximately 2 liters per minute using a soap film flowmeter to confirm the actual flow. The outlet from the needle valve was connected, again via Teflon tubing and fittings, to the inlet of the first impinger of the abbreviated Method 26 sampling train.

The contents of each impinger were transferred quantitatively to a separate 100-mL volumetric flask, diluted to the mark with deionized water, and the flask's contents were poured into separate pre-washed, 125-mL capacity, high-density polyethylene bottles. The labeled bottles were refrigerated at approximately 4 degrees Celsius until IC analysis for chloride began.

Analysis by Ion Chromatography

Impinger solutions were analyzed for chloride ion by IC by both RTI (as the QA laboratory) and Energy and Environmental Research Corporation (project's analytical laboratory). The laboratories both

used a Dionex DX300 ion chromatograph with a conductivity detector, sodium carbonate/sodium bicarbonate eluent solution, and a 5-point calibration curve. However, the analysis ranges of the two laboratories differed significantly. The QA audit laboratory operated on a fixed zero to 2 $\mu\text{g}/\text{mL}$ range and diluted all of the samples with eluent solution to adjust the chloride ion concentration to within this range. Eluent was used for dilution to minimize the “water dip” and other matrix effects which affect peak shape and thus quantitation. On the other hand, the project’s analytical laboratory calibrated over a much broader range, zero to 100 $\mu\text{g}/\text{mL}$, and analyzed samples without dilution. Quality control and quality assurance samples were analyzed by both laboratories.

RESULTS AND DISCUSSION

HCl Cylinder Gas Concentrations

Concentrations of HCl in six compressed gas cylinders were determined by IC analysis of Method 26 impinger solutions for chloride ions by the audit and contract laboratories. Results are given in Table 1. For individual cylinders, the best agreement between the manufacturer’s concentrations and those determined by either laboratory is for cylinders containing stated concentrations of 8.66, 20.5, 38.2, and 79.0 ppm. Seven of the eight analytical results were within 10% of the stated value and four of the eight results were within the manufacturer’s accuracy range of $\pm 5\%$. The largest differences were found for the two lower concentration cylinders (stated concentrations of 2.49 and 5.47 ppm); differences ranged from -9.6% to 28.5%. Due to the sampling protocol, impingers which collected HCl from these cylinders gave a less concentrated solution, with the result that the lower extreme of the IC calibration range (less than 3% of full scale in three of four cases) was used for analysis. Since matrix effects from the water and 0.1N to 0.03N sulfuric acid were present, the chloride ion area or peak height was more difficult to determine accurately at the lower concentrations. Figure 3 illustrates the IC chloride ion peak and the effect of the solution matrix on the baseline; Figure 4 shows the peak for higher concentrations.

The results of the cylinder analyses were also considered as a group by examining the fit of the linear regression of the manufacturer’s concentration values versus those found by the laboratories. At the 95% confidence level, and using Student’s t criteria, the slope of the regression equation for either set of laboratory data was found to be significantly different from a slope of 1.00. However, the slopes of the results were not significantly different from a slope of 1.05, a value representing the vendor’s stated accuracy of $\pm 5\%$.

Sampling Line Study

To assess the possibility for sampling or calibration line losses, calibration gas samples from cylinders were taken by Method 26 immediately downstream of the cylinder regulator and at the exit end of the approximately 75-foot (23-meter) long delivery tube, just prior to the CEMS inlet. The study of the lowest concentration cylinder (designated value 2.49 ppm) showed an apparent increase in concentration; however, the analytical results were so variable as to be uninterpretable. Results from studying the cylinder with a stated concentration of 38.2 ppm showed a diminishment of only 2.7%. Since this is well within the precision of the collection/measurement method at this concentration, it appears that no detectable line losses occurred.

Quality Assurance Samples

Each laboratory ensured that its analytical system was in control by analyzing control samples, blanks, and spikes at approximately 20-sample intervals. Two quality assurance solutions were also analyzed twice as blind samples. The first was a water-diluted acid precipitation standard with a chloride concentration of 2.31 $\mu\text{g}/\text{mL}$. This solution was suitable for the QA laboratory’s range of zero to 2 $\mu\text{g}/\text{mL}$.

(agreement within 1%) but was unsuitable as an audit solution for the project's analytical laboratory which operated over a zero to 100 $\mu\text{g}/\text{mL}$ range (high by 0.9 $\mu\text{g}/\text{mL}$ or 40%). The second solution was 12.0 $\mu\text{g}/\text{mL}$ of sodium chloride in 0.03N sulfuric acid. For analysis of this sample, the QA laboratory was high by 15%; the analytical laboratory was high by 12%.

CONCLUSIONS

Sampling and analysis difficulties were encountered in applying Method 26 to the analysis of gases in cylinders containing 5 ppm HCl or less. However, for concentrations in the range of 8 to 100 ppm, independent analysis gave results that were within 10% (and often within 5%) of the manufacturer's designated concentration. The results from this short quality assurance study point out the good potential for reliable production and use of compressed gas standards of HCl in a nitrogen matrix. To achieve higher confidence in compressed gas standards for HCl would require a program of development, multi-instrument analyses, and round-robin testing such as is used to certify NIST or EPA standard reference or research grade materials. In addition, explicit instructions would be required for the proper care and use of the HCl cylinder standards.

REFERENCES

1. Quality Assurance Test Plan. "Support of OAQPS HCl Monitoring Standards." Prepared by Acurex, Inc. for the U.S. Environmental Protection Agency; National Risk Management Research Laboratory, Research Triangle Park, NC. Document No. QTRAK CR06, 10/II. August 1995.
2. Code of Federal Regulations, Part 60, Appendix A. "Method 26-Determination of Hydrogen Chloride Emissions from Stationary Sources." Promulgated April 22, 1994.

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Table 1. HCl Cylinder Gas Concentrations as Determined by EPA Method 26

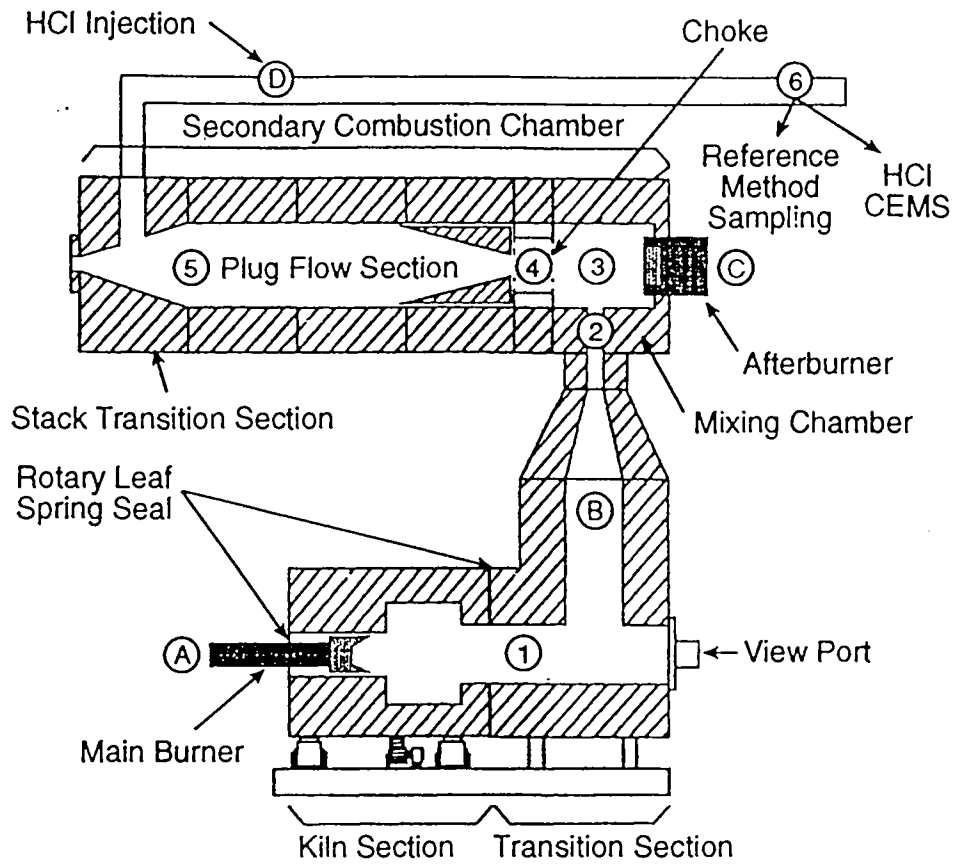
Cylinder Number	Manufacturer's Stated Concentration, ppm (a)	QA Audit Laboratory Results, ppm (% difference) (b)	Project Laboratory Results, ppm (% difference)
A020112	2.49	3.20 (28.5)	2.25 (-9.6)
A0200100	5.47	6.32 (15.5)	6.68 (22.1)
A020130	8.66	8.96 (3.5)	9.42 (8.7)
XA-1658	20.5	21.3 (3.9)	20.0 (-2.4)
A020015	38.2	40.7 (6.5)	39.0 (2.1)
A01980	79.0	84.2 (6.4)	88.9 (12.5)

(a) Certified working standard. Manufacturer's stated analytical accuracy +/- 5%.

(b) % difference = $100 \times (\text{laboratory result} - \text{manufacturer's value}) / (\text{manufacturer's value})$

Table 2. Comparison of HCl Cylinder Gas Concentrations as Determined at the Cylinder and at the Entrance to the CEMS (Line Loss Study)

Cylinder Number (Manufacturer's Value, ppm)	Concentration, ppm, as Found at the Cylinder	Concentration, ppm, as Found at the CEMS Inlet	Percent Change from Cylinder to CEMS Inlet
A020112 (2.49)	3.20	4.35	35.9
A020015 (38.2)	40.7	39.6	-2.7



Numbers = Sampling Points
 Letters = Injection Points

Figure 1. Schematic of Rotary Kiln Incinerator

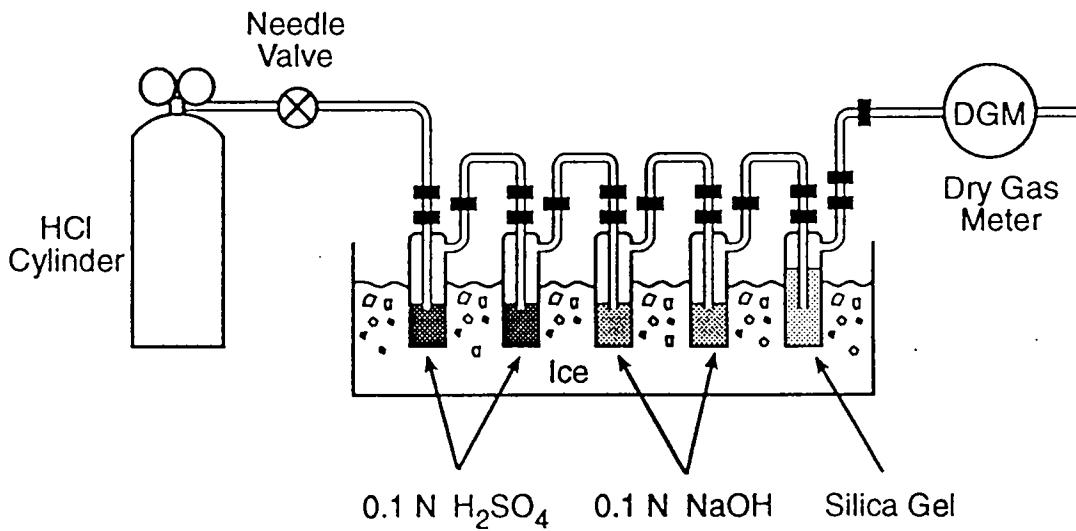


Figure 2. EPA Method 26 Sampling Train Modified to Collect Cylinder Gases

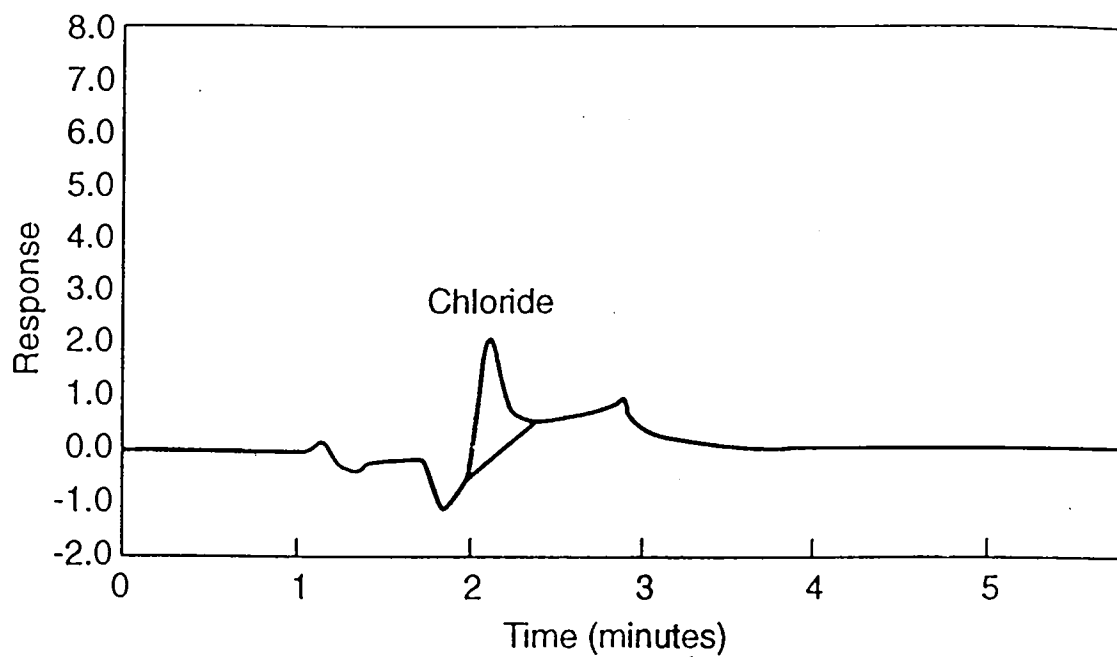


Figure 3. Ion Chromatograph Trace for Chloride Ion Showing Matrix Effects

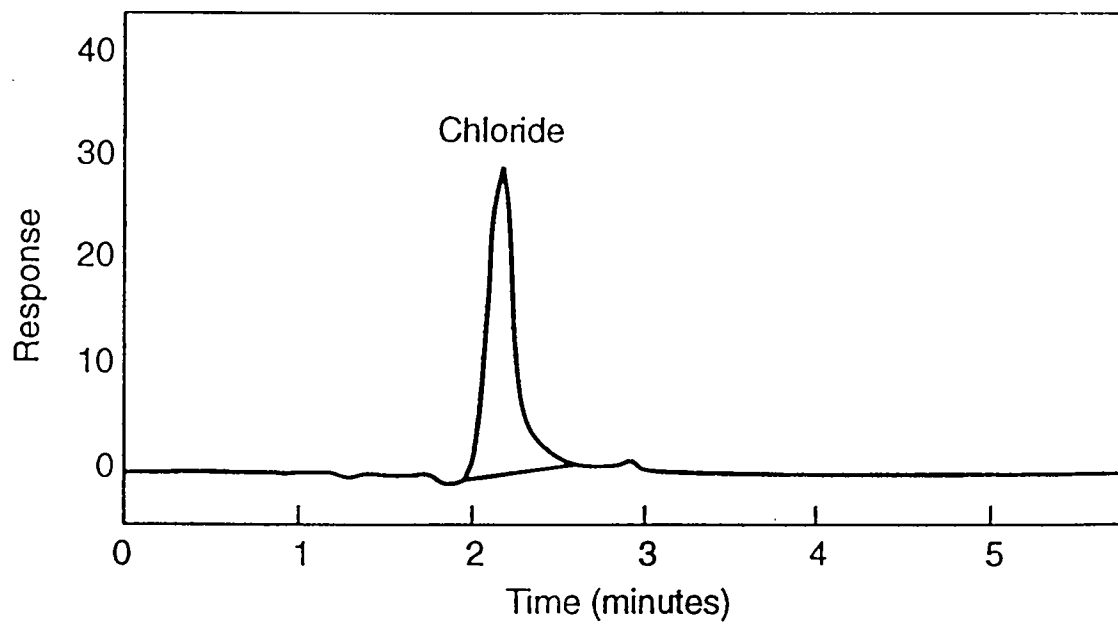


Figure 4. Ion Chromatograph Trace for Chloride Ion at Higher Concentrations

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17. KEY WORDS AND DOCUMENT ANALYSIS			
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