PPM-Level HCl Measurements from Cement Kilns and Waste Incinerators by FTIR Spectroscopy

Peter Zemek, PhD, MIDAC Corporation
Joe Van Gompel, PhD, MIDAC Corporation
Steven Plowman, MIDAC Corporation

Introduction

Fourier transform infrared (FTIR) spectroscopy is an accepted and well-known technique by the EPA to measure hydrogen chloride (HCl). Over the past 10 years, HCl by FTIR has been utilized successfully at many cement kilns and other incineration technologies using EPA Method 321 or 301. HCl is a common byproduct from cement kilns and municipal waste incinerators. Commonly, kilns will receive hazardous waste and other chlorinated compounds, under what the EPA calls the "Burning of Hazardous Waste in Boilers and Industrial Furnaces" (BIF) rule. Chlorine also enters the cement kiln in with the raw materials. In a municipal waste incinerator, many poly-chlorinated materials such old PVC piping are burned and HCl is produced, along with CO_2 and water vapor. HCl is considered a hazardous air pollutant (HAP) by the US EPA. A significant source is characterized as emitting HCl at greater than 10 tons / year.

FTIR spectroscopy is a powerful tool for analysis of HCl at sub-ppm levels. There have been many comparison tests to FTIR with wet chemical methods such as EPA Method 26 and 26A for HCl analysis. FTIR has also been described as a CEM by Performance Specification 15 (PS-15) and as a primary method when performing RATA analysis. The advantages of HCl by FTIR are the immediate near-real-time field results, reduction of laboratory error, and contamination reduction. The FTIR methods are self-validating when used with a spiking regimen and proven in the field and in the laboratory. This method requires the use of a high resolution FTIR instrument to obtain sub-ppm level detection limits. A resolution of 0.5 cm^{-1} to 1 cm^{-1} instrumentation is usually required.

The only drawback of HCl by FTIR in cement kilns is the possibility of kinetic reactions of the HCl with high ammonia levels in the stack, heated filter, or sampling system which can lead to the formation of ammonium chloride salts on the filter or in the heated line. This causes a certain amount of lag time in the spiking regimen but is usually overcome by the additional wait time while spiking to reach steady-state, need for a higher spiking concentration, or the need to place the FTIR instrument closer to the sample port. These issues can be overcome in the field with a review of the sampling system and field modifications. However, once a spike regimen is passed, the method, instrument, and sampling system has been validated and concentrations may be considered accurate and precise.

The projects described here were performed over many years at a cement kiln and a municipal waste combustor. The major goal of the study was to validate extractive FTIR spectroscopy for measurements of gaseous hydrogen chloride (HCl) as described in Environmental Protection Agency (EPA) Test Methods 301[1], 320, and 321[2]. Three different validation procedures were successfully performed; they were direct comparisons with EPA's manual Test Method 26[3], "single instrument" dynamic spiking, and "dual instrument" dynamic spiking.

HCl by FTIR

The infrared spectrum of HCl is distinctive and readily observed, even in the presence of water vapor interference. HCl appears as a series of doublet peaks that rise, fall to zero, then rise and fall to zero again. These regular peaks are observed between 2650 cm^{-1} and 3100 cm^{-1}. Each peak is split into a doublet with the ratio of 3:1 based on the ratio of ^{35}Cl:^{37}Cl isotopes. The mid-infrared spectrum of HCl is shown in Figure 1.
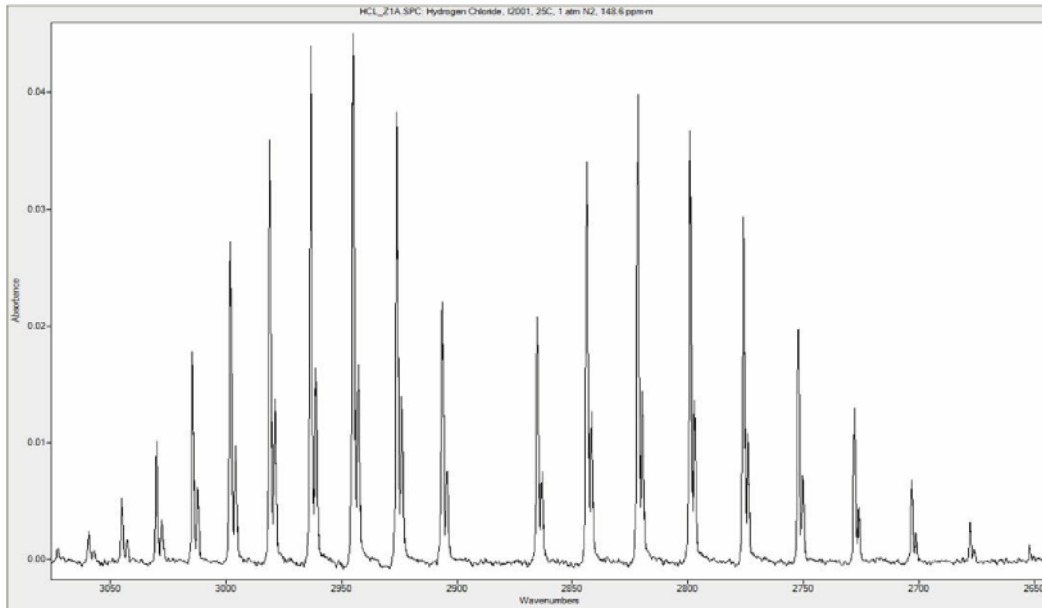

Figure 1. Hydrogen Chloride, 148.6 ppm-m, 25° C.

The ability to analyze HCl in the presence of water is imperative as water vapor concentrations are very high from combustion sources such as incinerators. Spectra incorporating these high concentrations of water are shown in Figures 2 - 4.
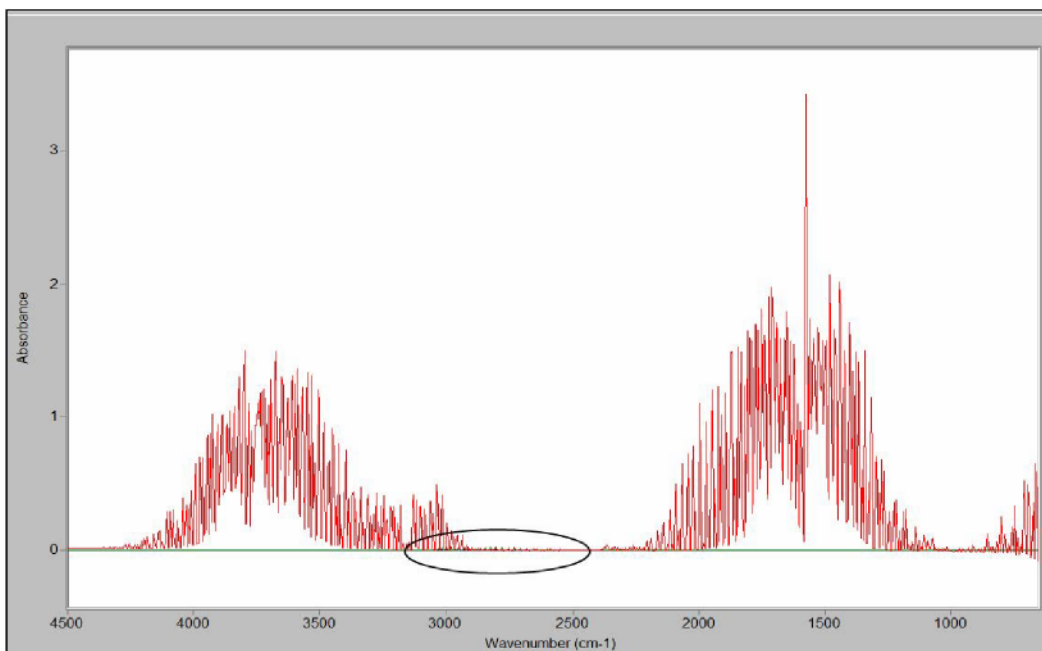

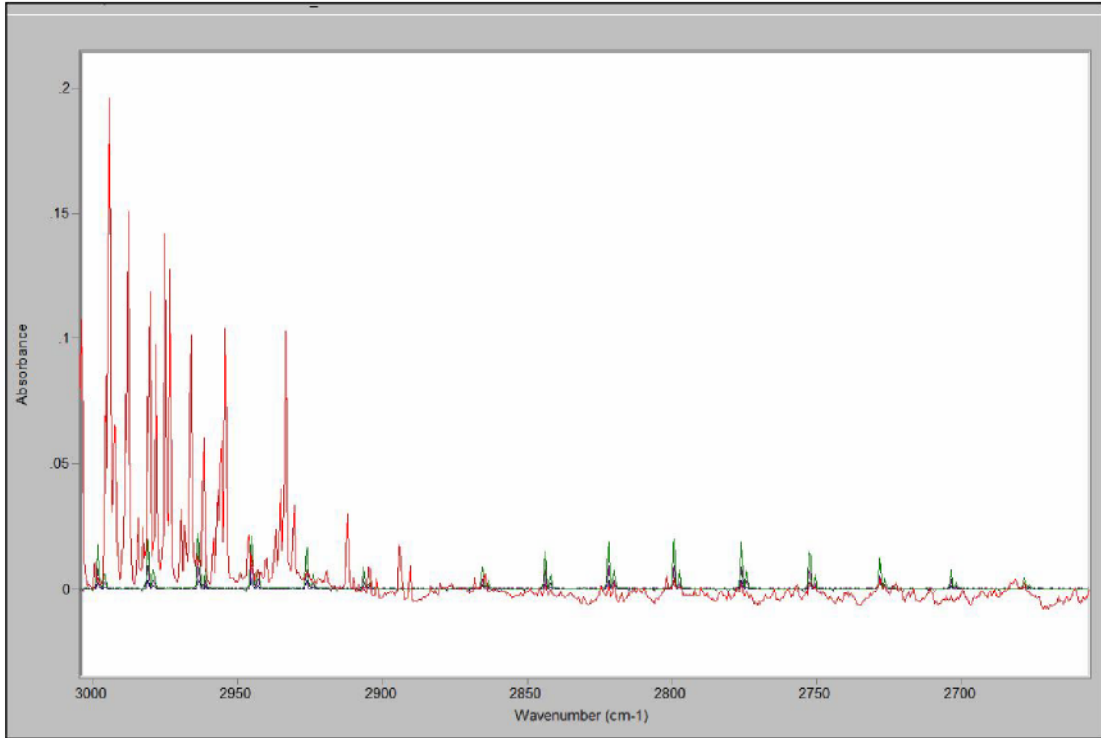Figure 2. 42 ppm-m HCl in baseline of 14% water vapor.

Figure 3. Figure 2 expanded to see HCl clearly in presence of high levels of water vapor.
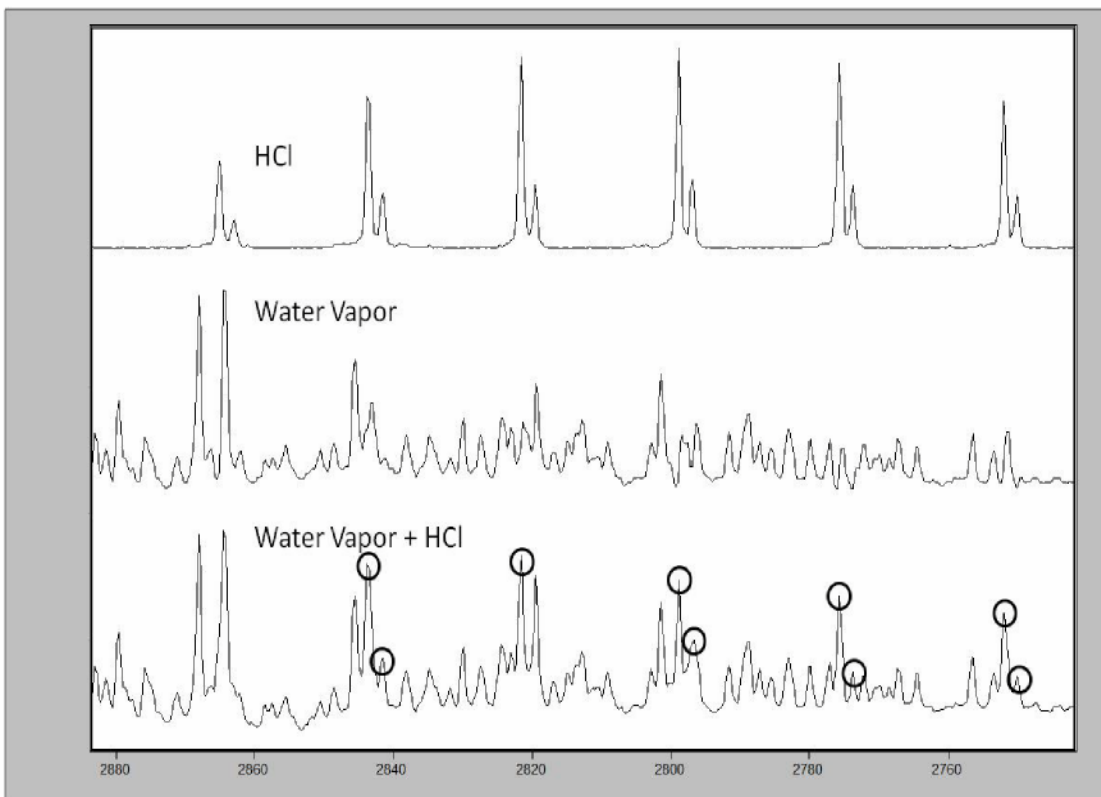

Figure 4. HCl in the presence of water vapor. HCl peaks are indicated which can be used for quantitation.

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The regular pattern of peaks for HCl is common for diatomic molecules such as HF, HBr, CO, and NO as well. It is due to rotational transitions between the ground and first excited vibrational states of the molecules. Known as the P-branch (lower energy) and the R-branch (higher energy), these fan-like spectral features surround the Q-branch, which is forbidden by quantum mechanics in the fundamental band of the heteronuclear diatomics. More complex materials, like NH_3 and CH_4, show prominent Q-branches.

Quantitative Analysis of HCl by FTIR
Test Facility
The test facility is a typical municipal waste combustor/generating station using refuse-derived fuel. The plant consists of several independent "units," two of which (referred to as "Unit 1" and "Unit 2") were sampled during this work. Each unit includes a boiler and a set of emissions control devices, notably a lime-slurry injection system for reducing the HCl emissions. All validation testing was performed at one of the two control-device outlet locations; the sampling ports were located in rectangular cross-section ducts connecting the outlets of the induced-draft fans to the base of the stack. Inlet testing was performed at a set of ports located just downstream of the Unit 1 boiler.

Sampling Systems
The sample streams passed through heated probe assemblies, heat-traced (~350° F, 181° C) PTFE sample lines, and the absorption cells of each of two FTIR spectrometers; a pump connected to the cell's outlet ports continuously drew sample gases through the cells at approximately 10 liters per minute (lpm). The only materials used in the sampling systems were Pyrex^R, Type 316 stainless steel, and Teflon^R. All Method 26 sampling was performed using equipment and techniques described in Reference 3; the resulting samples were submitted to Testar, Inc. (Raleigh, NC) for HCl analysis.

FTIR Analytical Systems
The two FTIR spectrometers used in this work are MIDAC Corporation (Costa Mesa, CA) Model I-2000 instruments (see Figure 1) with nominal one half wavenumber (0.5 cm^{-1}) spectral resolution; they are designated below as Instruments "A" and "B." Both systems employ Michelson interferometers, beam splitters and cell windows of zinc selenide (ZnSe), hot-wire infrared radiation sources, front-surface optical transfer mirrors, and multi-pass absorption cells. Mercury cadmium telluride (MCT) detectors were used for the majority of the testing described here; for the diluted inlet samples (only), an indium antimonide (InSb) detector was installed in Instrument B. In all cases, the detectors were cooled with liquid N_2 and their temperatures maintained at 77 K. The 10-meter path length "White" absorption cells use gold-surface internal mirrors, and their interior cell walls were made of polished nickel to minimize chemical interactions with the sample gas. Transducers and thermocouples connected directly to the insulated sample cells provide the pressures and temperatures of the sample streams. During testing, the temperature of the absorption cells was 181º C; the elevated temperature prevents gas condensation within the cell and minimizes HCl retention by the cell walls and mirrors. The volumes of the absorption cells are 2.0 liters, so at a flow of 10 lpm the sample gas in each cell is refreshed approximately five times per minute. Interferograms consisting of 50 co-added scans were recorded nearly continuously during the test periods, and provided one-minute average concentrations.
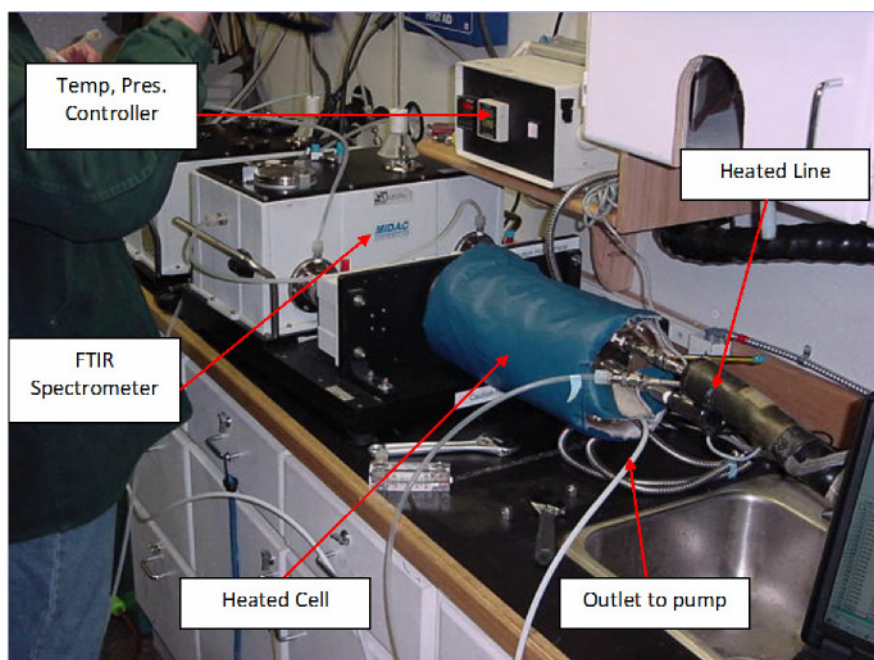
FIGURE 5. Typical FTIR spectrometer system during testing.

FTIR Spectral Analyses

The program AutoquantPro^R(hereafter "AQ," version 4.0.0.111,Midac Corporation, 2004) was used to control the FTIR, and collect and analyze all the infrared field data. AQ allows the development and storage of analytical "methods" for analysis of spectral data (absorbance) files. Various methods were generated for the instrument-detector combinations described above and used to for determine the absorption path lengths and the concentrations of the gaseous analytes. On every test day, at least one 128-scan background spectrum was recorded with dry N_2. Before and after each test run, spectra of a calibration transfer standard (CTS) gas were obtained and used to determine the effective absorption path lengths of the gas sample cells. A cylinder of ethylene C_2H_4 in N_2 (103 ppm) served as the CTS, and the absorption path lengths were determined by comparing the field CTS spectra to a well-characterized laboratory ethylene spectrum. All the absorption path lengths (for each instrument-detector combination) varied by less than 5% over the entire test period. The analytical results presented in this work are based on the average path length determined for each instrument-detector combination over the course of the field tests.

The HCl concentrations in the extracted FTIR samples were determined by mathematically comparing the samples' absorbance spectra to a number of HCl reference spectra; these reference spectra were recorded during the test period using the two field instruments and a cylinder standard of 86.2 ppm HCl and 5.03 ppm SF_6 (balance N_2). Using both a NIST-calibrated mass flow controller and standard barometric techniques, the reference samples were made by diluting the HCl/SF_6 standard gas to four lower volumetric concentrations. The absolute HCl concentration of the cylinder standard was determined in the laboratory according to the sampling and

analytical procedures of EPA Method 26; only the relative SF_6 concentrations are required for the validation procedures described below, so the SF_6 cylinder concentration was not independently confirmed.

Preliminary concentrations of three other analytes – carbon monoxide (CO), sulfur dioxide (SO_2), and nitric oxide (NO) – were also determined using quantitative FTIR reference libraries prepared in the laboratory from dilution of certified calibration gas standards. In some cases the observed concentrations of these compounds exceeded the calibration ranges of the spectrometers.

Table 1 presents the infrared wavenumber (cm^{-1}) analytical ranges and concentration-path length (ppm-meter) limits of the reference libraries employed to date.

TABLE 1. FTIR REFERENCE SPECTRA AND ANALYTICAL REGIONS

ANALYTE	WAVENUMBER RANGE	NUMBER OF SPECTRA	PPM-M RANGE
HCl	$2768.93 - 2849.00$ cm^{-1}	5	45 – 763 ppm-m
SF_6	$909.02 - 967.51$ cm^{-1}	5	2.67 – 44.57 ppm-m
CO	$2168.18 - 2180.62$ cm^{-1}	3	64 – 263 ppm-m
NO	$1872.50 - 1877.30$ cm^{-1}	3	563 – 2285 ppm-m
SO_2	$1068.96 - 1252.55$ cm^{-1}	2	217 – 441 ppm-m

HCl Method Validations

EPA's Test Methods 301 (Reference 1) and 320 (Reference 2) both provide statistical techniques for the validation of emissions test procedures. Three validation procedures for FTIR measurements of HCl were performed and are described below. Note that 1 ppm of a gas in a 10-m gas cell is 10 ppm-m.

Method 301: Reference Method Comparison

EPA Method 301 (Sections 5.2 and 6.2) allows the validation of a proposed test method (here, FTIR measurements of HCl) by a pair-wise comparison between the results of a simultaneously-performed EPA reference method (here, EPA Method 26). See Figure 6. A complete description of the validation requirements and calculations is given in Reference 1; only a summary is provided in this work. Briefly, the results S_R of nine test runs using the reference method are compared with results S_P of the proposed method and the relative standard deviation SD_P of the set of nine differences ($S_R - S_P$) is compared via an F-test to the published standard deviation of the reference method (here, $SD_R = 3.2\%$ at 15.3 ppm and $SD_R = 6.2\%$ at 3.9 ppm). Next, the bias B and a correction factor CF for the proposed method are calculated and a t-test is applied to determine whether the bias of proposed method is statistically significant. The criteria required for validation of the proposed method are: a) $SD_P \leq SD_R$ and, when the bias is found to be significant; and b) $0.9 \leq CF \leq 0.1$. Table 2 presents the nine pairs of concentration results used in these calculations.
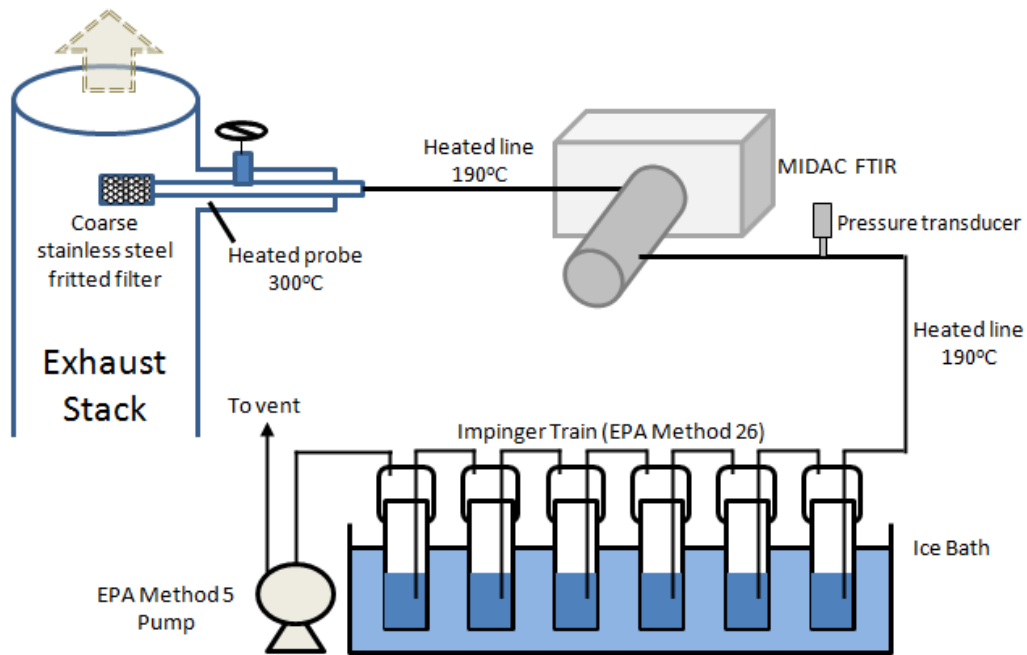
Figure 6. Validation of proposed test method using FTIR and EPA Method 26.

TABLE 2. METHOD 301 VALIDATION RESULTS (PPM)

SAMPLE PAIR	M 320 RESULTS S_R	FTIR RESULTS S_P
1	8.54	8.22
2	9.42	10.96
3	11.20	12.96
4	22.10	20.04
5	22.60	21.30
6	22.90	22.81
7	23.10	23.20
8	38.60	36.69
9	68.80	64.29

The paired results of Table 2 yield relative standard deviation SD_P = 4.3%, which lies between the two values (3.9% and 6.2%) published by EPA for the reference method. Although the t-test shows that the proposed method bias (2.0 ppm) is significant (t = 2.148), the F-test (F = 0.108) indicates good precision, and the correction factor (CF = 1.031) falls in the acceptable range $0.9 \leq CF \leq 1.1$.

METHOD 320: Dual Instrument Spiking Validation
EPA Method 320 (Reference 2, Section 13) allows validation of FTIR-based measurements by a pair-wise comparison between the results of two independent FTIR systems. One of these systems must provide the "native" (un-spiked) concentrations in 12 independent samples, and the other must provide simultaneous measurements of

samples which have been dynamically spiked to provide a calculable change in the analyte concentrations. The means of the spiked results and calculated spiked levels provide a bias estimate for the FTIR measurements, and a t-test is applied to the 12 differences in these values measurements to determine whether the bias is significant. If the bias is found significant, a correction factor is calculated and must be in the range $0.7 \leq CF \leq 1.3$.

In this work, one of the two FTIR spectrometers (Instrument A) was used to collect and analyze 12 unspiked gas samples. Simultaneously, Instrument B analyzed spiked samples collected from the same outlet sample port. Spike gas was introduced into the Instrument B sampling system by injecting gas from a cylinder standard of 86.2 ppm HCl and 5.03 ppm SF_6 (balance N_2) directly into the sample probe. The spike gas flow rate was adjusted (by monitoring the observed SF_6 concentration) so that the spike gas represented 10% to 20% of the total Instrument B sample flow rate. Table 3 presents the HCl and SF_6 results of these measurements for the spiked and unspiked samples.

Table 3. Method 320 Dual-Instrument Spiking Results (ppm)

SAMPLE PAIR	S_S (HCL)	S_U (HCL)	S_S (SF_6)
1	13.1	7.26	0.517
2	13.4	7.45	0.516
3	13.4	7.43	0.519
4	13.4	7.24	0.518
5	13.2	7.10	0.516
6	13.4	7.41	0.519
7	13.4	7.53	0.521
8	13.4	9.00	0.521
9	13.7	8.92	0.521
10	13.5	7.81	0.522
11	13.0	7.12	0.521
12	13.6	7.36	0.516
MEAN	13.4	7.62	0.520
STDEV	0.18	0.62	

From the mean of the S_S (SF_6) values and the cylinder SF_6 value concentration, the expected mean spiked concentration is CS = 16.5 ppm; the actual mean spiked concentration is 13.4, so the bias in the proposed method is B = 3.1 ppm. The t-test using the standard deviations of the values $S_S - S_U$ yields t = 5.76, indicating that a correction factor is required; the correction factor is

$$CF = [1 + B/CS]^{-1} = 1.236 \tag{1}$$

This value falls within the allowed range ($0.7 \leq CF \leq 1.3$).

Method 320: Single Instrument Spiking Validation

EPA Method 320 (Reference 2, Section 13) also allows validation of FTIR-based measurements by a pair-wise comparison between the results of a single FTIR system. The procedures and analyses are identical to those described above for the dual-instrument validation, except that the spiked-unspiked sample pairs are the results of sequential measurements on a single system (rather than simultaneous measurements on a pair of system). Table 4 presents the HCl and SF_6 results of these measurements for the spiked and unspiked samples.

Table 4. Method 320 Single-instrument Spiking Results (ppm)

SAMPLE PAIR	S_S (HCL)	S_U (HCL)	S_S (SF_6)
1	14.2	8.83	0.517
2	15.3	8.73	0.531
3	15.1	8.91	0.523
4	14.6	9.86	0.517
5	13.5	9.45	0.517
6	13.8	9.06	0.523
7	13.8	8.51	0.525
8	13.9	7.88	0.525
9	13.9	8.79	0.523
10	12.9	9.46	0.520
11	13.5	8.89	0.523
12	13.9	8.40	0.523
MEAN	14.0	8.90	0.522
STDEV	0.66	0.51	

From the mean of the S_S (SF_6) values and the cylinder SF_6 value concentration, the expected mean spiked concentration is CS = 17.6 ppm; the actual mean spiked concentration is 14.0, so the bias in the proposed method is B = 3.6 ppm. The t-test using the standard deviations of the values S_S – S_U yields t = 4.19, indicating that a correction factor is required; the correction factor is (see Equation 1) 1.257, which falls within the allowed range ($0.7 \leq CF \leq 1.3$).

Minimum Detectable Limits

The MDL is a critical parameter for any type of low-concentration analysis. A study according to ASTM D6348-98 was performed looking at the noise levels in the baseline of the MIDAC I-2000 FTIR spectrometer using a heated 10-meter pathlength gas cell in the presence of up to 20% water vapor. Under these conditions, the MDL for HCl was 0.150 ppm. Though not required by the ASTM method, a bias (average of the standard deviations of each measurement) was added to yield a more conservative 0.263 ppm MDL. Detection limits may be improved by using indium arsenide or indium antimonide detectors, though this would rule out analysis of compounds with showing absorbance only below 2000 cm^{-1}.

Conclusion

FTIR spectroscopy has been validated by direct comparison with accepted EPA Methods for the analysis of HCl at levels of less than 1 ppm in the presence of moisture, making this a suitable approach for use with incinerators and cement kilns. The principles established in EPA Methods 320 and 321 have been developed specifically for the analysis of HCl in Portland cement kilns.

References

1.   EPA Test Method 301, "Validation of Pollutant Measurement Methods from Various Waste Media", U.S. Code of Federal Regulations (40 CFR 61, Appendix B).

2.   EPA Test Method 320, "Measurement of Vapor Phase Organic and Inorganic Emissions By Extractive FTIR Spectroscopy", U.S. Code of Federal Regulations (40 CFR 61, Appendix B).

3.   EPA Test Method 26, "Determination of Hydrogen Chloride Emissions from Stationary Sources", U.S. Code of Federal Regulations (40 CFR 61, Appendix B).