



AP-157

VALIDATION STUDY OF FTIR-BASED EMISSIONS MEASUREMENTS AT A MUNICIPAL WASTE COMBUSTOR

Grant M. Plummer, Ph.D.
Special Projects Manager
Enthalpy Analytical, Inc.
2202 Ellis Road, Suite A
Durham, NC 27703

Peter Zemek, Ph.D.
Applications Manager
MIDAC Corporation
130 McCormick Ave #111
Costa Mesa, CA 92626

KEYWORDS

FTIR Spectroscopy, Emissions Measurements, Method Validation, HCl,
Relative Accuracy, RATA, CO, SO₂, NO

ABSTRACT

EPA Test Methods 301 and 320 include statistical techniques for validating sampling methods in specific gas matrices. Several of these techniques were used to analyze extractive FTIR data collected at a municipal solid waste incinerator and to validate the method for hydrogen chloride (HCl) measurements. FTIR results for carbon monoxide (CO), sulfur dioxide (SO₂), and nitric oxide (NO) were also compared to measurements recorded by the facility's continuous emissions monitors (CEMs). Presented are discussions of the equipment, spectral analyses, and statistical comparisons of the various test methods.

INTRODUCTION

The work described here was performed in October, 2004, at two sampling locations of a municipal waste combustor. The major goal of the study was to validate extractive Fourier transform infrared (FTIR) spectrometry for measurements of gaseous hydrogen chloride (HCl) as described in Environmental Protection Agency (EPA) Test Methods 301¹ and 320². Three different validation procedures were successfully performed; they were direct comparisons with EPA's "manual" Test Method 26³, "single instrument" dynamic spiking, and "dual instrument" dynamic spiking. A secondary goal of the study was the comparison of CO, NO, and SO₂ results obtained using the standard CEMs installed at the facility to those obtained using FTIR techniques. Four of the six Relative Accuracy Test Audits (RATAs) performed for these criteria pollutants were successful according to the statistical criteria required by EPA⁴; the average measured analyte concentrations for those (two) audits which failed were at the extremes of the CEM and FTIR instrument calibration ranges. A complete description of the method requirements and calculations is given in References 1 through 4; for brevity, only summaries are provided in this work. The referenced methods are available at the website <http://www.epa.gov/ttn/emc/promgate.html>.

TEST LOCATIONS AND EQUIPMENT

TEST FACILITY

The test facility is a typical municipal waste combustor/generating station utilizing refuse-derived fuel (RDF). The plant consists of several independent "units," two of which (referred to as "Unit 1" and "Unit 2" below) 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.

SAMPLING SYSTEMS

The sample streams passed through heated probe assemblies, heat-traced (~350°F) Teflon™ samples line, 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™, Type 316 stainless steel, and Teflon™. 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. MCT detectors were used for the testing described here. In all cases, the detectors were cooled with liquid nitrogen 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 are made of polished nickel in order 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 181° C; the elevated temperature prevents gas condensation within the cell and minimizes analyte adhesion to the cell walls and mirrors. The volumes of the absorption cells are 2.0 liters, so at a sample gas flow rate 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.

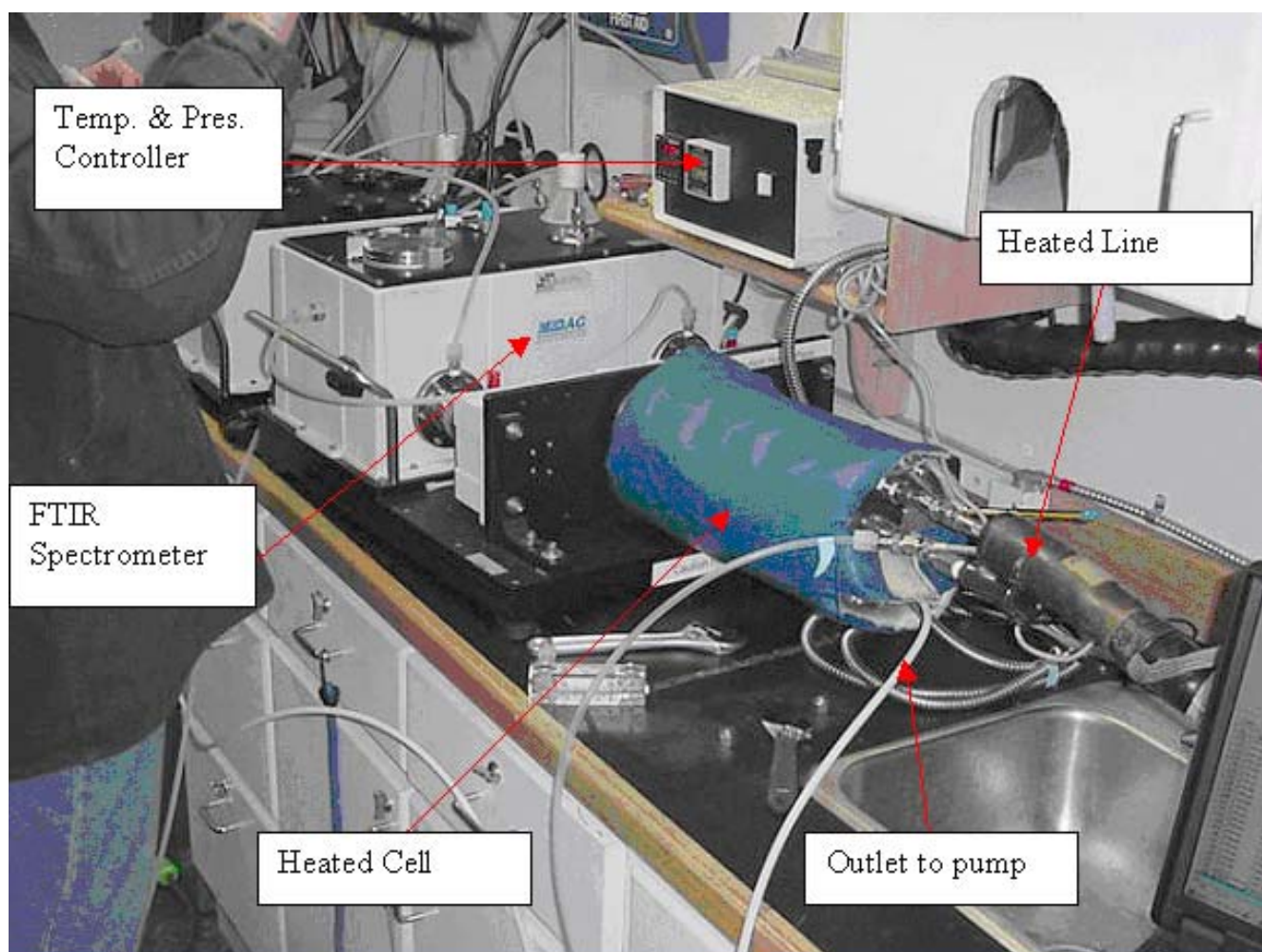


FIGURE 1. TYPICAL FTIR SPECTROMETER SYSTEM DURING TESTING

FTIR SPECTRAL ANALYSES

The program AutoquantPro™ (hereafter “AQ,” version 4.0.0.111, ©MIDAC Corporation, 2004) was used to collect and analyze all the infrared field data. The program 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 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 using nitrogen gas. 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 FTIR systems. A cylinder of ethylene in nitrogen (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 SF₆ (balance nitrogen). Details of the “classical least squares” mathematical comparison employed are described in Reference 5. Using both a NIST-calibrated mass flow controller and standard barometric techniques, the reference samples were made by diluting the HCl/SF₆ standard gas to four lower volumetric concentrations. The absolute HCl concentration of the cylinder standard was determined in Enthalpy’s laboratory according to the sampling and analytical procedures of EPA Method 26; only the relative SF₆ concentrations are required for the validation procedures described below, so the SF₆ cylinder concentration was not independently confirmed. Concentrations of three other analytes (CO, SO₂, and NO) were also determined using quantitative FTIR reference libraries prepared in Enthalpy’s laboratory, on Instrument B, from barometric dilutions of certified calibration gas standards.

Table 1 presents the infrared wavenumber (cm⁻¹) analytical ranges and concentration-path length (ppm-meter) limits of the reference libraries employed to date. Spectra representing the absorbance interferences from water and carbon dioxide were also employed as required over these same regions.

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.

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). Briefly, the results S_R of nine one-hour test runs using the reference method are compared to the corresponding results S_P of the proposed method. Next, a bias B and a correction factor CF for the proposed method are calculated. A t-test is applied to determine whether the bias of proposed method is statistically significant, and the relative standard deviation SD_P of the set of nine corrected differences ($S_R - S_P$) is compared via an F-test to the published standard deviation of the reference method³ (here, $SD_R = 3.2\%$ at 15.3 ppm and $SD_R = 6.2\%$ at 3.9 ppm). The criteria required for validation of the proposed method are a) $SD_P \leq SD_R$ and b) $0.9 \leq CF \leq 0.1$. Table 2 presents the nine pairs of concentration results and the (uncorrected) absolute differences used in these calculations. All these results presented in this section were calculated on a “dry, 7% O₂” basis using the Method 26 results for H₂O and O₂.

TABLE 2. METHOD 301 VALIDATION RESULTS (PPM)

SAMPLE PAIR	M 26 RESULTS S_R	FTIR RESULTS S_P	ABS($S_R - S_P$)
1	8.5	8.2	0.3
2	9.4	11.0	1.6
3	11.2	13.0	1.8
4	22.1	20.0	2.1
5	22.6	21.3	1.3
6	22.9	22.8	0.1
7	23.1	23.2	0.1
8	38.6	36.7	1.9
9	68.8	64.3	4.5
MEANS	25.3	24.5	1.5

Although the t-test shows that the proposed method bias ($B = 2.0$ 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 $0.9 \leq CF \leq 1.1$. The (corrected) differences between the paired results of Table 2 yield a relative standard deviation $SD_p = 4.3\%$, which lies between the two published values (3.9% and 6.2%) of the reference method.

METHOD 320: DUAL INSTRUMENT SPIKING VALIDATION

EPA Method 320 (Reference 2, Section 13) allows validation of FTIR-based measurements by a pairwise comparison between the results of two independent FTIR systems. One of these systems must provide the “native” (or “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. Briefly, 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 lie 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 un-spiked 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 SF₆ (balance nitrogen) directly into the sample probe; the spike gas flow rate was adjusted (by monitoring the observed SF₆ concentration) so that the spike gas represented 10% to 20% of the total Instrument B sample flow rate. Table 3 presents the HCl and SF₆ results of these measurements for the spiked and un-spiked samples. The results

presented in this section are “wet-basis” concentrations - that is, they have not been corrected for the presence of water vapor and oxygen.

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
MEANS	13.4	7.62	0.520

From the mean of the S_S (SF₆) values and the cylinder SF₆ 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 CF = 1.236 factor is required; this value falls within the allowed range (0.7 ≤ CF ≤ 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/un-spiked 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 SF₆ results of these measurements for the spiked and un-spiked samples. The results presented in this section are “wet-basis” concentrations - that is, they have not been corrected for the presence of water vapor and oxygen.

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
MEANS	14.0	8.90	0.522

Briefly, from the mean of the S_S (SF₆) values and the cylinder SF₆ 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 CF = 1.257 is required; this correction factor falls within the allowed range (0.7 ≤ CF ≤ 1.3).

RELATIVE ACCURACY TEST AUDITS

The FTIR spectra recorded during the Method 301 validation procedures described above were also analyzed for the presence of CO, NO, and SO₂. The FTIR – based concentrations of these compounds were corrected for the water vapor and oxygen content of the sample stream (as determined by the concurrent EPA Method 26 tests) and compared to the corresponding results of the two CEM systems operated by the facility. As required during the RATAs performed periodically on each unit⁴, the one-minute concentration averages of the two independent systems (a single FTIR spectrometer, and one set of three single-component gas analyzers) were obtained over nine 21-minute test periods, for each unit and for each analyte. Table 5 (Unit 1) and Table 6 (Unit 2) present the FTIR-based and CEM-based average concentration values over selected 21-minute subsets (“runs”) of the available data.

The nine pairs of run-average concentrations, for each analyte and each unit, were then mathematically compared as prescribed by Reference 4. Briefly, the mean absolute difference between the FTIR-

based results and those of the facility CEM systems was calculated, as well as both the standard deviations in those absolute differences and a related confidence coefficient. Both an “Absolute Relative Accuracy“ (ARA, based on the run-averaged results of the reference method) and a “Standard-Based Relative Accuracy” (SRA, based on the assumed emissions standards, taken as 100 ppm, 180 ppm, and 30 ppm for the compounds CO, NO, and SO₂, respectively) were calculated for each analyte. Each compound passes the audit, for a specific unit, if either ARA ≤ 20% or SRA ≤ 10%.

TABLE 5. CEM AND FTIR RUN-AVERAGE RESULTS FOR UNIT 1 (PPM)

RUN	CO		NO		SO ₂	
	CEM	FTIR	CEM	FTIR	CEM	FTIR
1	59.8	54.1	191	179	26.5	23.9
2	68.8	68.2	187	177	35.6	32.3
3	57.1	52.5	189	181	28.6	21.1
4	53.9	46.5	199	183	45.9	46.5
5	54.8	49.6	198	179	36.3	39.2
6	51.9	48.0	200	180	43.1	47.4
7	56.0	53.0	193	180	26.5	25.8
8	55.1	42.3	204	183	21.6	23.5
9	62.1	60.4	203	182	22.1	25.0

TABLE 6. CEM AND FTIR RUN-AVERAGE RESULTS FOR UNIT 2 (PPM)

RUN	CO		NO		SO ₂	
	CEM	FTIR	CEM	FTIR	CEM	FTIR
1	64.6	37.9	196	189	4.3	13.8
2	66.3	41.5	191	184	4.3	15.7
3	65.5	39.6	190	182	5.5	13.7
4	74.3	51.6	236	196	18.9	8.5
5	80.0	64.7	226	199	19.9	9.5
6	104	94.0	219	192	21.2	14.3
7	72.5	53.7	195	186	19.6	15.8
8	86.4	71.0	187	185	31.0	26.0
9	123	123	222	187	29.3	23.7

In the current case, Reference 4 provides no clear guidance as to which system (CEM or FTIR) is to be regarded as the “reference” and which as the “facility” method. The results quoted below are based on the assumptions that the CEM-based results comprise the “reference” system and that the FTIR-based results are those of the “facility” system. For the data collected during this work, this conservative assumption leads to the largest possible ARA and SRA values, but, as it turns out, affects none of the “pass/fail” audit results cited below. Table 7 presents the RATA results obtained for the two units, averaged over all nine runs. Each set of results was obtained using a separate pair of FTIR-CEM units; gas samples for each of the four analytical systems were supplied by four separate sampling systems.

As mentioned above, the audit is passed if either $ARA \leq 20\%$ or $SRA \leq 10\%$. Of the six sets of results presented in Table 7, four meet this criterion. Though it is not possible to draw any definitive conclusions based on the available data, the following points are of possible interest:

- All three compounds passed the audit for Unit 1, and on Unit 2 only one (NO) passed.
- Of the four passing results, only one – that for CO on Unit 1 – passes the audit on the basis of the “Standard-Based Relative Accuracy” (SRA).
- Three passing results (NO on both Units and SO₂ on Unit 1 only) are based on only the “Absolute Relative Accuracy” (ARA) value.
- For three of the four passing results (NO on both Units and SO₂ on Unit 1), the average FTIR concentrations fall within the FTIR calibration range.
- For both failing results (CO and SO₂ on Unit 2), the mean FTIR results fall outside the ppm calibration range.
- If the emission standard values for CO and SO₂ were 244 and 101 ppm, respectively (rather than 100 ppm and 30 ppm), then the results for all three compounds and both Units would meet the audit requirements.

TABLE 7. RATA RESULTS AVERAGED OVER ALL RUNS

PARAMETER	UNIT 1			UNIT 2		
	CO	NO	SO2	CO	NO	SO2
EMISSION STANDARD (PPM)	100	180	30.0	100	180	30.0
O ₂ (%)	9.9	9.9	9.9	11.2	11.3	11.3
H ₂ O (%)	19.0	18.8	18.8	16.1	16.0	16.0
FTIR RESULT (PPM)	57.7	196	31.8	81.8	207	17.3
CEM RESULT (PPM)	52.7	180	31.6	64.1	189	15.9
ABS. VALUE [CEM – FTIR] (PPM)	5.0	16	3.0	17.8	18	8.0
SRA	7.7%	10.8%	15.2%	24.4%	16.2%	33.6%
AUDIT STATUS – SRA	PASS	FAIL	FAIL	FAIL	FAIL	FAIL
ARA	14.6%	10.8%	14.4%	29.8%	14.1%	58.2%
AUDIT STATUS – ARA	PASS	PASS	PASS	FAIL	PASS	FAIL
OVERALL AUDIT STATUS	PASS	PASS	PASS	FAIL	PASS	FAIL
UPPER FTIR CAL. (PPM)	52.2	452	87.2	50.3	439	84.9
LOWER FTIR CAL. (PPM)	12.7	111	21.3	12.2	108	20.7

CONCLUSION

Three validation studies of FTIR spectrometry based on EPA reference methods indicate the suitability of the technique for the measurement of gaseous HCl in the emissions from municipal waste combustors using refuse-derived fuel. The three validation techniques were a) direct comparisons with EPA Method 26 according to EPA Method 301, b) dual-FTIR spiking procedures according to EPA Method 320, and c) single-FTIR spiking procedures according to EPA Method 320. Significant method bias was indicated in every case, but in all three cases the associated correction factors lie between 1.031 and 1.257, and all three fall within the limits allowed by the EPA validation procedures. The results of six relative accuracy test audits performed using the same FTIR spectra and data from two of the facility's CEM systems were mixed; the CO, NO, and SO₂ channels from one system (Unit 1) passed the audit requirements, while for Unit 2 only the NO results met the audit criteria.

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).
4. EPA, "CEMS Performance Specification 2 for SO₂ and NO_x" and "CEMS Performance Specification 4 for CO", U.S. Code of Federal Regulations (40 CFR 61, Appendix B).
5. D.M. Haaland, R.G. Easterling and D.A. Vopicka, "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Samples," Appl. Spectrosc. 39(1), 1985, pp.73-84.