Formaldehyde Emissions from a Siemens-Westinghouse 501F Combustion Turbine with Lean Pre-Mix Combustors, with SCR and CO Catalysts

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Technical Update, February 2003

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PRODUCT DESCRIPTION

This interim report presents a summary of formaldehyde emission measurements conducted at full operating load from a Siemens-Westinghouse 501F gas-fired combustion turbine with lean pre-mix low-NO_x combustors, and a selective catalytic reduction (SCR) and carbon monoxide (CO) catalysts.

Results & Findings

Formaldehyde concentrations, as measured by the California Air Resources Board (CARB) Method 430 using DNPH (dinitrophenylhydrazine) reagent, averaged 9 ppb in the turbine exhaust (before the SCR and CO catalysts) and 5 ppb at the stack. As measured by Fourier Transform Infrared (FTIR) Spectroscopy, formaldehyde concentrations averaged 47 ppb at the turbine exhaust and 42 ppb at the stack – over the same time periods. This discrepancy between the two methods could not be resolved based on the limited measurements and methods comparison. Although both sets of data met established QA/QC criteria, it is not known which, if either, method is providing accurate formaldehyde measurements.

Challenges & Objectives

The objectives of this study are:

- Characterize formaldehyde emissions from “utility-size” combustion turbines, with state-of-the-art lean premix low-NO_x combustors.
- Evaluate the impact of CO catalyst on formaldehyde removal.
- Compare the FTIR technique to the conventional DNPH reagent-based, manual CARB Method 430.

Applications, Values & Use

The results would assist in permitting new combustion turbines, as well as to support development of Maximum Achievable Control Technology (MACT) standards by the U.S. Environmental Protection Agency.

EPRI Perspective

These results summarize formaldehyde emissions data from a lean premix combustion turbine operating at full operating load. The results from the FTIR and CARB 430 methods do not agree. The QA/QC for both methods do not indicate any issues or concerns, thus it is not possible to determine which set of results accurately represents formaldehyde emissions.

Previous studies by Gas Research Institute and American Petroleum Institute have also indicated similar – but much smaller - discrepancies between FTIR and CARB Method 430. However these studies do not explain the differences in the two methods.

The intent of this report is to provide timely formaldehyde emissions data to support the development of a MACT standard. It is important to note that additional measurements were conducted during this study, but these results are still be analyzed and therefore are not included in this report. This includes the following emission measurements:

- VOCs (volatile organic compounds) by FTIR as well as by EPA TO-14A (canisters).
- Reduced operating load conditions.
- Transient conditions such as start-up and shutdown.

A comprehensive summary report is planned for Summer 2003. The reader is encouraged to follow-up when these results are available.

Additional measurements are planned to characterize organic air toxic emissions at other combustion turbine designs including a GE Frame 7FA.

Approach

Investigators measured formaldehyde emissions at the turbine exhaust and downstream of SCR and CO catalysts using two different sampling and analytical methods – FTIR and CARB 430.

Keywords

Air toxics, formaldehyde, combustion turbines, FTIR, CARB 430, HAPs, CO catalyst

ABSTRACT

Formaldehyde measurements were conducted at full operating load from a Siemens-Westinghouse 501F gas-fired combustion turbine with lean pre-mix low- NO_x combustors, and a selective catalytic reduction (SCR) and carbon monoxide (CO) catalysts. The California Air Resources Board (CARB) Method 430 using DNPH (dinitrophenylhydrazine) reagent and Fourier Transform Infrared (FTIR) spectroscopy were employed. Formaldehyde emissions using CARB Method 430 averaged 9 ppb in the turbine exhaust (before the SCR and CO catalysts) and 5 ppb at the stack. The CARB Method 430 results did not compare well with the FTIR results, which averaged 47 ppb at the turbine exhaust and 42 ppb at the stack – over the same time periods. The QA/QC for both methods do not indicate any issues or concerns, thus it is not possible to determine which, if either, set of results accurately represents formaldehyde emissions.

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1

INTRODUCTION

The Avogadro Group, LLC (Avogadro) and URS -Radian Corporation (URS) were contracted by the Electric Power Research Institute (EPRI) to perform a series of emission tests on a combined-cycle gas turbine with lean pre-mix low-NO_X combustors. The unit tested included a Siemens-Westinghouse 501F combustion turbine with lean pre-mix low-NO_X combustors, a heat recovery steam generator (HRSG), and selective catalytic reduction (SCR) and oxidation catalysts.

Tests were conducted at the gas turbine exhaust (i.e. upstream from any catalysts) and at the HRSG stack. The testing program was performed to meet several objectives, the most important of which were:

- To provide data for use by EPRI and EPA in evaluating MACT standards for gas turbines.
- To characterize emissions during operation at base load and lower load conditions, and during transients between loads.

URS provided monitoring of concentrations of formaldehyde, VOC and other gases using a Fourier Transform Infrared (FTIR) spectroscopy in accordance to pertinent sections of EPA Test Method 320 “Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy.”

Avogadro provided the “conventional” reference method sampling and analysis for measurement of formaldehyde and VOC, as well as continuous monitoring of NO_X, CO, Total Hydrocarbon, O_2 and CO_2 concentrations.

The tests were conducted on October 9 through 14, 2002. The Avogadro test team included Kevin Crosby and Jimmy Chan. The URS team included Walt Gray and Steve Hill. Process operations and data collection were coordinated by Leonard Angello of EPRI.

The results of the tests are presented in this report, which includes descriptions of the facility and the sampling locations, descriptions of the testing procedures, calculations and results, and a summary of quality assurance procedures.

2
EMISSION SOURCE INFORMATION

Facility Description

The gas turbine unit is a Siemens-Westinghouse 501F combustion gas turbine with dry low-NO_x combustors, and with a heat recovery steam generator (HRSG). The HRSG includes supplementary duct burners (with low-NO_x burners) for additional steam production, and SCR and oxidation catalysts for control of emissions.

Test Site Description, Gas Turbine Exhaust Duct

The gas turbine exhausts into the HRSG through a horizontal, rectangular duct that expands from 13 feet tall by 13 feet wide to 14 feet tall by 15 feet wide over a length of 13 feet (approximate dimensions). There is a single sampling port on the top of the duct. The port is a 1½-inch pipe section with a cap, and is located near the centerline of the duct. Access to the port was gained by ladder to a temporary scaffold across the top of the duct, and the probes were inserted vertically. A sketch of the duct layout is included in Figure 2-1.

A total of 8 sampling traverse points were located in the vertical cross-section of the duct according to EPA Method 1.

Test Site Description, Turbine / HRSG Stack

The turbine/HRSG exhausts through a vertical, cylindrical stack that is 99 feet tall. The stack has an inside diameter of 19 feet and has four sampling ports, located 90 degrees apart in the same horizontal plane. The ports are 6-inch pipe sections with flanges (150 psi rating type) and caps. Access to the ports is by stairway to the top of the HRSG, then by ladder the last 16 feet to a permanent platform approximately 84 feet above ground level. The ports are approximately 32 feet (1.7 stack diameters) downstream from (or above) the HRSG duct transition to the stack, and 9 feet (0.5 diameters) upstream from the top of the stack. A sketch of the stack layout is included in Figure 2-2.

A total of 12 sampling traverse points were located according to EPA Method 1 for a traverse to determine the amount of stratification of the stack gases. Three points were used in each of four sampling ports.

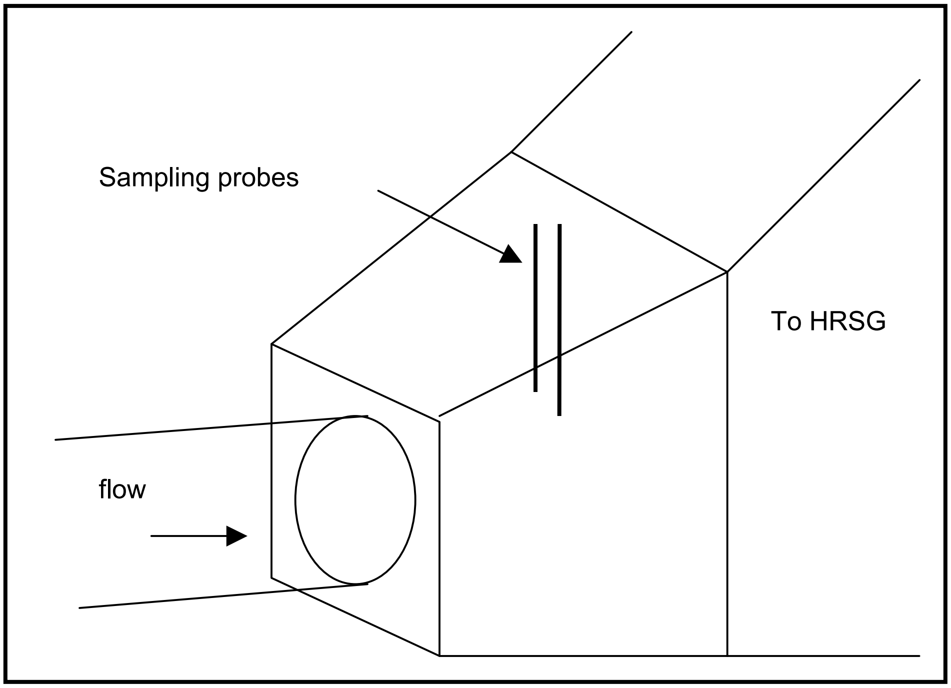

Figure 2-1
Sampling Location, Gas Turbine Exhaust

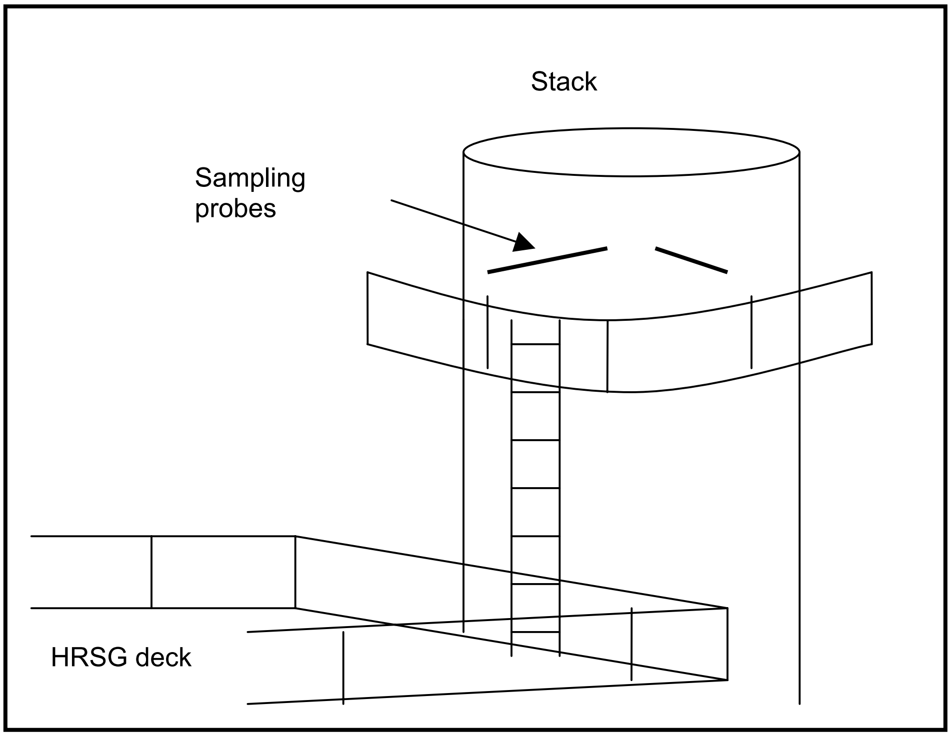

Figure 2-2
Sampling Location, HRSG Stack

3

TEST PROGRAM DESCRIPTION

Program Objective

The testing program was performed to meet several objectives, the most important of which were:

- To provide data for use by EPRI and EPA in evaluating MACT standards for gas turbines.
- To characterize emissions during operation at base load and lower load conditions, and to provide data using two test methods that are proposed by EPA for use in determining compliance with the MACT standard.

These objectives were met by testing during operation of the unit at base load. The second objective was enhanced by using both instrumental (FTIR) and "conventional" (DNPH/HPLC, GC, etc.) reference methods for measuring the emissions of formaldehyde (H_2CO) and other volatile organic compounds (VOC). The monitoring and testing of formaldehyde and VOC emissions were of critical importance in meeting the objectives. The monitoring and testing of the emissions of other compounds were of secondary importance; these compounds included NO_X (NO and NO_2), CO, NH_3, CH_4, H_2O and CO_2.

Avogadro provided measurements by "conventional" test methods:

- Sampling and analysis for formaldehyde and VOC emissions using CARB Method 430 and EPA Method TO-14A,
- Monitoring of concentrations and emissions of NO_X, CO, and total hydrocarbon using standard continuous emission monitoring analyzers,
- Monitoring of concentrations of O_2 and CO_2 using standard continuous emission monitoring analyzers.

URS provided measurements by FTIR:

- Monitoring of formaldehyde and VOC concentrations,
- Monitoring of concentrations of NO, NO_2, CO, CH_4, NH_3, and H_2O,
- Monitoring of concentrations of CO_2 by FTIR, and of O_2 with a standard continuous emission monitoring analyzer.

This interim report primarily presents the results of the formaldehyde measurements at full operating load, and is being issued to assist in the MACT development. A comprehensive final report is expected in Summer 2003 which would summarize the VOC measurements, as well as the transient and low operating load tests, after the data analyses have been completed.

Process Conditions

The testing program was conducted during operation of the gas turbine at base load, with no duct burner firing in the HRSG. Tests were also conducted during unit shutdown, startup, and low load operations. The results of those tests are not presented in this report. The process conditions were determined and controlled by the facility’s operators. Coordination of the testing and operation schedule was provided by EPRI.

Test Schedule

The test schedule was adapted to fit the operation schedule of the gas turbine as shown in Table 3-1.

Table 3-1
Testing Schedule

1. Date	2. Testing Activity, Reference Methods	3. Testing Activity, FTIR
October 9, 2002	1117-1135 Preliminary Traverse 1500-1800 Base Load Test, GT Exhaust 1505-1805 Base Load Test, GT / HRSG	1522-1810 Base Load Test, GT Exhaust 1953-2339 Base Load Test, GT Exhaust
October 9 to 10	2345-0107 Shutdown Test, GT Exhaust (NO_x, CO, THC only)	2344-0130 Shutdown Test, GT Exhaust
October 10	Unit Down	Unit Down
October 11	1858-2053 Startup Test, GT Exhaust (NO_x, CO, THC only) 1927-1932 Startup Formaldehyde Test 1950, 1954, 1958 Startup VOC Tests 2004-2009 25 MW “Level-off” Formaldehyde Test 2242-0042 95 MW Test, GT Exhaust 2236-0036 95 MW Test,, GT / HRSG	1858-2053 Startup Test, GT Exhaust 2058-0901 95 MW and Base Load Test, GT Exhaust
October 12	1450-1750 Base Load Test, GT Exhaust 1445-1745 Base Load Test, GT / HRSG 1817-2117 Base Load Test, GT Exhaust 1811-2111 Base Load Test, GT / HRSG	1420-2359 Base Load Test, switching between GT Exhaust and HRSG Stack
October 13	--	0000-1429 Base Load Test, switching between GT Exhaust and HRSG Stack 2139-2359 Base Load Test, HRSG Stack
October 14	--	0000-1007 Base Load Test, HRSG Stack

4
REFERENCE METHOD TESTING

Overview

The testing program conducted by Avogadro included measurement of the emissions of criteria pollutants and toxic air contaminants. The tests included the measurement of gaseous emissions from the gas turbine exhaust duct and from the gas turbine/HRSG stack. Some samples were taken from both locations concurrently, but most were taken from one location or the other.

Avogadro provided measurements by “conventional” test methods:

- Sampling and analysis for formaldehyde and VOC emissions,
- Monitoring of concentrations and emissions of NO_x, CO, and total hydrocarbons using standard continuous emission monitoring analyzers,
- Monitoring of concentrations of O_2 and CO_2 using standard continuous emission monitoring analyzers.

4.1 Test Methods

Avogadro used standard EPA or CARB reference methods for the measurements made during the program. A list of the test methods is provided in Table 4-1.

Table 4-1
Reference Test Methods and Detection Limits

Parameter	Reference Methods	Principle	Detection Limit
NO_x	EPA 7E	Chemiluminescent Analyzer	0.2 ppm vol dry
CO	EPA 10 (modified)	NDIR / Gas Filter Correlation Analyzer	0.2 ppm vol dry
Total Hydrocarbons	EPA 25A	Flame Ionization Detector Analyzer	0.2 ppm vol dry
O_2	EPA 3A	Electrochemical Cell Analyzer	0.05 % vol dry
CO_2	EPA 3A	NDIR Analyzer	0.05 % vol dry
Volumetric Flow Rate and Emission Rates	EPA 19	Calculated from Stoichiometric Fuel Factor and measured Fuel Flow	N/A
Formaldehyde	CARB 430	Absorption in DNPH solution, Analysis by HPLC	2 to 7 ppb vol dry (CARB DL 7 ppb vol dry) (CARB Reporting Limit 75 ppb vol dry)
Benzene	EPA TO-14A	Sampling into SUMMA Canister, Analysis by GC/FID/MS	0.3 ppb vol dry
Toluene, Ethylbenzene, *m* + *p* Xylenes *o*-Xylenes	EPA TO-14A	Sampling into SUMMA Canister, Analysis by GC/PID/MS	0.5 ppb vol dry 0.3 ppb vol dry 0.5 ppb vol dry 0.4 ppb vol dry

4.1.1 Gaseous Emissions / Diluent Gases

NO_x, CO, CO_2, and O_2 concentrations were quantified by means of an extractive continuous emission monitoring (CEM) system maintained in a mobile laboratory. The CEM system is comprised of four basic subsystems. These subsystems are: 1) the sample conditioning and delivery system, 2) the calibration gas system, 3) the electronic analyzers, and 4) the data recording and acquisition system.

The sample conditioning and delivery system includes components to extract a representative sample from the source, remove the moisture and particulate matter from the sample stream, and transport the sample to the analyzers. The primary components of this subsystem are: 1) A stainless steel or glass probe - heated or insulated as necessary to avoid condensation, 2) Teflon tubing - connecting the probe to the sample conditioner and the sample conditioner to the analyzer manifold - heated or insulated as necessary to avoid condensation, 3) sample conditioner - glass or stainless steel flasks immersed in an ice bath to remove the moisture from the sample gas stream, 4) vacuum pump - a leak-free pump with Teflon diaphragm to transport the sample gas through the system, 5) sample manifold - a distribution system, constructed of stainless steel and Teflon tubing, to direct sample gas to the analyzers, and 6) sample flow rate control - a series of rotameters, vacuum gauges and pressure gauges connected to the manifold used to maintain the appropriate sample flow rates.

The calibration gas system utilizes only US EPA Protocol One gases to verify the operation, linearity, and range settings of the electronic analyzers. The sample gas system allows for the introduction of the protocol gases to the analyzers either directly through the manifold (calibration error check - performed once daily) or through the sampling system (system bias check - performed with each run).

The electronic analyzers are rack mounted and are maintained in the mobile lab. The data recording and acquisition system is based on a digital system known as STRATA. It includes software for controlling the collection of calibration and emission monitoring data, and hardware for connection of the analyzer outputs to the recording system. Test results can be provided in three forms; on-site printouts of the digitized data, diskette recordings of the digitized data, and printouts of strip charts from the monitoring data.

4.1.2 Total Hydrocarbons (THC)

Concentrations of THC were monitored using a direct flame ionization detector (FID) analyzer according to EPA Method 25A. Sample was drawn from the sampling probe through a length of heated Teflon tubing by the analyzer’s internal heated pump. Calibration gases were introduced at the connection between the probe and the heated Teflon line.

4.1.3 Formaldehyde

The concentrations of formaldehyde were measured using CARB Method 430. Sample gas was drawn through DNPH solution in midget impingers at a known flow rate using a vacuum pump and a calibrated critical orifice. Field blank and field spike samples were taken in the same manner as the samples. The DNPH solution was prepared and analyzed by Air Toxics, Ltd. of Folsom, CA

The sample volume and sampling time for each test run was determined using the pre-test planning calculations of Method 430. The test runs at base load were 3 hours in duration and collected approximately 70 liters of sample gas. The test results were calculated at the blank-corrected value.

4.1.4 Volatile Organic Compounds (VOC)

Concentrations of volatile organic compounds were measured using EPA Compendium Method TO-14A. Samples were drawn into evacuated SUMMA canisters, which were shipped to the laboratory for analysis. The GC/FID/PID/MS analyses included benzene, toluene, ethylbenzene and xylenes (BTEX). The VOC results will be summarized in the final report planned for Summer 2003.

4.1.5 Volumetric Flow and Emission Rates

Emission rates were calculated in units of lb/MMBTU from the measured concentrations and fuel factors using EPA Method 19. The stack gas volumetric flow rates were calculated from the measured fuel flow rates. The EPA factor Fd (dscf/MMBTU at stoichiometric conditions), the stack gas O_2 concentration, and the fuel higher heating value was used in the flow rate calculations. Emission rates were calculated in units of lb/hr where applicable using the measured concentrations and the calculated volumetric flow rates. The daily emission rates were calculated assuming 24-hour operation.

4.1.6 Mobile Laboratory

For the purposes of this test program, Avogadro mobilized a mobile laboratory to the site for the testing period. The mobile lab is equipped with storage cabinets and the CEM system. There is sufficient room to work in the mobile van with spacious counter tops for sample recovery, calculation of results and completion of the sample chain of custody forms.

4.2 Test Results

The results of the emission tests are summarized in Tables 4-2 and 4-3. The tables present the results of the tests conducted during operation of the gas turbine at base load conditions. The symbol “<” denotes that the analyte was detected in some samples or fractions but not in all samples or fractions. The symbol “ND<” denotes that the analyte was not detected at the level stated, which represents the detection limit for that test run. For compounds that result below the detection limit, ½ the reported MDL was used for calculating the average concentrations.

Table 4-2
Emission Test Results, Conventional Test Methods (Criteria Pollutants)

Base Load	**Gas Turbine Exhaust**				**HRSG Stack**			
Test number	Run 1	Run 9	Run 10	**Avg**	Run 2	Run 7	Run 8	**Avg**
Date 2002	10-9	10-12	10-12	**--**	10-9	10-12	10-12	**--**
Start / Stop time	1117-1135	2012-2042	2111-2141	**--**	1658-1728	1607-1637	1643-1713	**--**
O_2, % volume dry	13.77	13.65	13.62	**13.68**	13.40	13.78	13.86	**13.68**
CO_2, % volume dry	N/A	4.132	4.095	**4.114**	4.314	4.071	4.094	**4.160**
Fuel flow, kscfh	1,939	1,936	1,936	**1,937**	1,939	1,938	1,938	**1,939**
Stack flow rate, dscfm	833,873	818,390	815,353	**822,539**	791,979	834,359	843,603	**823,313**
Turbine Gross Output, MW	155	160	160	**158**	155	161	161	**159**
Aqueous Ammonia Rate, Klb/hr	294	304	304	**301**	294	322	322	**313**
CO, ppm vol dry	0.7	1.1	1.0	**0.9**	<0.2	<0.2	<0.2	**<0.2**
ppm @ 15% O_2 dry	0.6	0.9	0.8	**0.8**	<0.2	<0.2	<0.2	**<0.2**
lb/hr	2.7	3.8	3.5	**3.3**	<0.7	<0.7	<0.7	**<0.7**
lb/day	64	92	83	**79**	<17	<17	<18	**<17**
lb/MMBtu	0.0014	0.0020	0.0018	**0.0017**	<0.0004	<0.0004	<0.0004	**<0.0004**
NO_x, ppm vol dry	34	35	33	**34**	3.2	3.2	3.3	**3.3**
ppm @ 15% O2 dry	28	28	27	**28**	2.5	2.7	2.7	**2.7**
lb/hr as NO_2	204	204	191	**200**	18	19	20	**19**
lb/day as NO_2	4900	4892	4582	**4792**	441	466	474	**460**
lb/MMBtu as NO_2	0.104	0.104	0.098	**0.102**	0.0094	0.0099	0.0101	**0.0098**
THC, ppm vol dry	--	2.2	<0.2	**1.2**	--	--	--	**--**
ppm @ 15% O_2 dry	--	1.8	<0.2	**0.9**	--	--	--	**--**
lb/hr as CH_4	--	4.5	<0.4	**2.4**	--	--	--	**--**
lb/day as CH_4	--	108	<9.8	**56**	--	--	--	**--**
lb/MMBtu as CH_4	--	0.0023	<0.0002	**0.0012**	--	--	--	**--**

Note: The symbol “<” denotes detection below the practical detection limit, which is the value shown.

Table 4-3
Emission Test Results, Conventional Test Methods (Hazardous Air Pollutants)

Base Load	**Gas Turbine Exhaust**				**HRSG Stack**			
Test number	Run 1	Run 9	Run 10	**Avg**	Run 2	Run 7	Run 8	**Avg**
Date, 2002	10-9	10-12	10-12	**--**	10-9	10-12	10-12	**--**
Start / Stop time	1500-1800	1450-1750	1817-2117	**--**	1505-1805	1445-1745	1811-2111	**--**
O_2, % volume dry	13.40	13.82	13.64	**13.62**	13.40	13.82	13.64	**13.62**
Fuel flow, kscfh	1,939	1,936	1,936	**1,937**	1,939	1,938	1,938	**1,939**
Stack flow rate, dscfm	791,979	834,359	818,390	**814,909**	791,979	834,359	818,390	**814,909**
Turbine Gross Output, MW	155	161	160	**159**	155	161	160	**159**
Aqueous Ammonia Rate, Klb/hr	294	322	304	**307**	294	322	304	**307**
Formaldehyde								
ppb vol dry (raw)	<10.4	21.3	7.8	**11.4**	9.5	4.1	<7.0	**5.7**
ppb @ 15% O_2 dry	<8.2	17.8	6.3	**9.4**	7.5	3.4	<5.6	**4.6**
lb/hr	<0.02	0.08	0.03	**0.04**	0.04	0.02	<0.03	**0.02**
lb/day	<0.9	2.0	0.7	**1.1**	0.9	0.4	<0.7	**0.5**
lb/MMBtu	<2.0E-5	4.3 E-5	1.5 E-5	**2.3 E-5**	1.8 E-5	0.8 E-5	<1.4 E-5	**1.1 E-5**

Note: The symbol "<" denotes less than the practical detection limit, which is the value shown. ½ of the detection limit was used for purposes of calculating an average.

5

FTIR MONITORING

Overview

The testing program conducted by URS included continuous emission monitoring using a Fourier Transform Infrared (FTIR) Spectrocopy. The tests included the measurement of gaseous emissions from the gas turbine exhaust duct or from the gas turbine/HRSG stack. There were no concurrent samples from both locations, as sample could be drawn from just one location at a time.

URS provided measurements by FTIR:

- Monitoring of formaldehyde and VOC concentrations,
- Monitoring of concentrations of NO, NO_2, CO, CO_2, CH_4, NH_3, and H_2O,
- Monitoring of concentrations of O_2 with a standard continuous emission monitoring analyzer.

5.1 Introduction

Testing at this facility consisted of monitoring a natural gas-fired combustion turbine at varying loads during the time-span of October 7th through the 14th. The analytes of most interest for this testing were formaldehyde (H_2CO) and the “BTEX” VOC compounds (benzene, toluene, ethylbenzene, and the o-, m-, p-xylenes). Testing for formaldehyde was conducted according to pertinent sections of EPA Test Method 320 “Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy.” The primary objectives of this testing were:

- Provide data for EPRI and the EPA for use in setting MACT standards for gas turbines.
- Compare FTIR and wet-chemistry based methodologies (i.e., CARB Method 430) for measuring formaldehyde and other volatile organic compounds.

Of critical importance in meeting these objectives were the monitoring of formaldehyde and VOC emissions from the gas turbine during normal (base load) operation and start-up and shutdown procedures. Of secondary importance was the monitoring of other compounds such as NH_3, NO_X [nitric oxide (NO) and nitrogen dioxide (NO_2)], methane (CH_4), and carbon monoxide (CO). The major constituents in combustion exhaust, water (H_2O) and carbon dioxide (CO_2), were also monitored via FTIR. To achieve these objectives, the following was accomplished:

- A laboratory study to document the performance of the FTIR system to monitor the analytes of interest and to determine the minimum detection limits (MDLs) for each.
- Data collection in accordance with EPA Method 320 guidelines to document the formaldehyde emissions from the gas turbine.
- Data collection using a sample conditioning system (for water and carbon dioxide removal) to monitor for the BTEX compounds.
- Develop a functioning FTIR analysis method to quantify all other constituents of interest.

Sampling of the exhaust gas stream was performed on a continuous basis using an extractive FTIR system. This sampling technique enables highly sensitive, real-time monitoring of all target compounds simultaneously. In addition to Method 320, pertinent sections of URS's ISO 9001 document "Protocol for Extractive FTIR Monitoring"[1] and its accompanying "Extractive FTIR System Checklist" were followed to ensure data were collected at a known quality. Descriptions of the FTIR method and calibration data obtained before continuous monitoring commenced at the test site, discussion of the validation results, sampling data collected, and the special considerations noted throughout testing are provided below.

5.2 Principles of Extractive FTIR Monitoring

Almost every chemical compound has a unique absorption pattern of infrared (IR) light that can be used to identify and quantify that species in a complex mixture of gases. As governed by Beer's Law, the magnitude of a compound's IR absorbance is directly proportional to the product of its concentration in the mixture and the sample cell optical path length. The extractive FTIR instrument is able to achieve parts-per-billion (ppb) detection levels because a cell is used that reflects the IR beam between a series of mirrors before it reaches the detector. The optical path that the gas sample is exposed to can then be set to a desired length before measurements are taken. The path length, once field calibrated, is an important parameter in the infrared spectrum analysis method used to determine compound concentrations.

5.2.1 Spectrum Analysis Method

An infrared spectrum analysis is performed by matching the features of an observed spectrum to those of reference standards. If more than one feature is present in the same region, a linear combination of references is used to match the compound features. The standards are scaled to

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[1] Radian International LLC, *Protocol for Extractive FTIR Monitoring.* DCN 96-133-403-01 Revision 1.0. Austin, Texas, Oct. 1996.

match the observed band intensities; this scaling also matches the unknown concentrations. The scaled references are added together to produce a composite that represents the best match with the sample. A classical least squares mathematical technique is used to match the standards' absorption profiles with those of the observed spectrum in specified spectral analysis regions. Compounds of interest and any known compounds expected to present spectral interference are included in the analysis region.

An infrared spectrum can be collected and analyzed in approximately one second, but data are typically averaged over a five-minute integration period to produce adequate signal-to-noise and ppb level detection limits.

5.2.2 Creating the Spectrum Analysis Method

The spectrum analysis method used for the turbine testing was developed by selecting the spectral regions and sub-regions that minimize interference from the primary IR absorbers (H_2O and CO_2, in this case) while also optimizing the detection of the target compounds. Typically, an analysis method will be iteratively refined by using it to analyze a representative set of infrared spectra, while varying the method. The optimum method is indicated when both the error bars and the bias on the individual compounds are minimized. Table 5-1 summarizes the references used in the method (described in terms of the compound's concentration and cell path length used when the reference was recorded). In addition to the compounds listed in Table 5-1, formic acid (HCO_2H) and hydrochloric acid (HCl) were also observed during the routine spectral analysis done as part post-test data QC.

Of the compounds listed in Table 5-1, all but H_2O, CO_2, and CO had periods where their concentrations fell below the detection limit of the FTIR. For those compounds, which were observed near the instrument's noise level, MDLs were calculated. This was achieved by analyzing sets of spectra from the turbine exhaust when only interferants were present (the compounds of interest were absent by spectral investigation). When applied to this series, the analytical method should return a set of values centered about zero. The MDL is then estimated by taking three times the standard deviation of that data scatter. If the data scatter is scattered about a non-zero value, it is indicative of a method bias and bias correction procedures are invoked. These field MDL results obtained for each target compound are provided below.

Table 5-1
FTIR Analysis Method Parameters

Analyte	**Reference Used**
CO (carbon monoxide)	50 ppm @ 10.0 m
CH_4 (methane)	2000 ppm @6.0 m
NO (nitric oxide)	248 ppm @ 10.8 m
NO_2 (nitrogen dioxide)	14 ppm @ 26 m
H_2CO (formaldehyde)	4.2 ppm @ 10.0 m
CH_3CHO (acetaldehyde)	50 ppm @ 6.7 m
CH_3OH (methanol)	48 ppm @ 13 m
C_7H_8 (toluene)	97 ppm @ 3.4 m
C_6H_6 (benzene)	100 ppm @ 3.4 m
C_8H_{10} (m-Xylene)	305 ppm @ 1.0 m
C_8H_{10} (o- Xylene)	313 ppm @ 1.0 m
C_8H_{10} (p- Xylene)	286 ppm @ 1.0 m
C_8H_9 (ethyl benzene)	17.7 ppm @ 3.6 m
NH_3 (ammonia)	33 ppm @ 26 m
Interferents:	
H_2O (Water)	9.92% @ 57.0 m
CO_2 (Carbon Dioxide)	4.0% @ 68.5 m

m = meters, ppm = parts per million

5.3 FTIR Procedures

5.3.1 Laboratory Evaluation

The objective of the laboratory evaluation was to document the FTIR measurement performance for formaldehyde and the BTEX compounds in a sample matrix similar to that of combustion turbine exhaust. An apparatus was set up to simulate the expected gas stream concentrations of the most prominent interferents, water and carbon dioxide. This was accomplished by generating a heated, humidified gas stream and blending it with nitrogen and carbon dioxide gas standards. This gas stream was then monitored by the FTIR for several hours to determine any biases as well as to detection limits based on 3 times the standard deviation. A NIST traceable standard of the formaldehyde was injected, at known volumes, into this gas stream and subsequently reduced to a point where it was no longer possible to maintain a constant injection flow of the formaldehyde standard (1.7 ppm formaldehyde/13.4 ppm SF_6). Based on limitations of the mass flow controller, the minimum formaldehyde concentration spiked was approximately 20 ppb. This gas stream was also spiked with a NIST traceable BTEX standard and directed through a water and CO_2 scrubber. Again the biases were determined and MDLs were calculated. The MDL results are presented in Table 5-2.

5.3.2 Field Measurements

Independent measurements of the inlet and exhaust gas streams of the combustion turbine were sampled for both formaldehyde and BTEX compounds. The effectiveness of the FTIR in monitoring low levels of BTEX compounds strongly depends on the ability to remove (scrub) CO2 from the sample. Therefore, a soda lime scrubber and Perma-Pure dryer were put inline as a scrubbing device for CO_2 and water respectively. The soda lime scrubber also removes all polar compounds (formaldehyde, HCl, NH_3, etc.). It was not possible to monitor for these components during times when the sample was conditioned.

The samples were extracted from two sampling locations available on the turbine. While the outlet location was ideal (no flow disturbances - 8 duct diameters down or 2 duct diameters up stream), the inlet sampling location did not meet these requirements. However, velocity measurements were made and the probe was positioned such that it was central to the mean of the flow with respect to velocity. Due to high temperatures at the inlet location, a glass-lined probe was used, whereas, at the cooler outlet location, a stainless probe was used to extract the gas sample. The outlet probe was positioned such that it drew sample from the central axis of the airflow of the stack. Heated extraction lines (150 feet long at the outlet and 100 feet at the inlet), containing polyfluoroalcohol (PFA) grade Teflon™ tubing, were used to deliver stack gas to the heated FTIR sample cell. All compounds were analyzed on a hot/wet basis to ensure that no analyte losses occurred due to condensation.

5.3.3 Analytical Method Characterization

An analytical method was developed for monitoring the analytes expected in the turbine exhaust stream. The estimates of the MDLs for the target compounds displayed in Tables 5-2 were determined via the procedures described above.

Table 5-2
FTIR MDL Evaluation

Compound	Laboratory Evaluation MDL (ppm)	Actual Field MDL (ppm)	Method 320 Quantitation Limit (ppm)
CO (carbon monoxide)	0.010	Not Available	0.251
CH_4 (methane)	0.035	0.090	0.317
C_2H_4 (ethylene)	Not Included	0.027	0.268
NO (nitric oxide)	0.052	0.258	1.51
NO_2 (nitrogen dioxide)	0.050	0.360	0.327
H_2CO (formaldehyde)	0.008	0.012	0.0135
CH_3CHO (acetaldehyde)	0.009	0.169	0.816
CH_3OH (methanol)	Not Included	0.033	0.097
C_7H_8 (toluene)*	0.028	0.428	0.131
C_6H_6 (benzene)*	0.016	0.260	0.128
C_8H_{10} (m- Xylene)*	0.030	0.260	0.369
C_8H_{10} (o- Xylene)*	0.022	0.501	0.126
C_8H_{10} (p-Xylene)*	0.017	0.212	0.266
C_8H_9 (ethyl benzene)*	0.024	0.189	0.289
NH_3 (ammonia)	0.010	0.018	0.093

*Derived from scrubbed data

Although most of the laboratory-based MDLs were comparable to those observed in the field, there were significant differences observed in some compounds. The gas stream generated in the laboratory contained approximately half (5% in laboratory to 10% actual) the moisture content that was observed in the field, and the laboratory study was conducted in a controlled and stable environment. These are contributing factors for the slight differences in MDLs for most compounds. However, for compounds such as BTEX, the differences were greater and are related to the ability to remove CO_2. During the laboratory study, the CO_2 was removed more effectively than was possible in the field due to higher water concentrations.

5.3.4 Extractive FTIR System

A description of the URS extractive FTIR system used for this project, as well as the steps followed in validating the FTIR spectrometer/analysis method, are included in the following subsections.

5.3.4.1 System Description

A fully integrated system consisting of a Nicolet FTIR spectrometer and a 12.5-liter sample cell (with an infrared path length set to approximately 60 m) was used to perform the testing. The approximate cell mirror spacing was 0.8 meters, and the 0.13-meter ID cell chamber was a nickel-coated aluminum tube. Gold-coated glass mirrors were used to minimize degradation of the reflective surface from moisture or any reactive gases in the exhaust stream. The IR beam exiting the sample cell was detected by a liquid nitrogen-cooled Mercury/Cadmium/Telluride detector, a photoconductive device that produces an electrical voltage proportional to the amount of IR light that strikes it. The FTIR scans were recorded while sampling a dynamic flow (at ~8 liters per minute) of gas using a diaphragm pump through the probe assembly, the heated (185^{o}C) Teflon™ line, and the heated (185^{o}C) FTIR cell. The cell pressure was continuously monitored during measurement periods using an Omega pressure sensor calibrated over the 200 to ~800 torr range and incorporated in each spectral analysis. Instrumental resolutions were set at approximately 0.5 cm^{-1} and signal averaging was performed over five minute intervals.

The probe and extraction system diagrammed in Figure 5-1 was similar to the one used for sampling throughout data collection at the gas turbine. The only difference was that the sampling system used on site had the heated extraction connected directly to the probe without any unheated sections. It accommodated for sampling both scrubbed and unscrubbed samples. This was done using a series of heated solenoid valves that, when turned on, redirected the sample through a Perma-Pure dryer and soda lime scrubber prior to entering the FTIR cell. A diaphragm pump at the outlet of the FTIR continuously drew the samples through the extractive system.

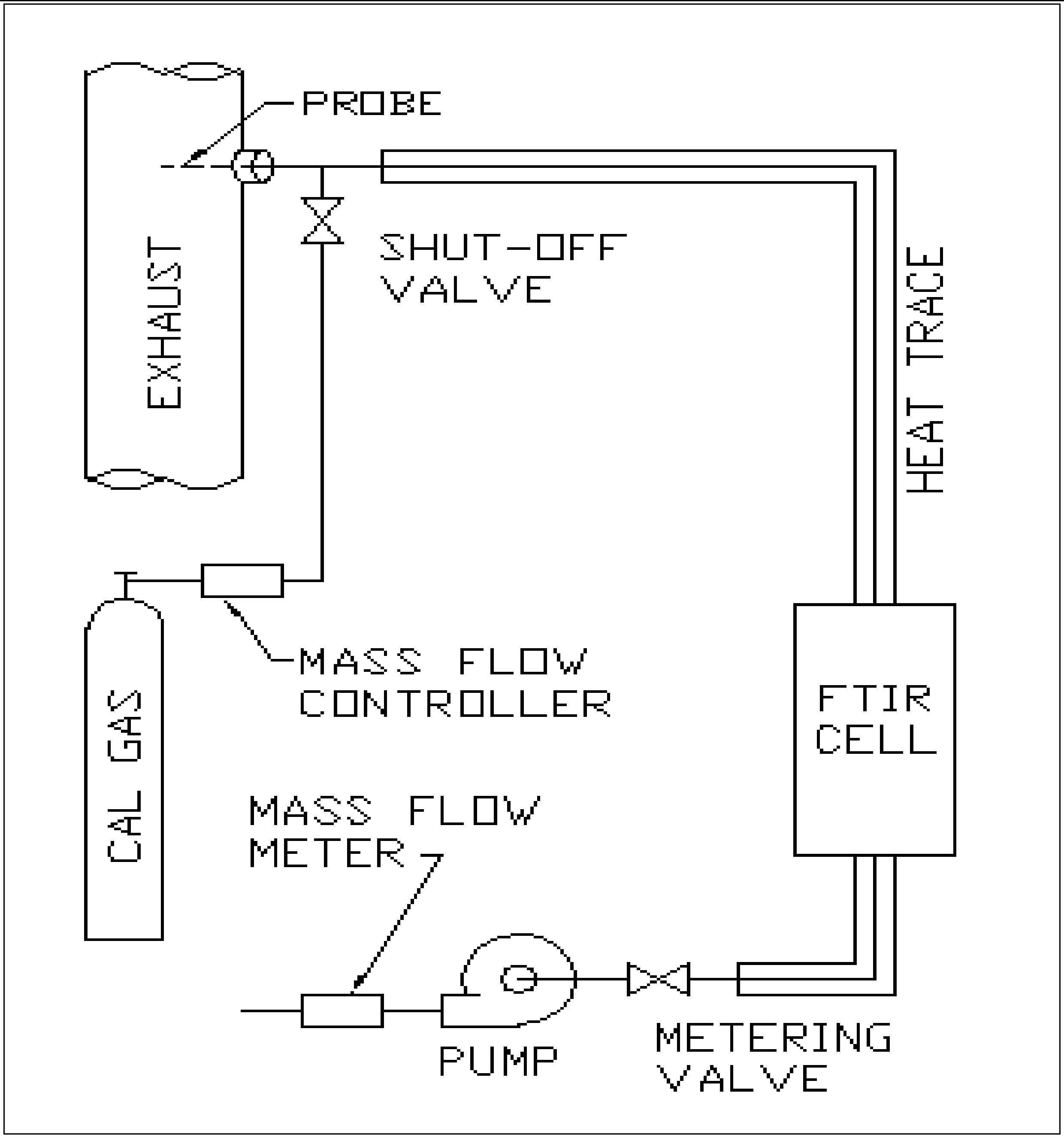

Figure 5-1
FTIR Sampling System Schematic

5.3.4.2 FTIR Calibration/Validation Procedures

A series of field calibrations was completed with the extractive FTIR system in order to ensure data of highest quality. A description of these calibrations/validations is given below.

5.3.4.2.1 Field Validation

As per EPA Method 320 and the URS Protocol, the following on-site procedures were performed to validate the analysis method before sampling began:

1. **Calibrated cell path length using a gas mixture containing R-22 in nitrogen with NIST certified concentrations**

   The NIST certified R-22 gas cylinder was attached directly to the FTIR's cell using a gas regulator and PFA Teflon™ tubing. After the sample cell was sufficiently flushed with the certified gas mixture, a 1.5-minute signal averaged spectrum (64 scans), at ~0.5 cm^{-1} resolution was recorded. The integrated area of the main R-22 absorption band (centered at ~1120 cm^{-1}) was then measured and compared to a reference spectrum obtained from the URS spectral library. The ratio of the two areas, (A_{cell}/A_{ref}), was computed and the cell path length could then be calculated by invoking the relationship described in Equation 5-1:

   $$path = \frac{C_{ref} * L_{ref} * P_{ref} * T_{cell}}{C_{cell} * P_{cell} * T_{ref}} * \left(\frac{A_{cell}}{A_{ref}} \right) \qquad (5\text{-}1)$$

   where $C_{ref} * L_{ref}$ is the concentration-path length product for the reference spectrum, P_{ref} and T_{ref} the absolute pressure and temperature at which the reference was measured, P_{cell} and T_{cell} the absolute pressure and temperature of the cell, and C_{cell} is the R-22 concentration in the gas mixture used to perform the calibration. Inserting the values recorded on-site gave a path length of approximately 60 meters. This calibrated value was then used for all subsequent measurements.

2. **Checked for spectrometer resolution and frequency line shifts using ambient air.**

   According to the URS protocol, the FTIR spectrometer was verified to have met resolution specifications before testing commenced. After sufficiently purging the sample cell with ambient air, a 0.5 cm^{-1} resolution, five-minute signal-averaged spectrum was recorded. The resolution was checked by measuring the line-width, at half-maximum, of two isolated water absorption bands centered at 1187.02 cm^{-1} and 1149.46 cm^{-1}, respectively. The half-widths were then entered into Table 5-3 for comparison with the predicted line widths.

The extractive FTIR spectrometer resolutions were deemed acceptable for turbine exhaust testing, since the observed line widths were found to be no larger than 1.1 times the predicted line widths for this type of FTIR.

Table 5-3
Predicted vs. Measured Line Widths for 0.5 cm^{-1} Resolution

Line Type Position (cm^{-1})	Predicted Line Width (cm^{-1})	Observed Line Width from FTIR (cm^{-1}) Inlet/Outlet
H_2O @ 1187.02	0.513	0.535
H_2O @1149.46	0.510	0.542

The same ambient air spectra recorded for resolution verification were analyzed for the existence of spectrometer line shifts. The deuterated water (HDO) absorption lines in the 2776.0 cm^{-1} to 2780.7 cm^{-1} region were compared with the same bands present in the water reference spectrum used in the analysis method. No line shifts greater than 1/10 of the operating resolution were observed, so line shifting algorithms were not needed for the analysis method.

3. **Recorded periodic cell backgrounds consisting of dynamic fills with dry nitrogen.**

   The sample cell "blanks" (backgrounds) were recorded by purging the cell thoroughly with ultra-high purity nitrogen before testing commenced. Subsequent sample spectra were then ratioed against the new backgrounds prior to quantification. Backgrounds were collected on a daily basis at a minimum.

5.3.4.2.2 System Validation

Field validation of select target compounds, at various concentration levels, was conducted while on site. The validations were conducted using NIST traceable standards spiked on top of stack gas. The QA standard for all the formaldehyde Method 320 spikes was a 1.7 ppm formaldehyde/13.4 ppm SF_6 mix. The QA validations were necessary in both characterizing the extraction apparatus and cell interactions toward the primary compounds of interest, and verifying that the analysis method would return accurate concentrations. The validation results and pertinent discussions are presented below.

5.3.5 FTIR Data Handling

FTIR raw and processed data were stored on computer hard disk, transferred to backup storage media, and kept in a secure location after the completion of the testing. All quantification routines used to process the data were backed up on compact disks and saved on the system hard drive.

5.4 Discussion of FTIR Results

5.4.1 Methodology

In accordance with EPA Method 320, QA and Calibration Transfer Standard (CTS) tests were performed to ensure the FTIR system was operating correctly and producing data of the highest integrity. Deviations from this method were minor and are as follows;

- Pre-test calculations, with the exception of instrument operating calculations, were not necessary. A laboratory study was conducted and FTIR data had been collected on many occasions at similar sites, therefore expected concentration levels had been established and analytical quantification methods developed. The quantification methods were slightly improved after testing began to better account for spectral line shifts and interferences. All data collected prior to the final method improvements were reanalyzed with the finalized quantification method.
- The QA spike done on October 11 was done on top of stack gas as dictated by EPA Method 320 however, the turbine was not running as the QA spike was done.
- There was no inline filter used during sampling. The particulate loading was not expected to be high and the extraction line temperature was not sufficient to decompose most particulate. Therefore, the absence of an inline filter should not have any effect on the sample.
- The Teflon™ calibration line, which delivered the QA standards to the inlet spiking "T", was unheated. This line was virgin Teflon™ and had been purged with nitrogen to ensure that no water was present. These precautions ensured that the formaldehyde was delivered to the spiking tee dry and contaminant free.
- The tests were defined by the Avogadro Group’s sampling team in conjunction with the plant and were based on the ability to coordinate data collection at the required operating conditions. Since the FTIR is automated, it ran while Avogadro staff collected data for multiple tests. Method 320 QA spikes and CTS tests were done within 24-hours of the sampling runs but not immediately prior to or after each individual test.
- The gas bottle regulator used on the formaldehyde QA standard was not a purgeable regulator. However the regulator used was corrosive resistant, heated, and solely used for formaldehyde.

5.4.2 QA Spiking

As per EPA Method 320 QA spikes of formaldehyde were done at three different levels. In addition to the analyte of interest, each QA spiking gas standard contained a component to be used as a spectroscopic tracer. Common properties to all spectroscopic tracers are that they exhibit a broad absorption profile over a large concentration range and they are chemically inert. The linear behavior of the spectroscopic tracer allows a precise measurement of the dilution ratio of the spiked gas to native gas. For the Method 320 QA spike this dilution ratio was determined using SF_6 and applied to calculate the theoretical formaldehyde concentration using the following equation:

$$H_2CO_{Theoretical} = \left(\frac{SF_{6sample}}{SF_{6cylinder}}\right)(H_2CO_{Cylinder}) + \left[1 - \left(\frac{SF_{6sample}}{SF_{6cylinder}}\right)\right](H_2CO_{stack})$$

Where:

$H_2CO_{Theoretical}$ = Theoretical H_2CO concentration (ppm)
$SF_{6sample}$ = SF_6 concentration (ppm) as seen by the FTIR during QA spiking
$SF_{6cylinder}$ = The concentration (ppm) of SF_6 in the NIST traceable gas standard
$H_2CO_{cylinder}$ = The concentration (ppm) of H_2CO in the NIST traceable gas standard
H_2CO_{stack} = The concentration (ppm) of H_2CO in the stack during stable conditions

The criterion for a successful QA test is a measured concentration within 0.7-1.3 times the calculated theoretical concentration[1]. Spikes at three levels were conducted and each spike met the Method 320 criterion. The results of the QA spiking are present in Table 5-4.

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[1] "Test Method 320 – Vapor Phase Organic and Inorganic Emissions by Extractive FTIR".
[1] http://www.epa.gov/ttn/emc/Promgate.html

Table 5-4
Method 320 Formaldehyde QA Spiking Results

Spike Level	QA Run	Date/Time	Calculated (ppm)	Actual (ppm)	Recovery	Comments
High	#1 Pre Test	10/8/2002 16:54	0.361	0.430	119.2%	Pass
Mid	#1 Pre Test	10/8/2002 17:03	0.094	0.113	119.4%	Pass
Low	#1 Pre Test	10/8/2002 17:14	0.048	0.058	120.1%	Pass
	TEST #1	Start: 8/16:54				
High	#1 Post Test	10/9/2002 19:01	0.735	0.870	118.4%	Pass
Mid	#1 Post Test	10/9/2002 19:11	0.403	0.450	111.8%	Pass
Low	#1 Post Test	10/9/2002 19:22	0.202	0.211	104.5%	Pass
	TEST #2	Start: 10/1749				
High	/#2 Pre Test	10/11/2002 11:34	0.526	0.600	114.1%	Pass
Mid	#2 Pre Test	10/11/2002 11:58	0.399	0.452	113.3%	Pass
Low	#2 Pre Test	10/11/2002 11:46	0.270	0.338	124.9%	Pass
	TEST #3	Start: 11/1449				
High	#2 Post Test/#3 Pre Test	10/12/2002 10:30	0.510	0.466	91.3%	Pass
Mid	#2 Post Test/#3 Pre Test	10/12/2002 10:42	0.360	0.341	94.6%	Pass
Low	#2 Post Test/#3 Pre Test	10/12/2002 10:54	0.194	0.202	103.8%	Pass
	TEST #4	Start: 12/1628				
High	#3 Post Test	10/13/2002 16:06	0.568	0.410	72.2%	Pass
Mid	#3 Post Test	10/13/2002 16:31	0.382	0.272	71.4%	Pass
Low	#3 Post Test	10/13/2002 16:21	0.195	0.189	96.9%	Pass

5.4.3 Calibration Transfer Standard (CTS) Results

Calibration transfer standard (CTS) tests were conducted on a daily basis. The primary purpose of the CTS tests is to verify that the FTIR instrument conditions are stable throughout the testing period. Two parameters, the integrated area of a selected absorbance band and frequency position of a narrow absorbing band, were measured to insure that the FTIR did not change throughout the course of sampling. The criteria for a successful CTS run is a difference in the integrated area of no greater than 5% between pre- and post-test CTS standards and a frequency reproducibility of +/- 0.06 wave numbers (cm^{-1}). A NIST traceable standard containing 10.0 ppm R22 (integrated area) and 10.0 ppm CO (frequency position) was used as the CTS standard. Table 5-5 lists the results of the pre- and post- CTS runs.

Table 5-5
Method 320 CTS Results

Date/Time	R22 Integrated Area	% Difference	CO Line Position	Comments
10/9 12:12	30.789	N/A Initial setting	2094.836	Pre Test # 1
10/10 16:58	30.672	0.4	2094.836	Post Test #1
10/11 09:42	31.019	-1.1	2094.836	Pre Test #2
10/12 09:48	29.530	4.8	2094.836	Post Test #2/ Pre Test #3
10/13 15:15	28.447	3.7	2094.836	Post Test #3

5.4.4 FTIR Testing Results

The results, as well as all other testing considerations, are presented chronologically in this section. Table 5-6 is a timeline for the FTIR monitoring that shows which test site (gas turbine exhaust or “inlet,” HRSG stack or “outlet”) was monitored and which gas stream (e.g., scrubbed/unscrubbed, turbine down) was flowing to the FTIR. A data point was collected every 5-minutes. Tables 5-7 and 5-8 present summaries of data collected throughout the testing:

- Unless otherwise stated, all concentrations are provided on a wet basis in units of ppmv. Those compounds having values less than their respective field MDL are listed as BDL - Below Detection Limit.
- For compounds that had periods where the FTIR concentration result was below the detection limit of the FTIR, ½ the reported field MDL was used for calculating the average concentrations.

Table 5-6
Timeline of Collected FTIR Data

Date/Time	Turbine Operation	FTIR Sample	Comments
10/8-10/9 1522	Base Load	Inlet /Setup	Calibrations and Meth. 320 QA spike
10/9 1522-1810	Base Load	Inlet/Unscrubbed	
10/9 1810-1953	Base Load	Inlet/Unscrubbed	Meth. 320 QA spike
10/9 1953-2339	Base Load	Inlet/Unscrubbed	
10/9 2349 – 10/10 0130	Shut Down	Inlet/Unscrubbed	Initial Shut Down
10/10 0130-1408	Turbine Down	Inlet/Unscrubbed	Stagnant Turbine Exhaust
10/10 1408-1825	Turbine Down	No Sampling	
10/10 1825 - 10/11 0253	Turbine Down	Inlet/Unscrubbed	Stagnant Turbine Exhaust
10/11 0258-0528	2 Cold Start Attempts	Inlet/Unscrubbed	Both Attempts Failed
10/11 0258-0854	Turbine Down	Inlet/Unscrubbed	Stagnant Turbine Exhaust
10/11 0854-1206	Turbine Down	Inlet/ Meth. 320 QA spike	Stagnant Turbine Exhaust
10/11 1206-1449	Turbine Down	No Sampling	
10/11 1454-2053	3 Cold Start Attempts	Inlet/Unscrubbed	Turbine Up after 3rd Start
10/11 2058 - 10/12 0901	To 95 MW	Inlet/Unscrubbed	
10/12 0905-1415	Base Load	Inlet & Outlet Unscrubbed	Meth. 320 QA spike
10/12 1415-1604	Base Load	Outlet/Both*	30-min. cycle time*
10/12 1608-1725	Base Load	Inlet/Both*	30-min. cycle time*
10/12 1731-2018	Base Load	Outlet/Both*	30-min. cycle time*
10/12 2018-2353	Base Load	Inlet/Both*	30-min. cycle time*
10/12 2353 - 10/13 1453	Base Load	Outlet/Both*	30-min. cycle time*
10/13 1453-1651	Base Load	Outlet	Meth. 320 QA spike
10/13 1651-2139	--	--	Generate Water Reference
10/13 2139 - 10/14 1007	Base Load	Outlet/Unscrubbed	Additional Data

Table 5-7
Daily FTIR Results of Unscrubbed Data, Base Load (Wet Basis)

		CH2O (ppm)	H2O (ppm)	CO2 (ppm)	CO (ppm)	CH4 (ppm)	NH3 (ppm)	NO2 (ppm)	NO (ppm)	NOx (ppm)
10-13 Outlet	*Min*	0.024	88,698	36,280	1.58	0.55	7.82	2.88	BDL	3.12
begin 10/13 2139	*Max*	0.047	113,514	37,754	1.88	0.75	11.18	3.67	1.36	5.03
end 10/14 1007	*Avg*	0.031	99,899	37,153	1.68	0.62	9.22	3.41	0.73	4.14
10-12 Inlet	*Min*	0.040	92,335	35,612	2.26	0.94	BDL	5.34	23.46	28.80
begin 10/12 1702	*Max*	0.052	111,332	39,518	3.49	1.34	BDL	6.72	34.99	41.71
end 10/13 1133	*Avg*	0.048	101,580	38,082	3.17	1.09	-	6.09	27.14	33.23
10-12 Outlet	*Min*	0.031	102,173	31,726	0.70	0.68	7.88	3.15	BDL	3.38
begin 10/12 1420	*Max*	0.065	118,938	37,620	1.68	1.10	12.41	3.82	1.23	5.05
end 10/13 1429	*Avg*	0.050	105,901	36,273	1.19	0.90	10.57	3.51	0.42	3.93
10-9 Inlet	*Min*	BDL	101,361	36,738	1.90	BDL	BDL	BDL	32.85	33.03
begin 10/9 1522	*Max*	0.098	124,737	39,684	2.31	0.17	BDL	BDL	34.34	34.52
end 10/9 1800	*Avg*	0.064	112,970	38,673	2.10	0.06	-	-	33.63	33.81

CH2O – formaldehyde
CH4 – methane
NH3 – ammonia
BDL – below detection limit; see Table 5-2 for the field MDL values for each analyte.

6

RESULTS

Emissions

A summary of the average test results for each test site and method is provided in Tables 6-1 and 6-2. The results from individual test runs are presented in Tables 6-3 through 6-6.

The average results shown in Tables 6-1 and 6-2 represent the average of two or three test runs at base load. The O_2 concentration measured by the conventional method was used for correction of all the measured concentrations to 15% O_2.

The calculation of the percent reduction for CO measured by conventional methods is an estimate based on the practical detection limit (DL) for CO of 0.2 ppm volume dry. Lower concentrations of CO can be detected, but the uncertainty in the measurement remains at approximately 0.2 ppm. If the actual downstream (stack) concentration of CO were 0.2 ppm, then the upstream concentration (gas turbine exhaust) would need to be 4 ppm or higher in order to show at least 95% reduction of CO.

A summary of the results for the individual test runs is presented in Tables 6-3 through 6-6. The results of both the FTIR tests and the conventional tests are provided as average concentrations for each test run period. Note that the test run times shown for the conventional methods are those for the formaldehyde tests. The concurrent NO_X and CO test runs were shorter in duration.

Table 6-1
Summary of Average Results, Conventional Methods

Sample Location	Upstream from Catalysts – Gas Turbine Exhaust	Downstream from Catalysts – HRSG Stack	Percent Reduction
Load, MW	158	158	--
O_2, % vol dry	13.6	13.6	--
NO_x, ppm vol dry @ 15% O_2	28	2.7	90
CO, ppm vol dry @ 15% O_2	0.8	<0.2	>78
Formaldehyde, ppb vol dry @ 15% O_2	9.4	4.6	51
Note: The symbol "<" denotes results below the practical detection limit value shown. ½ of the detection limit was used for purposes of calculating an average. The results shown are for the average of 2 or 3 runs at base load. * The practical detection limit for CO concentrations was approximately 0.2 ppm. The percent reduction shown is an estimate based on that detection limit.			

Table 6-2
Summary of Average Results, FTIR Analyzer

Sample Location	Upstream from Catalyst - Gas Turbine Exhaust	Downstream from Catalyst – HRSG Stack	Percent Reduction
Load, MW	158	160	--
O_2, % vol dry	13.6	13.7	--
NO_x, ppm vol dry @ 15% O_2	32	3.5	89
CO, ppm vol dry @ 15% O_2	2.0	0.9	57
Formaldehyde, ppb vol dry @ 15% O_2	46.8	41.8	11
Note: The results shown are for the average of 2 or 3 runs at base load. All O_2 concentrations were determined by EPA Method 3A using a conventional CEM analyzer.			

Summary

The results for the upstream location show that the formaldehyde measurements taken by FTIR were greater than the proposed MACT standard (43 ppb vol dry @ 15% O_2). The basis of the proposed MACT standard was existing data that was nearly all derived from tests conducted by CARB Method 430 (the “conventional” method), which provided lower results than FTIR in every case in this study.

The two test methods show different results, especially for formaldehyde, with the FTIR results significantly higher than those from the CARB Method 430 measurements. Although these results are not surprising, the magnitude of the differences is higher than anticipated. Previous studies have shown that elevated levels of NO_2 and/or NO in a sample matrix, relative to that of formaldehyde, result in depressed levels of formaldehyde as measured by the CARB Method 430 (GRI 2001, API/GRI 1998). The NO_2 and NO interfere with the method's chemistry and cause the formaldehyde results to be biased low. One study was conducted on natural gas-fired internal combustion engines where much higher concentrations of formaldehyde, NO_2 and NO comprised the sample matrix as compared to those measured during this gas turbine testing. The second study was conducted on a GE LM2500 combustion turbine, and the concentrations of formaldehyde, NO_2 and NO measured after a CO catalyst were on the order of 300 ppbv for formaldehyde (FTIR) and 43 ppmv for NO_x. Note that the stack location in the current test was downstream of an SCR, and the concentrations of NO and NO_2 were much lower, about 2-3 ppmvd for NO_x.

These two studies do not conclusively explain the discrepancies between the FTIR and CARB Method 430 results from this gas turbine testing. However, these two studies do confirm that the two methods have been shown to provide different results, and that there are measurable technical reasons for the difference.

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Table 6-3
Results Summary, Conventional Methods, Emissions from Gas Turbine Exhaust

Upstream from Catalyst – Gas Turbine Exhaust	Run 1	Run 9	Run 10	Average
Date / Time	10-9-02 1505-1805	10-12-02 1445-1745	10-12-02 1811-2111	
Load, MW	155	160	160	158
O_2, % vol dry	13.4	13.8	13.6	13.6
NO_x, ppm vol dry @ 15% O_2	27	29	27	27
CO, ppm vol dry @ 15% O_2	0.6	0.9	0.8	0.8
Formaldehyde, ppb vol dry @ 15% O_2	<10.4	17.8	6.3	9.4
Note: The symbol "<" denotes results below the practical detection limit value shown. ½ of the detection limit was used for purposes of calculating an average. The run times shown are for the formaldehyde test runs; the O_2, NO_x and CO runs were shorter.				

Table 6-4
Results Summary, FTIR, Emissions from Gas Turbine Exhaust

Upstream from Catalyst – Gas Turbine Exhaust	Run 1	Run 9	Run 10	Average
Date / Time	10-9-02 1522-1810	10-12-02 1702-1722	10-12-02 2102-2117	
Load, MW	155	160	160	158
O_2, % vol dry	13.4	13.8	13.6	13.6
NO_x, ppm vol dry @ 15% O_2	30	34	32	32
CO, ppm vol dry @ 15% O_2	1.7	1.9	2.4	2.0
Formaldehyde, ppb vol dry @ 15% O_2	56.7	39.3	44.3	46.8
Note: See Table 5-2 for details on detection limits for the FTIR analyzer. The run times shown are the periods averaged for the FTIR. The O_2 concentrations shown are from conventional analyzer as in Table 6-3.				

Table 6-5
Results Summary, Conventional Methods, Emissions from HRSG Stack

Downstream from Catalyst – HRSG Stack	Run 2	Run 7	Run 8	Average
Date / Time	10-9-02 1500-1800	10-12-02 1450-1750	10-12-02 1817-2117	
Load, MW	155	160	160	158
O_2, % vol dry	13.4	13.8	13.6	13.6
NO_x, ppm vol dry @ 15% O_2	2.6	2.7	2.7	2.6
CO, ppm vol dry @ 15% O_2	<0.2	<0.2	<0.2	<0.2
Formaldehyde, ppb vol dry @ 15% O_2	7.5	3.4	<5.6	4.6
Note: The symbol "<" denotes results below the practical detection limit value shown. ½ of the detection limit was used for purposes of calculating an average. The run times shown are for the Formaldehyde test runs; the O_2, NO_x and CO runs were shorter.				

Table 6-6
Results Summary, FTIR, Emissions from HRSG Stack

Downstream from Catalyst – HRSG Stack	Run 2	Run 7	Run 8	Average
Date / Time	N/A	10-12-02 1457-1603	10-12-02 1817-2012	
Load, MW	N/A	160	160	160
O_2, % vol dry	N/A	13.8	13.6	13.7
NO_x, ppm vol dry @ 15% O_2	N/A	3.4	3.5	3.5
CO, ppm vol dry @ 15% O_2	N/A	0.7	1.0	0.9
Formaldehyde, ppb vol dry @ 15% O_2	N/A	50.5	33.0	41.8
Note: See Table 5-2 for details on detection limits for the FTIR analyzer. The run times shown are the periods averaged for the FTIR. The O_2 concentrations shown are from conventional analyzer as in Table 6-5.				

7 REFERENCES

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1. National Emission Standards for Hazardous Air Pollutants for Stationary Combustion Turbines; Proposed Rule, Federal Register, 40 CFR Part 63, January 14, 2003. http://www.epa.gov/ttn/atw//turbine/turbinepg.html.

2. Gas Research Institute, *Investigation of Interferences with Aqueous 2,4-DNPH Based Methods for Measurement of Aldehydes in Natural Gas Combustion Exhaust*, GRI Report GRI-00/0048, January 2001.

3. American Petroleum Institute/Gas Research Institute, *Preliminary Results from Natural Gas-Fired Combustion Turbine Testing*, Technical Note, August 1998.

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