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DISTRIBUTED GENERATION CERTIFICATION TEST METHOD DEVELOPMENT

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PREFACE

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Distributed Generation: Certification Test Method Development is the final report for the Study of Peak-Load Energy Production Potential and Air Quality Impacts of Backup Generators (BUGs) project (contract number POM 026-R69) conducted by University of California, Riverside, Bourns College of Engineering—Center for Environmental Research and Technology (CE-CERT). The information from this project contributes to Energy Research and Development Division's Energy-Related Environmental Research Program.

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ABSTRACT

Many California cities fail to meet federal and state air quality standards; therefore, they face strict emission limits on their power-generating equipment. Cities and businesses, in addition to getting electrical power from central power stations, often install smaller generating units close to their needs. These smaller units are referred to as *distributed generation.* The convergence of stricter emission limits and need for distribution power generation has created a whole new group of power generation units with very low emissions. The goal of this research was to learn whether existing regulatory methods accurately measured the flow rate and concentration of gases in the exhaust of the new generation power sources. The gases of particular interest were: nitric oxides (NOx), carbon monoxide (CO), and hydrocarbons. Furthermore, the project sought new methods if existing concentration and flow methods did not accurately measure the desired property.

The project examined five sources: a microturbine (65 kilowatts [kW]); a Solar Turbines turbine with selective catalytic reduction (SCR) (14 megawatts [MW]); a Solar Turbines turbine with the SCONOx™ catalytic reduction technology (14 MW); a molten salt fuel cell (300 kW); and a General Electric turbine with selective catalytic reduction and a CO catalyst (50 MW). Measured concentrations of CO and NOx were well below the lower limit for instruments specified in the California Air Resources Board's (ARB) Method 100 (M-100). Testing with existing commercial instruments designed for ambient measurements of NOx and CO proved satisfactory. Total hydrocarbons were measured by South Coast Air Quality Management District (SCAQMD) Method 25.3, as ARB's M-100 was out of range. Values measured by Method 25.3 were often < 10 parts per million, highly variable, and sometimes inaccurate. Tests with U.S. Environmental Protection Agency (U.S. EPA) Method 25a proved satisfactory, even at < 5 parts per million levels. This method was recommended for future field measurements of total hydrocarbons. In any case, whether canister or gas chromatography methods are used, the recommendation is to use U.S. EPA protocol gases to calibrate the total hydrocarbon method. Overall, all gaseous measurements should be made between 10 and 90 percent of the instrument range.

Keywords: distributed generation, emissions, ARB Method 100, measurements near low detection limit, emission measurement, flow measurement

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EXECUTIVE SUMMARY

Introduction

Many populated California cities are classified as non-attainment areas with respect to federal and state air quality standards; therefore, they face strict emissions limits on their power-generating equipment. In addition to getting electrical power from central power stations, some cities or businesses often install smaller generating units referred to as *distributed generation.* Distributed generation resources are small-scale power generation technologies (typically in the range of 3 kilowatt [kW] to 10 megawatts [MW]) located close to where electricity is used. To meet the strict emissions limits, these new distributed generation installations are using the latest low-emission technology. However, the newest distributed generation technologies have such low emission concentrations that there was a question as to whether the existing tests methods offered by the California Air Resources Board (ARB) are sufficient to accurately measure emission at such low levels; especially as experience has shown that some methods are inaccurate at the concentration levels being measured. This project's goals were to (1) test existing concentration and flow methods with various distributed generation sources and identify test methods that accurately measure voltaic organic compounds, nitrogen oxides (NOx), and carbon monoxide (CO) concentrations down to 0.10 part per million by volume, and (2) test methods that can accurately measure exhaust gas velocity and flow rate within +/-5 percent, similar to the voltaic organic compounds, NOx, and CO analyzers.

Project Purpose

Emissions testing was conducted at a number of distributed generation sites that were selected by an Advisory Committee. The technologies tested included a 65 kW Capstone microturbine, a 300 kW FuelCell Energy unit, two 13.5 MW Solar Turbines turbines fired with natural gas (one with selective catalytic reduction and the other with the SCONOx catalytic reduction technology), and a 50 MW natural gas turbine with selective catalytic reduction. Gas concentrations and flow rates were measured with existing ARB regulatory methods for distributed generation and with alternative methods designed for very low concentrations. For example, ambient instruments were used to measure CO and NOx, and canister methods were used to measure total hydrocarbons. Flow was measured using International Standards Organization (ISO) method 8178, which relies on mass balances.

Project Results

Gaseous Measurements

Carbon monoxide, NOx, and hydrocarbons. All of the units tested had very low concentrations of NOx, CO, and hydrocarbons, as is evident in Table ES-1.

Table ES-1: Summary of Results for Measured Concentrations (parts per million)

			Hydrocarbons*		
DG Unit	**NOx**	**CO**	**SCAQMD 25.3**	**EPA TO-12**	**EPA 25A**
Microturbine (65 kW)	1.40	1.66	16.3	1.6	~2.
Fuel Cell (300 kW)	0.2	28	7.3	4.6	890
Turbine (14 MW) + SCR	1.21	1.28	7.2	1.8	1.9
Turbine (14 MW) + SCONOx	1.15	0.63	3.0	0.3	3.56
Turbine (50 MW) + SCR	2.32	3.69	1.54	0.10 and 0.29**	0.46

* Methods SCAQMD 25.3 and EPA TO-12 report non-methane, non-ethane, organic carbon (NMNEOC), and EPA Method 25A reports THC (total hydrocarbons).

** Measured by two laboratories

When following regulatory protocols, field instruments measuring CO, carbon dioxide (CO_2), NOx, and hydrocarbons are expected to operate between 10 to 90 percent of their range. The results showed that when the instruments were operating within the specified range, there was good agreement between the published values from the manufacturer and the values measured with the continuous emission monitors installed on the unit. However, measuring CO and NOx at lower levels required instruments designed for ambient ranges. Measuring hydrocarbons at low levels (< 10 parts per million) proved especially challenging, and values reported from the various qualified labs using different regulatory methods did not agree. For example, values from the South Coast Air Quality Management District's Method 25.3 were always higher than values reported by EPA TO-12 and by EPA 25A.

Flow Measurements

This project investigated the accuracy of the exhaust gas flow rate, since the contribution of the source emissions to a local emissions inventory is determined by multiplying the measured concentration and the measured exhaust gas flow rate. During this project, flow rate was determined by two independent methods. One method followed ARB Methods 1 to 4 and is based on the measured velocity and the calculated molecular weight of the exhaust. Velocity is measured using Bernoulli's principle, which states that the pressure in a stream of fluid is reduced as the speed of the flow is increased. The other method is from the International Standards Organization (ISO 8178) and is based on the principle of mass balances. For example, the commonly used Carbon Balance Method relies on the measured fuel flow and the concentration of carbon dioxide in the stack. Each method has advantages and disadvantages, but as indicated in Table ES-2, as shown in the last column, the two methods agreed within ARB's 5 percent goal.

Table ES-2: Comparisons of Volumetric Flow Methods

DG Unit	Methods 1–4	ISO8178-1	Diff. (%)
Microturbine (65 kW)	57.27 kSCFH	57.41 kSCFH	0.2
Turbine (14 MW) + SCR	4.76 mmSCFH	4.63 mmSCFH	1.7
Turbine (14 MW) + SCONOx	5.25 mmSCFH	5.01 mmSCFH	4.4
Fuel cell, 300 kW	52.86 kSCFH	49.91 kSCFH	1.8
~50 MW turbine + SCR	14.02 mmSCFH	13.90 mmSCFH	0.9

Note: kSCFH = thousand standard cubic feet per hour; mmSCFH = million standard cubic feet per hour

Particulate Matter Measurement

Measurement of the particulate matter mass on a filter proved problematic, so a continuous scanning mobility particle sizer was used to provide a snapshot of the particle size distribution of the source and the local ambient air. The project results showed the following:

1. Pre-filters on the Capstone DG were not effective in removing small particles.
2. Water-based condensation particle counters measured about the same number of particles as a butanol-based condensation particle counter for ambient air but measured approximately 1 percent of the particles found in a turbine exhaust; presumably because the exhaust particles were too small to be seen or were not wetted by the water-based system.
3. Scanning mobility particle sizer particulate matter mass data for turbines with selective catalytic reduction suggested that the exhaust air from the combustion process has less particulate matter mass than the ambient air. For the 50 MW unit, both the number and mass of the exhaust was less than the particulate matter found in the ambient air. Basically the results suggest that the air coming from the gas turbine is cleaner than the air going into the turbine.
4. Scanning mobility particle sizer data for the SCONOx and fuel cell plants showed a lot of very small (< 5 nanometer) particles but low mass amounts.

Project Benefits

Based on this project's findings, there are several recommendations for measuring the low levels found in modern distributed generation sources.

1. Rather than the current instruments specified in Method 100, the regulation should state that the measured concentration of CO, CO_2, NOx, and total hydrocarbons should fall between 10 to 90 percent of the instrument range. This change would allow the use of commercial instruments that measure near ambient levels and yield accurate numbers.

2. U.S. EPA Method 25A should be considered as a replacement method for the canister sampling methods for measuring the total hydrocarbons in the field. When combined with a methane splitter, then the non-methane hydrocarbons levels are available. Using Method 25A in the field would allow a field determination of whether the exhaust is within compliance values for CO, NOx, non-methane hydrocarbons, and total hydrocarbons. This changed approach would mean that users would know whether the equipment passed or failed the field test immediately, instead of weeks later.
3. If canister methods (EPA TO-12 and SCAQMD 25.3) are continued, then for non-methane non-ethane organic compounds values < 10 parts per million:
    a. Samples sent to the lab for analysis should include a zero gas sample and a sample with a certification gas near the expected levels in the exhaust.
    b. Even more stringent canister cleaning methods are likely needed.
    c. The minimum fill requirement for SCAQMD 25.3 should be lowered from 15 inches of vacuum to a level near 5 inches of vacuum, to minimize the error introduced by dilution when pressurizing the canisters in the lab.

Current flow methods work well. However as part of a quality assurance program, some flows should be checked with the ISO-8178 methods that are based on mass balance.

CHAPTER 1:
Project Background, Objectives and Approach

1.1 Background

Distributed generation (DG) resources are small-scale power generation technologies (typically in the range of 3 kilowatt [kW] to 10 megawatts [MW]) located close to where electricity is used.1 Examples of DG technologies include reciprocating engines, turbines, fuel cells, and photovoltaic cells. Some businesses choose to operate DG technologies with heat recovery systems that capture the heat produced from the electrical generation process; so-called combined heat and power units. This captured heat can then be used to heat water, provide steam or space heating, or power a chiller at the facility. Distributed generation can be used at various types of businesses such as hospitals, schools, libraries, breweries, utilities, and laundries.

Senate Bill (SB) 12982 requires ARB to establish a DG Certification program for electrical generation technologies that are exempt from local air district permits. Pursuant to SB 1298, the ARB adopted a DG Certification Regulation in 2001 and amended the regulation in 2006. In addition to establishing emission standards, the DG Certification Regulation includes testing protocols, calculation procedures, and other specified requirements that manufacturers must satisfy to certify DG technologies.

Testing for compliance within the DG Certification Regulation requires the following methods (Table 1-1), as outlined in Section 94207 of the California Code of Regulations (CCR):

Table 1-1: Test Measurements and Methods

Measurement of Interest	Test Method
Nitrogen Oxides (NO_x), Carbon Monoxide (CO), and Oxygen:	ARB Test Method 100 (CCR, Title 17, Section 94114)
Carbon Dioxide (CO_2)	ARB Test Method 100 (CCR, Title 17, Section 94114)
Voltaic Organic Compounds (VOC)	South Coast Air Quality Management District (SCAQMD) Method 25.3 (as published in March 2000)
Gas Velocity and Flow Rate	ARB Test Methods 1, 2, 3, and 4 (CCR, Title 17, Sections 94101, 94102, 94103, and 94104)

1 California Distributed Energy Resources Guide. See http://www.energy.ca.gov/distgen/.

2 Senate Bill 1298, Bowen, Chapter 741, Statutes of 2000.

1.2 Objectives

The objectives of this research are to evaluate the accuracy and precision of current ARB test methods used for distributed generation and to determine if new instrumentation and/or test methods need to be developed. Specifically, the project addressed the following tasks:

1.2.1 Evaluate ARB Test Methods 1–4 and 100, and SCAQMD Test Method 25.3

Current test methods used in the DG Certification program were evaluated, with the goal of identifying weaknesses in the methodologies or technologies within the test methods that cause inaccuracy among emission measurements.

1.2.2 Evaluate ARB Test Methods 1–4 for Accuracy in Measuring Velocity and Flow Rate

Current exhaust gas velocity and flow rate test methods used in the DG Certification program were evaluated, with the goal of identifying weaknesses in the methodologies or technologies within the test methods that cause inaccuracy among measurements.

1.2.3 Evaluate Other Test Methods for Both Stationary Sources and Ambient Sources

Once current test methods and technologies were evaluated, the project assessed other test methods, for both stationary sources and ambient sources, from government agencies (both domestic and foreign), and private entities. This evaluation sought to identify test methods that can accurately measure VOC, NO_x, and CO concentrations down to 0.10 parts per million by volume (ppmv) preferably, but would be acceptable at 0.1 ppmv. It also sought to identify test methods that can accurately measure exhaust gas velocity and flow rate within +/-5 percent, similar to the VOC, NO_x, and CO analyzers.

1.2.4 Determine if New Instrumentation and/or Test Methods Need to be Developed:

If the project evaluation determined that current test methods could not accurately measure VOC, NO_x, and CO concentrations or measure exhaust gas velocity and flow rate with the same accuracy (+/-5 percent) as the VOC, NO_x, and CO analyzers, then the project was to determine if new instrumentation and/or test methods needed to be developed.

1.3 Approach

The California Energy Commission and the University of California agreed to the following approach:

1.3.1 Literature Review and Mining of Existing Data

The first task was to review existing test methods and literature reports for similar source projects. For example, since most of the distributed generation units studied in this program were based on turbine technology, we reviewed existing literature, the U.S. Environmental Protection Agency (EPA) AP-42 Tables, and the status of the test methods being developed for aircraft turbines by the British standards group, since those turbines were about the same power level as the largest turbines studied in this project.

1.3.2 Trial Test

A trial test was added, given the importance and complex requirements of the project and the limited number of test opportunities. The trial test run had multiple goals:

learn the time and techniques needed to test a DG in the field,

explore several particulate matter (PM) measurement methods; and

sample gases with M-100 instruments to learn the applicability to the planned DG sources.

1.3.3 Field Testing

The field tests consisted of testing five units in commercial operation, including: a 65 kilowatt (kW) microturbine, a 300 kW fuel cell operating with molten salt on biogas, two 13.5 megawatt (MW) Solar Turbines turbines with different exhaust controls, and a near 50 MW unit with exhaust controls. Accurate measurement of the exhaust flow rate and concentration of the gases were the desired outcome.

1.3.4 Data Analysis

Data were analyzed and compared with external sources such as continuous emissions monitor (CEM) data or parallel testing with an outside test lab, if available.

1.3.5 Reporting

This report contains the recommended plans for modifying current test methods and the development of new test methods and/or instrumentation, as applicable.

CHAPTER 2:
Results from the Literature Review and Trial Test

2.1 Literature Review and Mining of Existing Data

The project started with a review of existing test methods and literature reports for similar sources. For example, since most of the DG units in this project were based on turbine technology, the status of the test methods being developed for aircraft turbines by the Society of Automotive Engineers (SAE) were reviewed. Those turbines operate similarly and have about the same power level as the largest turbines studied in this project.

The literature review reviewed three areas: (1) current efforts by U.S. EPA to measure exhaust emissions at low levels; (2) existing advice and measured values imbedded in the U.S. EPA's AP 42, *Compilation of Air Pollutant Emission Factors,* and (3) current standard testing protocols from measuring emissions from airplane turbines, since they are the same technology used for power generation. Results of the literature survey indicated that the exhaust concentration levels are getting lower all the time, with new standards driving technology to ever lower levels. Basically no single report addressed the issues of this research, so the attached literature review was used as a guidance document of the issues associated with measuring low concentrations from modern combustion sources, like distributed generation units.

2.2 Trial Test

The first test was a trial test, given the importance and complex requirements of the project and the limited number of costly test opportunities. It was run on July 1, 2010, with multiple goals:

1. Learn the time and techniques needed to test a DG in the field.
2. Explore several PM measurement methods to select one for the project.
3. Sample gases with M-100 instruments to learn the applicability to the planned DG sources.

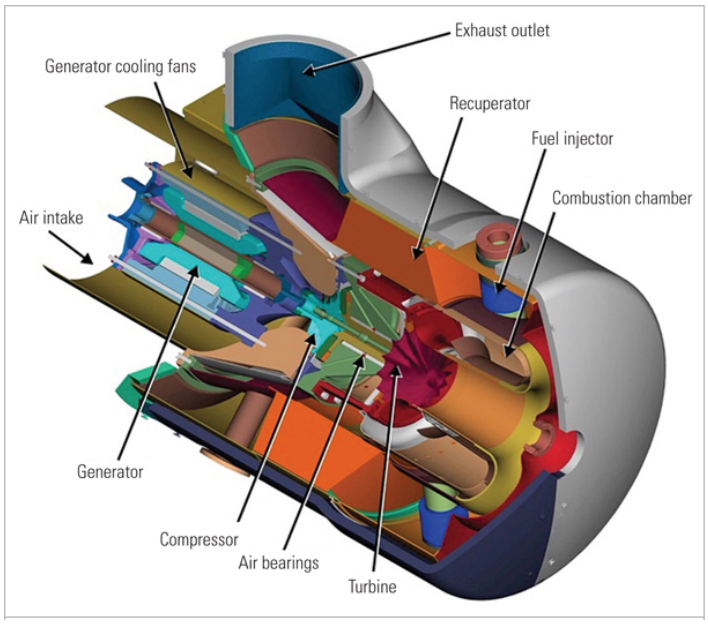
2.2.1 Description of the Test Unit

For the trial test, a Capstone C65 microturbine was selected, as it was easily accessible and was one of the units in the planned test matrix. The Capstone C65 microturbine is a simple gas turbine, featuring a radial compressor and turbine rotors and using just one stage of each. These turbines recover exhaust energy to preheat compressed inlet air, thereby increasing electrical efficiency compared with a simple-cycle machine. The air-to-air heat exchanger is termed a *recuperator,* and the entire system is typically called a *recuperated cycle.* The Capstone unit uses maintenance-free air bearings, so there are no lubricants. The inlet is air cooled, so no coolants are needed (see Figure 2-1).

The microturbine can run on a variety of fuels, including: natural gas, biogas, flare gas, diesel, propane, and kerosene. According to the manufacturer's brochure, the exhaust gas flows are approximately 1.0 pound per second (lb/sec) of air (nominally 800 standard cubic feet per

minute [scfm]) at a typical temperature of 550°F to 600°F (260°C to 320°C). The exhaust gas exits through a 10-inch diameter stainless steel stack. The unit, shown in Figure 2-2, operates quietly and has a small footprint and high power density.

Figure 2-1: Schematic of a Capstone Simple Cycle Turbine



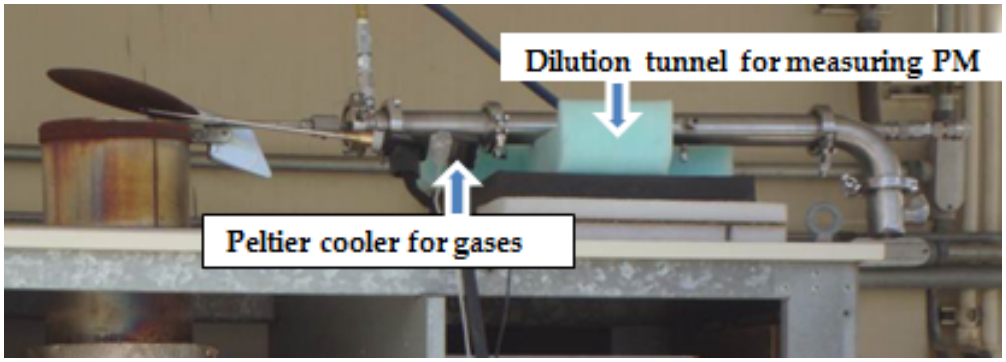
Source: Capstone Turbine Corporation (www.microturbine.com)

One of the benefits of Capstone microturbine technology is its design achieves extremely low exhaust emissions levels without the need for exhaust after treatment. Continuous lean premix combustion provides low levels of NO_x, CO, and unburned hydrocarbons. The 65-kW Capstone C65 has a heat rate about 11,800 Btu/kilowatt-hours (kWh) lower heating value (LHV) and produces NO_x at a rate of approximately 9 ppm, dry basis; a fraction of the rate of a large natural gas–fired reciprocating generator set and about half of the average utility-scale power generation system.

Figure 2-2: Photograph of Capstone C65 Microturbine Unit

Figure 2-3 shows the gaseous and PM sampling systems. The gaseous sampling probe included a Peltier cooler to remove the moisture before the gaseous analyzers. However, for the PM measurement, a dilution tunnel was used to reduce the moisture in the sample. The dilution ratio was about 3 or 4. The dilution air was cleaned of hydrocarbons, moisture, and PM before being sent to the dilution tunnel.

Figure 2-3: Photograph of the Gas and PM Sampling Systems



2.2.2 Trial Test – ARB Method 100 Gaseous Results

The heart of the gaseous instruments used in the trial or pilot test and subsequent tests was a Horiba PG-250, with the specifications shown in Table 2-1 and Table 2-2. As part of the Quality Assurance Project Plan (QAPP) the instrument was serviced by Horiba every six months to ensure that it met all operating specifications. On return of the instrument, the University of California, Riverside (UCR) verified that the instrument met the Horiba specifications in the lab before deploying it in the field.

Table 2-1: Detectors and Ranges for the Horiba PG-250

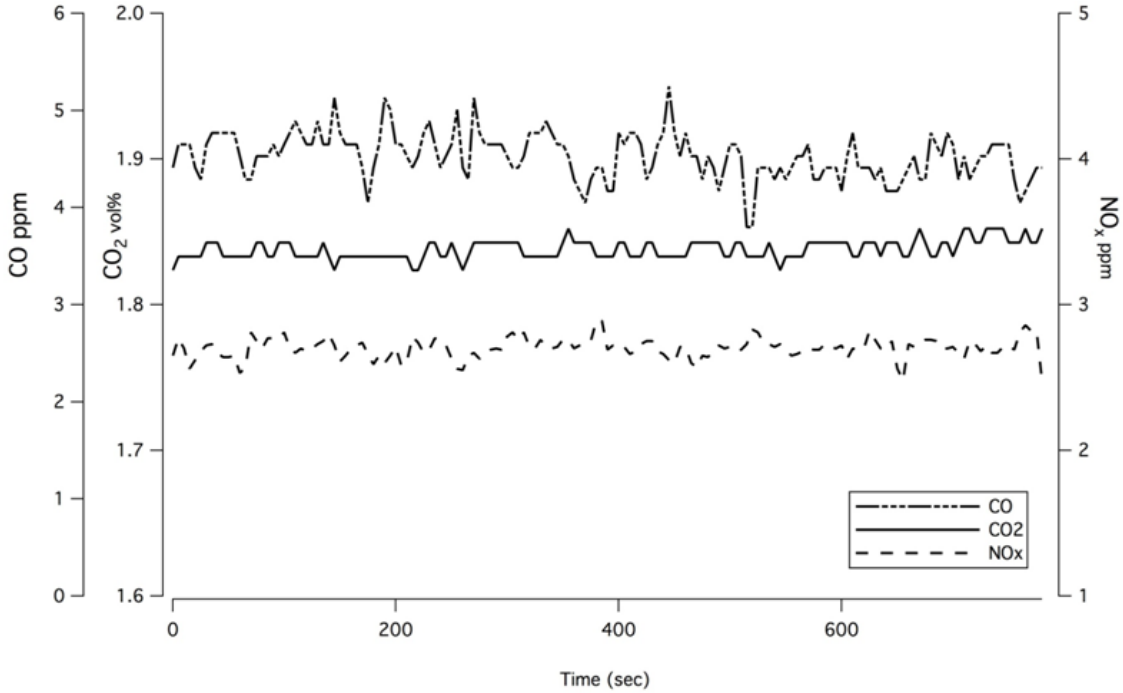
Component	Detector	Ranges
Nitrogen Oxides (NOx)	Heated Chemiluminescence Detector (HCLD)	0–25, 50, 100, 250, 500, 1,000, and 2,500 ppmv
Carbon Monoxide (CO)	Non-dispersive Infrared Absorption (NDIR)	0–200, 500, 1,000, 2,000, and 5,000 ppmv
Carbon Dioxide (CO_2)	Non-dispersive Infrared Absorption (NDIR)	0–5, 10, and 20 vol%
Sulfur Dioxide (SO_2)	Non-dispersive Infrared Absorption (NDIR)	0–200, 500, 1,000, and 3,000 ppmv
Oxygen	Zirconium oxide sensor	0–5, 10, and 25 vol%

Table 2-2: Quality Specifications for the Horiba PG-250

Repeatability	±0.5% Full Scale (F.S.) (NO_x: </= 100 ppm range; CO: </= 1,000 ppm range) ±1.0% F. S.
Linearity	±2.0% F.S.
Drift	±1.0% F. S./day (SO_2: ±2.0% F.S./day)

Measured concentrations of CO, CO_2, and NOx are shown in Figure 2-4 from the trial test.

Figure 2-4: Sample Measurements of CO, NOx, and CO_2 from a 65 kW Microturbine



Data as recorded and later corrected using the calibration curves were averaged over the test period and values listed in Table 2-3. As expected, results showed the concentrations of NOx and CO were below 10 ppm. Results also showed the need to follow calibration procedures carefully at these low levels to get accurate data. In this study's protocol, calibration gases were injected during the testing and at the end of the day to check for instrument drift. Thus, the scale knob on the analyzer was rarely mechanically adjusted; instead, the raw data were adjusted with the measured calibration curves. Note the magnitude of the corrections. For example, the raw value of 0.36 for the NOx data increased to 1.20 after correcting for the calibration by 1.2/.36 = 333 percent—a most significant change. Also note that the coefficient of variation (COV) for all gases was < 10 percent, indicative of how steady the turbine operated during the test period.

Table 2-3: Trial Run Shows Data Corrections Are Significant

	Raw Data		Corrected Data		
	NOx (ppm)	CO (ppm)	NOx (ppm)	CO (ppm)	CO_2 (ppm)
Average	0.36	2.52	1.20	2.86	4410
STDEV	0.05	0.18	0.05	0.21	121.3
COV	14%	7%	4%	7%	3%

STEDV = standard deviation

The next step in the analysis was to compare the values measured in this trial with values for a microturbine listed in the Capstone brochure and in U.S. EPA's AP-42, their *Compilation of Air Pollutant Emission Factors.* The Capstone brochure indicates the turbine exhaust should have < 9 ppmv NOx, in agreement with what was measured. From this work, the average NOx (g)/CO_2 (kg) = 0.29, as indicated in Table 2-4 and the EPA AP-42 lists a range of 0.83 to 2.69 NOx (g)/CO_2 (kg). We considered this comparison to validate the approach and that this unit is representative of a properly operating unit.

Table 2-4: PM Filter Mass Measured in Triplicate

	PM(g)/CO_2 (kg)	**NOx (g)/CO_2 (kg)**	**CO (g)/CO_2 (kg)**
Test 1	0.02	0.31	0.45
Test 2	0.01	0.29	0.39
Test 3	0.01	0.29	0.39

2.2.3 Trial Test: Particulate Matter Results

A number of PM test methods were used during the trial test (see Table 2-5). A primary objective during the trial was to find a PM method that would quickly characterize the PM without taking attention from measuring the gaseous emissions, as those data were the project's primary focus. The trial used both (1) a filter-based mass measurement using protocols outlined by the International Standard Organization (ISO 8178-1), and (2) electronic, real-time methods, although these were not reference methods. Some of the electronic methods are being considered for SAE AIR6037, the measurement of non-volatile PM from jet turbines.

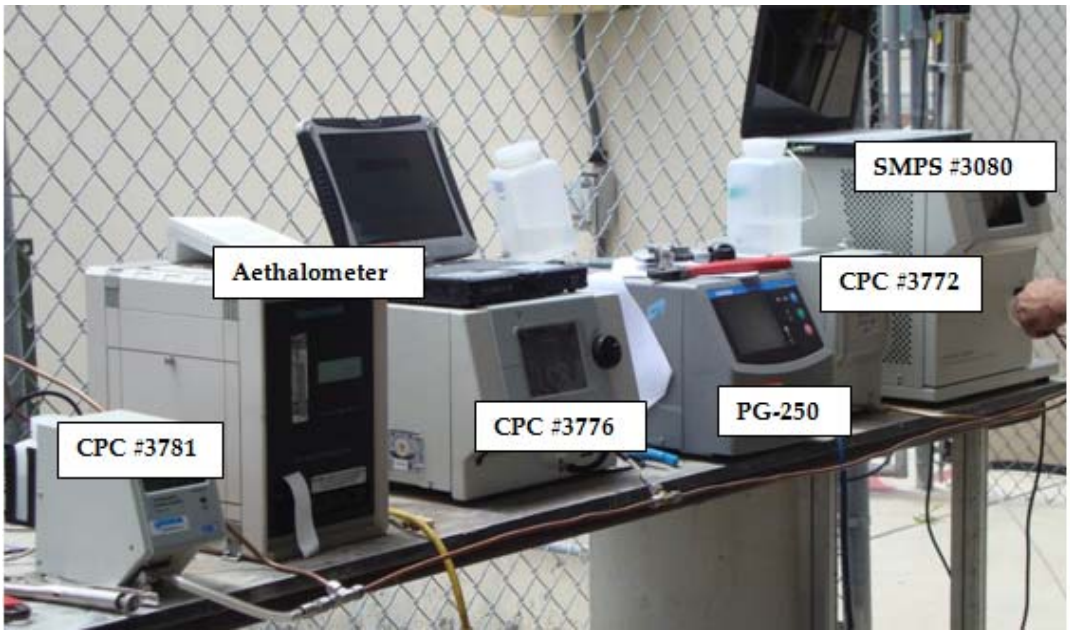
Table 2-5: List of PM Measuring Methods Used in the Trial Test

Instrument	**Model Number Measures**
Teflon filter and partial dilution tunnel	PM mass by a reference method, ISO 08178-1
Aethalometer, Magee Scientific AE-42, Portable	Measures optical absorption by suspended aerosol particles at two wavelengths: 880 nanometers (nm) (IR), quantitative for the mass of "Black" Carbon; and 370 nm (ultraviolet), indicating aromatic organic compounds.
CPC Model: TSI 3781	Water-based Condensation Particle Counter (CPC) capable of measuring particles larger than ~6 nm
CPC Model: TSI 3776	Butanol based ultra-fine CPC designed to detect particles as small as ~ 2.5 nm
Scanning Mobility Particle	Range altered to measure from 7–260 nm, composed of a

Sizer (SMPS) Model: TSI 3081	Differential Mobility Analyzer (DMA) and a CPC

Figure 2-5 shows the bench with the instruments lined up for the testing. A Peltier cooler was used at the sample point of the turbine exhaust, and the treated exhaust was feed for the PG-250, used for continuously measuring gas concentrations. All the other instruments measured PM using the same sample coming from the dilution tunnel.

Figure 2-5: Lineup of PM Instruments for the Trial Test



Even though the turbine ran at 100 percent power for about 60 minutes to reach steady state before measuring gas concentration and PM mass, we were especially concerned about the repeatability of the PM measurements, as the microturbine had not been used for some time. Accordingly triplicate measurements of the PM mass were made, and the results in Table 2-4 report the mass of emissions per mass of fuel burned.

PM by filter mass: As is evident in Table 2-4, the gaseous and PM values for the second and third runs were near steady state, so the turbine operation was viewed as a process that was under statistical control. Earlier PM values were higher, suggesting the unit was not run long enough. Values measured for the PM mass per mass of fuel consumed were compared with those reported in U.S. EPA's AP-42. This study measured 0.01g PM/kg of CO_2, a value significantly less than the 0.06 g PM/kg CO_2 reported in U.S. EPA's AP-42. However, the new Capstone microturbine is likely to be cleaner.

PM by electronic measurement: Before the trial test, the CPC was expected to be the most credible continuous analyzer for measuring PM during the project, based on three factors: (1) the Europeans are using PM number as criteria for exposure, (2) the Society of Automobile Engineers (SAE) specification for measuring solid PM emissions from aircraft turbines uses the CPC, and (3) it would be a simple instrument to install and would run unattended after initial setup during the rest of the testing.

Data for the SMPS and two CPCs are shown in Table 2-6. Analysis of the data revealed some interesting findings:

1. Measurements of ambient concentrations PM varied widely for the various analyzers.
2. The PM concentrations for the filtered air going into the turbine were greater than those for the ambient air. Figure 2-6 shows that the filter effectively removes particles greater than 30 nm but there are a greater number of small particles in the filtered air. The reason for this filter artifact is undetermined.
3. Water-based condensation particle counters measured about the same number of particles as a butanol-based condensation particle counter for ambient air but measured approximately 1 percent of the particles found in a turbine exhaust; presumably because the exhaust particles were too small to be seen or were not wetted and counted by the water-based system.

Table 2-6: PM Data for the SMPS and Two CPCs

	CPC-SMPS (#/cm³)		**CPC-3781 (#/cm³)/water**		**CPC-3776 (#/cm³)/butanol**	
CPC min. (nm)	10		6		2.5	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Ambient	5,623.5	1,739.0	3,390.0	200.8	9,470.0	1940.0
Filtered Air	21,479.9	8639.7	32,556.6	32573.3	25,267.0	6382.3
Exhaust	8,452.1	1233.4	652.8	243.2	57,128.2	32081.0

The real-time data allowed a measure of the transient nature of the turbine exhaust. Figure 2-7 shows that the emissions are relatively stable. Note that in this figure the butanol scale had to be multiplied by 10,000 to fit the chart, while the y-axis for the water system was not multiplied. Another correction needs to be made for the 3.2 dilution ratio in the tunnel.

Figure 2-6: Typical SMPS Data for (a) Ambient air; (b) Filtered air; (c) Turbine Exhaust

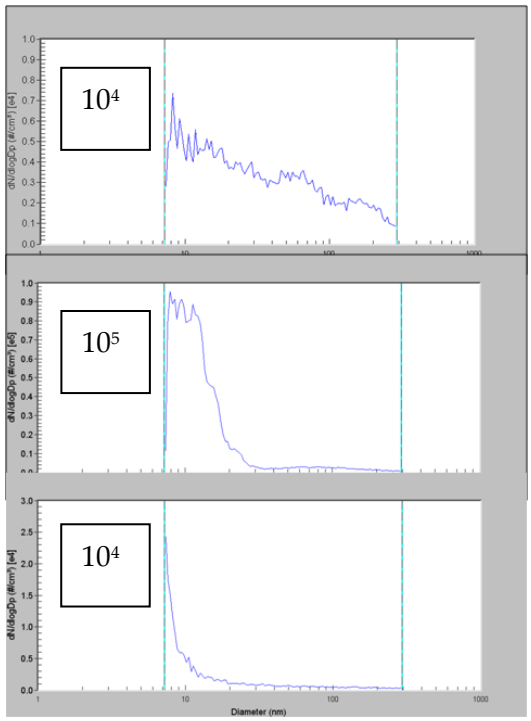
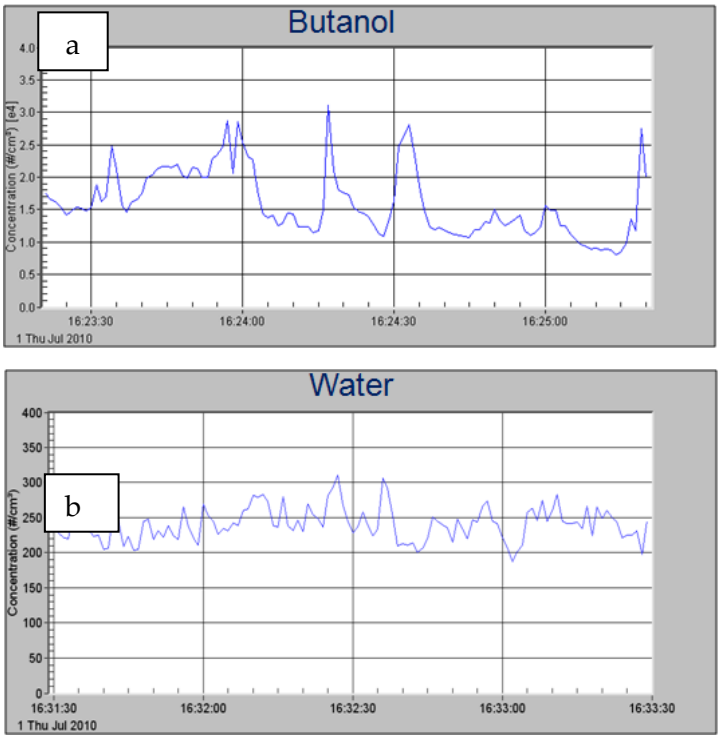


Figure 2-7: Real-Time CPC Data for Turbine Exhaust Showing Difference Between the: (a) Butanol and (b) Water CPCs



(Note that the butantol Y axis scale is 10,000 times the water Y axis scale.)

The trial run also looked at the use of a Scanning Mobility Particle Sizer (SMPS) to characterize the PM properties. The range for the SMPS instrument, which is composed of a Differential Mobility Analyzer (DMA) and a CPC, was tailored to measure from 7–260 nm. Figure 2-7 below shows the particle size distribution for the ambient and filtered air and the exhaust. Note the filter removed some of the larger particle diameter material; however, most of particles in the exhaust were < 10 nm. Based on the comparative results in the trial test, the SMPS was selected as the instrument for the project, as it provided both particle size distribution and magnitude. Further, there is a way to estimate the PM mass from the SMPS data. In any case, the electronic monitoring methods provided a more accurate way to monitor the physical nature of the PM mass rather than reliance on filter weights.

2.3 Design of Integrated Sampling System, Including Hydrocarbons

One critical component of the project was the design of an integrated field system that allowed the simultaneous measurement using protocols specified in existing regulations and instruments proposed from this project. Special attention was afforded to the accurate measurement of concentrations at low levels, especially hydrocarbons, as those measurements are quite challenging. During this project, the samples of exhaust were measured with a number of hydrocarbon methods, including: SCAQMD Method 25.3,3 U.S. EPA TO-12,4 and provisions to sample for carbonyls with 2,4-Dinitrophenylhydrazine (DNPH) cartridges and light hydrocarbons using selective sorption tubes. Commercial firms on the SCAQMD approved vendor list were selected for the off-line canister analysis. Furthermore, a member from one of the SCAQMD approved labs was included during the field testing to take advantage of their considerable field experience. In addition to the canister methods, UCR set up a Flame Ionization Detector (FID) with a heated line to continuously measure THC or non-methane hydrocarbons (NMHC), per U.S. EPA Method 25A,5 as a continuous check on the hydrocarbon levels. The design of the complicated field system is shown in Figure 2-8.

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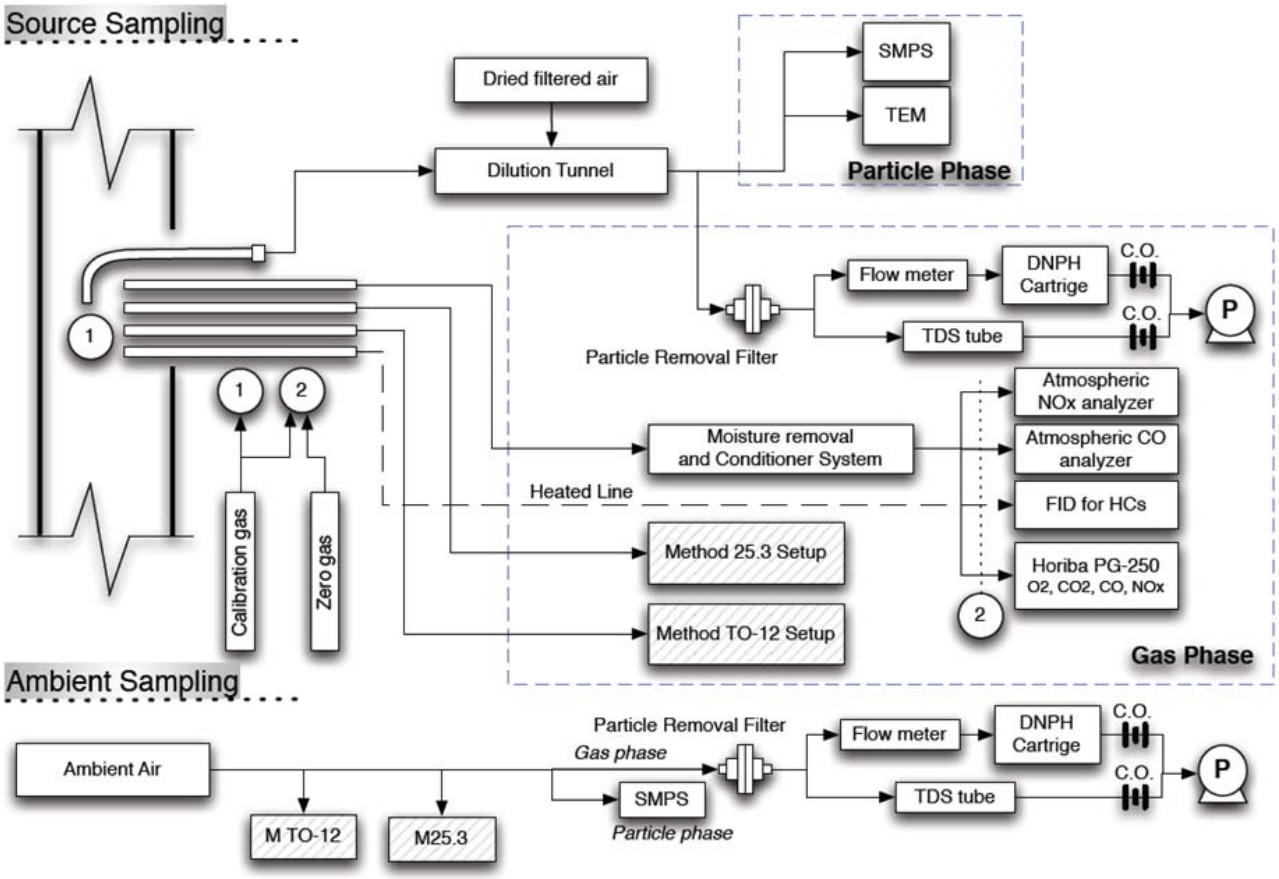
3 SCAQMD Method 25.3 is the method for the Determination of Low Concentration Non-Methane Non-Ethane Organic Compound Emissions from Clean Fueled Combustion Sources.

4 EPA TO-12 is the mMethod for the Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID).

5 EPA 25A is the Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer.

Figure 2-8: Schematic of the System for Source and Ambient Sampling



CHAPTER 3:
Results from the Field Testing

Following the completion of the trial test, the California Energy Commission project manager and the Advisory Committee reviewed the results from the trial test and approved the sampling system and PM measurement method. Subsequent discussion in the meeting was about the specified units to test (see Table 3-1).

Table 3-1: Recommended List of Distributed Generators to Test

Test	Distributed Generator
1	Capstone C-65 microturbine (65 kW)
2	Fuel Cell Energy's DFC300 (300 kW) on natural gas (NG) or biogas
3	Solar Turbines Titan™ 130 Turbine + SCR (13.5 MW) on NG
4	Solar Turbines Titan™ 130 Turbine + EMx (13.5 MW) on NG
5	Large NG Turbine (~50 MW) + control

3.1 Test of the Microturbine (Capstone 65 kW)

On September 24 and 25, 2010, UCR tested the same Capstone microturbine used in the trial testing, with the goal of measuring gaseous concentrations, the flow rate, and the PM characteristics, following the methods approved in the advisory meeting. However, before testing, the exhaust configuration was changed from that seen in Figure 3-1. Pipe lengths were attached to the turbine exhaust and straight pipe sections were directed through the roof, in order to make the flow measurements. The additional pipe lengths allowed enough ports to simultaneously measure both the EPA TO-12 samples and the SCAQMD 25.3 samples. See Figure 3-1. Characteristics of the microturbine were previously provided in Section 2.2.1.

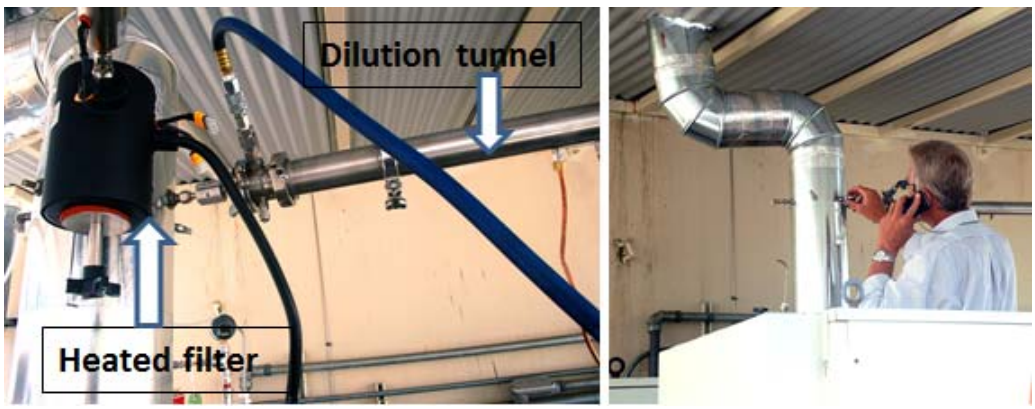
3.1.1 Measuring NOx, CO, and CO_2 with Method 100 and Ambient Instruments

In addition to the Method 100 instruments, the following analytical instruments were added to measure concentrations at much lower levels (see Table 3-2).

Table 3-2: Properties of New Analytical Instruments

Instrument	Method of Detection	Range
NO_x analyzer, TECO Model 42	Chemiluminescence	0–5000 parts per billion (ppb)
CO analyzer - Thermo Environmental Instruments Model 48C	Infrared detection at 4.6 m	1, 2, 5, 10, 20, 50, 100, 200, 1,000 ppm
J.U.M. Engineering HFID Model 3-200	Flame ionization detector	0–10,100, 1,000, 10,000, 100,000 ppm

Figure 3-1: Installed Exhaust Conduit with Heated Filter and Dilution Tunnel



From Figure 3-2 it seems clear that the measured values of NOx and CO with the Method 100 instrument are biased high when compared with the ambient instruments. This is not surprising given that the NOx analyzer is working on a 0–25 ppm scale, so the low values for this source are well below the generally accepted operating range of 20 percent * 25 ppm = 5 ppmv. Similarly the CO range was 0–200 ppm, so the useful lower limit was 40 ppm. Further analysis of the data indicated the COV was about the same for all instruments, as shown in Table 3-3.

Figure 3-2: Measurements of NOx, CO, and CO_2 by ARB Method 100 and Ambient Instruments

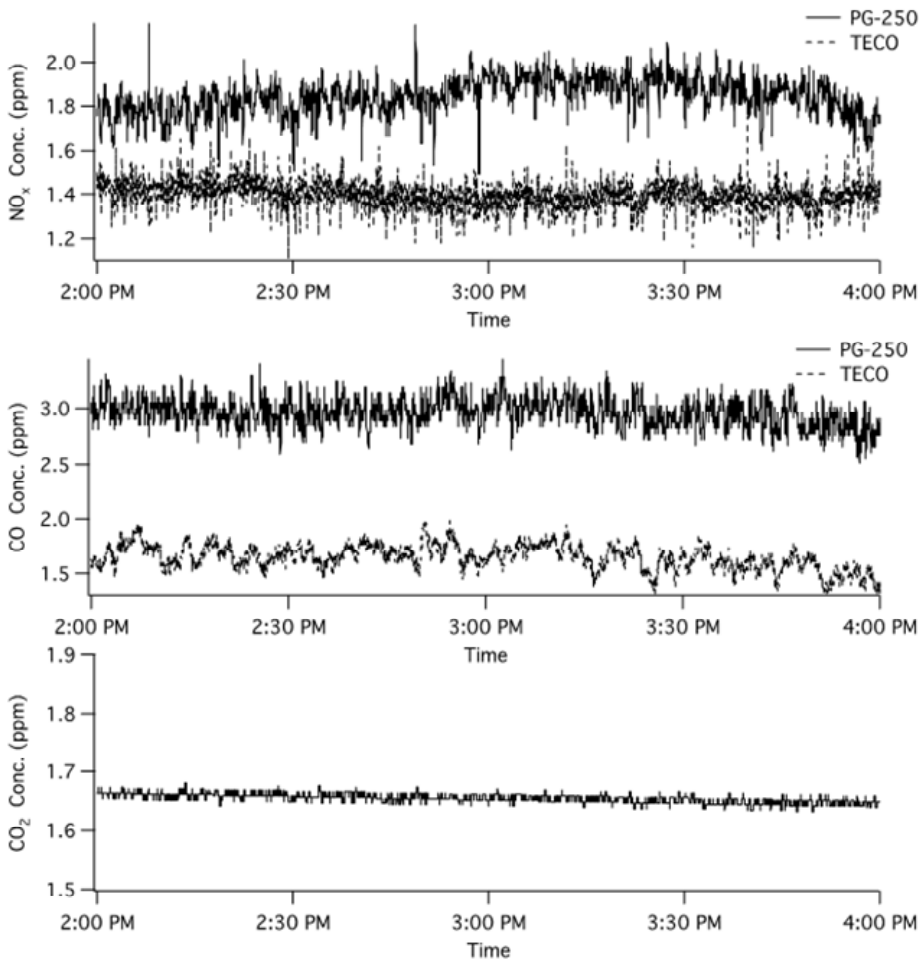


Table 3-3: Average Concentration of CO and NOx by ARB Method 100 and Ambient Monitors

Measurements	Instrument	Average (η)	Stdev (σ)	COV, %
CO (ppm)	PG-250	2.971	0.126	4
	TECO	1.661	0.109	6
NO_x (ppm)	PG-250	1.853	0.081	4
	TECO	1.396	0.049	3

3.1.2 Measurement of Hydrocarbons by SCAQMD 25.3 and U.S. EPA TO-12

As mentioned previously, measuring < 10 ppm of total hydrocarbons in the exhaust of modern DG units has proven quite challenging. Samples of empty canisters and impingers for SCAQMD 25.3 were ordered from a lab on the SCAQMD approved list. The methods require extensive care in the pre-sampling leak checks and in the sampling itself (Figure 3-3). Sampling

takes over an hour in order to obtain a representative sample. As indicated in Section 2.3, UCR sampled both exhaust and ambient air with the expectation that the ambient sample would be near 4 ppm and serve as the baseline to compare with the exhaust values.

Figure 3-3: Pretest Leak Checking SCAQMD 25.3 and Sampling with U.S. EPA TO-12

All canisters passing the leak test were filled to about 15 inches of vacuum or about 50 percent of the evacuated values as prescribed in the method. After the test and sampling, the canisters were returned to the qualified lab for analysis after the testing using chain of custody forms. Results are provided below. While SCAQMD 25.3 requires simultaneous parallel samples, some parallel samples were compromised when the water vials broke on shipment back to the lab, so only one set of data is provided (see Table 3-4).

Table 3-4: Analysis of Exhaust by SCAQMD Method 25.3, Both Canister and Water Vials

	Canister				Impinger	
Test	**Methane (ppm)**	**Ethane (ppm)**	**TGNMO (ppm)**	**CO_2 (ppm)**	**Carbon (ppmv)**	**Volume (ml)**
1/Ambient air	3.97	<1	17.59	1180[outlier]	1.85	2.16
	1.74	<1	10.86	443	1.32	2.62
2/Ambient air	2.36	<1	4.42	494	3.5	2
2/Source	<1	<1	10.65	17100	0.65	2.8
3/Source	<1	<1	15.75	15700	1.88	2.64
4/Source	<1	<1	14.77	16000	1.53	2.67
	<1	<1	18.90	15600	1.04	2.5
5/Source	<1	<1	16.07	15600	0.57	2.76

Source (Average±STDEV)	<1	<1	15.0 ± 3.4	16100 ± 688	1.3 ± 0.5
Ambient (Average±STDEV)	2.7 ± 01.2	<1	11.0 ± 6.6	468.5 ± 36.1	2.2 ± 1.1

TGNMO = total gas non-methane organics

Given the high combustion efficiency of this turbine, results for the exhaust emissions showed very low concentrations of methane and ethane, as expected. However, values for TGNMO (total gas non-methane organics) of 15 ± 3.4 ppm seemed surprisingly high for a natural gas-fired turbine. Note the COV for the TGNMO of 3.4/15 = 22 percent, a rather high value that might be representative of the method. The impinger value of 1.3 ± 0.5 seemed about right, based on reports of field test companies.

A review of the results for CO_2 concentrations in the ambient air shows the first sample was far from the expected results of ~400 ppm, so it was identified as a statistical outlier and excluded from the analysis. While the measured methane concentration in the ambient air samples seemed about right, the TGNMO value of 11 ± 6.6 ppm was higher than the expected value of ~2 ppm. We cannot offer a definite explanation for the high value for the TGNMO but suggest that the high COV value of 6.6/11 = 60 percent is indicative of a process with wide variations and uncontrolled parameters. Given the low COV values of ~5 percent for NOx and CO, it is clear the turbine is operating near steady state, so it is the canister analytical methods where the uncontrolled parameters exist.

Results showed that the values of TGNMO by EPA TO-12 for the exhaust samples were 89 percent lower (1.6/14 = 11 percent) than values measured by SCAQMD 25.3 (see Table 3-5). Values of ~1.5 for EPA TO-12 were similar to those expected. The fixed gas analysis, measured by the standard EPA Method 3C (Determination of carbon dioxide, methane, nitrogen, and oxygen from stationary sources using gas chromatography) in Table 3-5, shows values near those expected and excellent COVs.

Table 3-5: Analysis of Exhaust for TGNMO by EPA TO-12 and Fixed Gases by U.S. EPA 3C

	Canisters (EPA TO-12)		Fixed gas analysis (EPA 3C)	
Test ID	Canister ID	TGNMO(ppmv)	Nitrogen (%v)	Oxygen (%v)
1/Ambient	SUMMA 147	1.16	76.9	20.4
2/Ambient	SUMMA 161	1.78	77.3	20.2
2/Source	SUMMA 135	1.83	77.1	17.1
	SUMMA 107	1.09	77.1	16.9
3/Source	SUMMA 399	1.41	77.3	17.2
4/Source	SUMMA 382	1.94	77.8	17
Source (Average±STDEV)		1.6 ± 0.4	77.3 ± 0.3	17.1 ± 0.1
Ambient(Average±STDEV)		1.5 ± 0.4	77.1 ± 0.3	20.3 ± 0.1

3.1.3 Measurement for Carbonyl and Other Trace Light Hydrocarbons

Results in Table 3-6 show the analysis for aldehydes and ketones. Results show that exhaust levels of aldehydes and ketones are in the parts-per-billion range, less than those in the ambient air and primarily consisting of formaldehyde, presumably from the partial oxidation of

methane in the natural gas fuel. Clearly aldehydes in the parts per billion levels account for an insignificant level of the exhaust hydrocarbons, which according the canister results are in parts per million levels, or 1,000 times greater.

Table 3-6: Analysis for Aldehydes and Ketones Using DNPH Cartridges (ppbv)

	Test No	Formaldehyde	Acetaldehyde	Acetone	Acrolein	Propionaldehyde	Crotonaldehyde
Ambient	1	12.47	11.23	18.69	3.51	-	-
	2	14.54	24.70	12.75	48.29	11.12	3.38
	3	18.30	10.32	20.22	2.76	-	-
Source	1	11.07	8.35	9.48	-	-	-
	2	5.40	2.15	3.38	-	-	-
	3	6.13	1.67	3.57	-	-	-
	4	4.19	1.99	1.96	-	-	-
	5	3.56	1.25	1.00	1.60	-	-
Ambient		15.10±2.95	15.41±8.05	17.22±3.95	18.18±26.07	11.12	3.38
Source		5.46±3.05	2.57±2.93	3.23±3.35	1.6	-	-

Note: The shadowed sample was collected overnight.

Table 3-7 shows the results for the analysis of selected trace light hydrocarbons. Note that results for the light hydrocarbons, such as benzene, were in parts per trillion concentrations as compared with the aldehydes in parts per billion levels. Clearly the sum of the concentrations of aldehydes and light hydrocarbons only account for an insignificant level of hydrocarbons found in the canisters.

Table 3-7: Analysis for Selected Trace Hydrocarbons Using TDS Tubes (pptv)

Sample	1*3-Butadiene	Benzene	Toluene	m&p-xylene	Ethyl-benzene	o-Xylene	Naphthalene
Ambient	48.6	901.3	1222.2	374.5	144.0	156.1	50.4
	29.1	370.7	764.5	356.4	96.6	119.0	21.0
	263.5	1175.8	961.0	318.3	111.1	142.8	21.3
Source	164.0	1821.6	1037.5	422.1	140.8	235.6	108.0
	150.0	548.2	74.1	20.0	15.7	55.6	45.6
	143.7	361.8	75.0	75.8	17.4	32.3	32.3
	38.7	1979.8	124.3	76.1	29.0	74.1	50.2
Ambient	156.0 ±152.0	1038.6 ±194.1	1091.6 ±184.7	346.4 ±39.8	127.6 ±23.3	149.5 ±9.4	35.9 ±20.6
Source	124.1 ±57.6	1177.8	327.7 ±473.7	148.5	50.7 ±60.4	99.4	59.0 ±33.6

±840.6	±184.3	±92.4

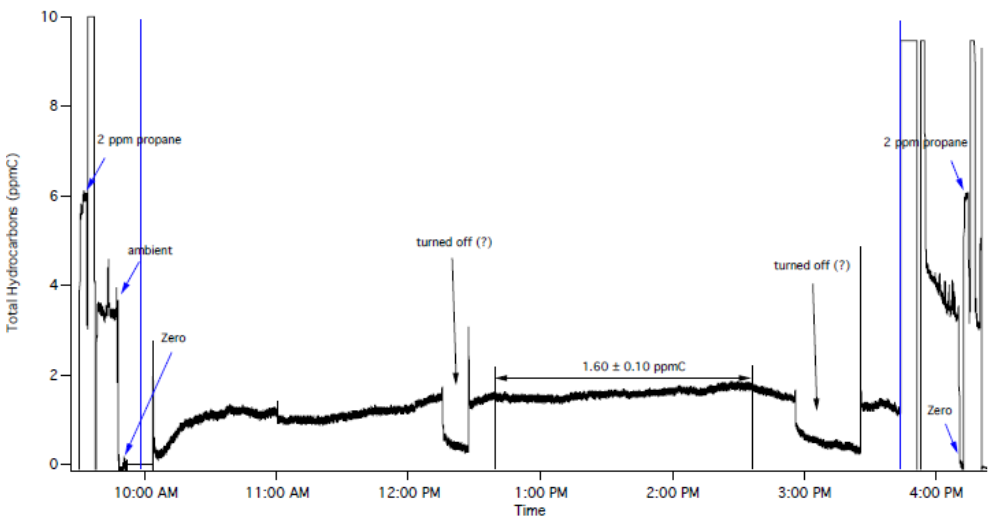
Note: The gray-shaded sample was collected overnight.

3.1.4 Measurement of Hydrocarbons by EPA 25A

Measurement of total and non-methane hydrocarbons with the FID proved problematic during the testing, so the quantity of data were quite limited on the first day. Some data were lost because the electrical circuit with the heated filter element and instrument often tripped the breaker, and at other times, the flame went out on the FID.

Data taken the last 30 minutes of the first day were stable and showed that the level of hydrocarbons was much less than 10 ppm. Data from the second day are illustrated in Figure 3-4 and show the total hydrocarbons (THC) is ~2 ppm, a value closer to that measured with EPA TO-12.

Figure 3-4; Total Hydrocarbon Data from Microturbine on the Second Day



3.1.5 Measurement of the Flow Rate

Flow properties were measured across the 8-inch diameter stack using ARB Methods 1–4, and the data are shown in Table 3-8. Values in Table 3-8 were converted to the flow rate by using equations in Table 3-9.

Table 3-8: Stagnation Pressure and Temperature of Stack Gas at a Point

Point	ΔP (in H_2O)	T (° C)
1	1.3	258
2	1.4	257
3	1.1	258

Point	ΔP (in H_2O)	T (° C)
4	1.2	258
5	1.3	257
6	1.4	257
7	1.25	257
8	1.2	257

Stack velocity at each traverse point (V) is calculated based on pressure difference in inches of water from Table 3-8. An average temperature of 257.37°C (495.27°F)and ΔP of 1.27 in H_2O lead to a stack velocity of 100.96 ft/sec. To calculate molecular weight of stack exhaust (M_d), concentrations of CO_2, nitrogen (N_2), oxygen (O_2), and CO from Method 100 were used. These values resulted in an average molecular weight (M_d) equal to 27.84. Referring to the recorded test data, the pressure correction factor (F_p) turns out to be 0.982, based on barometric pressure of 29.94 in Hg. Gas density correction factor (F_d) is a function of standard dry molecular weight (M_{std} - lb/lb-mole) and molecular weight of stack gas (M_d - lb/lb-mole), with the value of 1.0196 based on M_d = 27.84.

Table 3-9: Equations for Calculating Volumetric Flow Rate

Parameter	Method	Equation
Molecular weight of exhaust (unitless)	SCAQMD M3.1	$M_d = \%CO_2\ (0.44) + \%O_2\ (0.32) + (\%N_2 + \%CO)\ (0.28) = 27.84$
Gas density correction factor (unitless)	SCAQMD M2.1	$F_d = \sqrt{\frac{M_{std}}{M_d}} = \sqrt{\frac{28.96}{M_d}}$
Pressure correction factor (unitless)	SCAQMD M2.1	$F_p = \sqrt{\frac{P_{std}}{P_{bar} \pm P_{static}}} = \sqrt{\frac{29.92}{P_s}}$
Stack velocity at each traverse point (ft/sec)	SCAQMD M2.1	$V = 2.90\sqrt{H(T_s + 460)}$
Stack gas volumetric flow rate (scfm)	SCAQMD M2.1	$Q = 60\ C_p V_c F_d F_p A$
Dry standard volumetric flow rate (scfm)	SCAQMD M2.1	$Q_{std} = \frac{Q P_s (520)(1 - 0.01 B_w)}{29.92 (T_s + 460)}$

where:

A: Cross sectional area, m^2 (ft^2)

C_p: Pitot tube coefficient (dimensionless)

H: Velocity head measured by S-type pitot tube, cm (in) H_2O

B_w: Water vapor in the gas stream, proportion by volume (Method 4.1 or Method 5.1)

T_s: Stack temperature (°F)

T_{std}: Stack Absolute Temperature 293 K (528 R)

M_d: Molecular weight of stack gas (lb/lb-mole)

M_{std}: Standard dry molecular weight (28.95 lb/lb-mole)

P_{static}: Stack static pressure, mm Hg (in Hg)

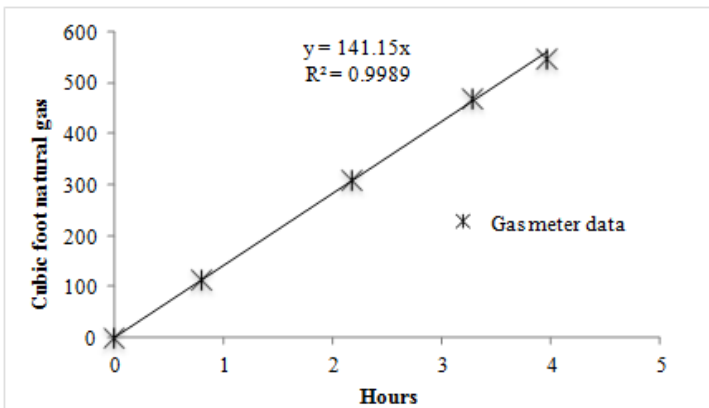
P_s: Absolute Stack pressure ($P_{bar} + P_g$), mm Hg (in Hg)

P_{std}: Standard Absolute Pressure, 760 mm Hg (29.92 in Hg)

Substituting F_d, F_p, and C_p in the stack volumetric flow rate (Q) results in stack volumetric flow rate value of 108.62 kSCFH at the measured exhaust temperature. When these values are substituted into the last equation, the dry standard volumetric flow rate (Q_{std}) is calculated as 57.27 kSCFH.

Flow was also calculated from the Carbon Balance Method outlined in ISO 8178-1 using the data in Figure 3-5. A graph was constructed from the several gas meter readings taken over time, and it showed that with a power output of 58.5 kW, the turbine consumed 141.15 standard cubic feet of natural gas per hour.

Figure 3-5: Gas Usage cu ft Per Hour for this Microturbine at 70 psi



Based on the carbon dioxide concentration in the stack and fuel flow measurements, the calculated flow rate using the ISO Carbon Balance Method was 57.41 kSCFH, about 0.3 percent higher than from Methods 1–4 (see Table 3-10).

Table 3-10: Flow Rates from ARB and ISO Methods

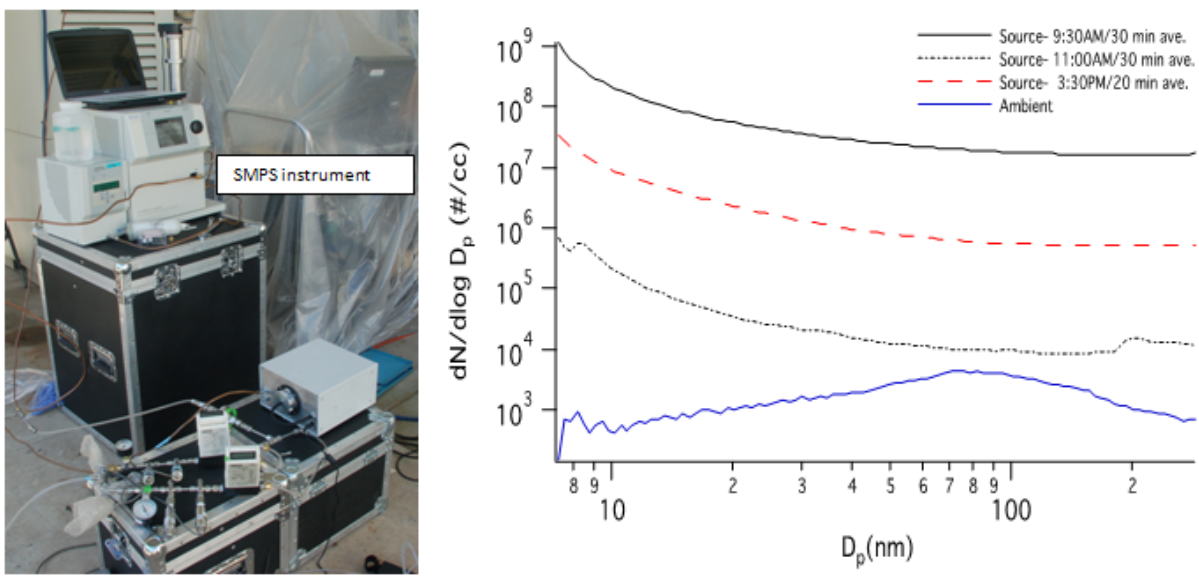
Parameter	Value	Unit
ARB Method		
Stack diameter	8	inch
Stack exhaust temperature	495.3	°F
Stack exhaust Velocity	101.0	ft/sec
Stack Volumetric Flow rate (dry basis)	57.27	kSCFH

Parameter	Value	Unit
ISO Carbon Balance Method		
Fuel rate	141.15 @70 psi	CFH
CO_2 concentration	1.65	vol%
Calculated flow rate	57.22	kSCFH

3.1.6 Particle Size Distribution of the Capstone 65kW Microturbine

Results from the SMPS for the source and the ambient air indicated that the source has smaller diameter for the particles and more particles than in the ambient air (see Figure 3-6). Further, the source levels varied greatly during the test period, by a thousand fold. We did not anticipate such a wide range for the microturbine during the day, as it was operated at full power during the day. Note that the filtered air had a significant amount of bypass air reaching the exhaust.

Figure 3-6.: (a) Field Setup for SMPS, and (b) Data from SMPS During the Test Period



3.2 Test of Solar Turbines Titan™130 Turbine with SCR; First Test

The second unit tested on October 13, 2010, was a natural gas- fired Solar Turbines Titan™ 130 Turbine with selective catalytic reduction (SCR) for NOx control. The power system included a heat recovery generator. There were several advantages of testing at this site:

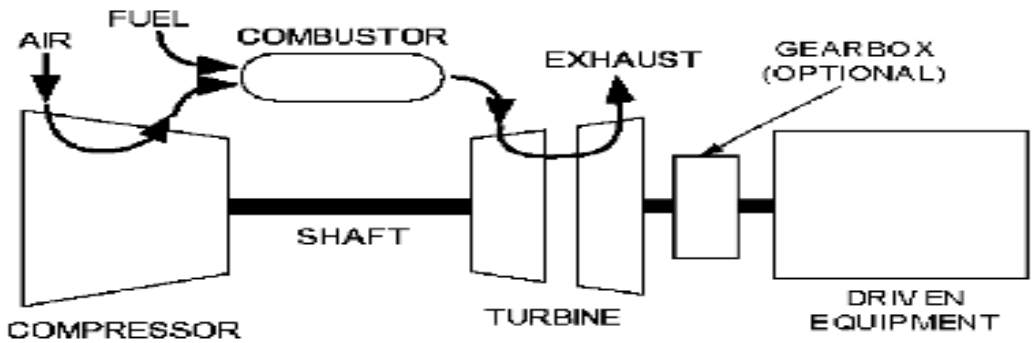
1. The unit had controls and low emissions and was on the Advisor test list
2. The unit had a CEM (continuous emission measurement) for CO, NOx, and oxygen providing an additional and independent check on the concentration levels of our measurements.

3. The unit had accurate and continuous monitors for the natural gas flow.

3.2.1 General Description for a Solar Turbines Turbine Operation

In the Solar Turbines turbine operation shown in Figure 3-7, air is drawn into and compressed by a multi-stage, axial-flow engine compressor. Compressed air is directed at a steady flow into the annular combustion chamber, where fuel is injected and mixed with the compressed air. The mixture is ignited during the start cycle, and combustion is continuous as long as there is an adequate flow of pressurized air and fuel. Hot-pressurized gas from the combustor expands through and drives the turbine, dropping in pressure and temperature as it exits the turbine. The gas turbine only requires approximately one-fourth of the total air it compresses, so the excess air is mixed with the combustion products to reduce the gas temperature at the turbine first stage inlet. The excess air lowers the metal temperatures in the combustor and turbine assembly to prolong service life. The combustion cycle converts the energy in the fuel into kinetic rotating power at the turbine output shaft.

Figure 3-7: Schematic of a Typical Turbine Combustion Unit6



3.2.2 General Description of a Solar Titan 130 Mechanical Drive Package

The second unit tested was a Solar Turbines Titan™ 130 Turbine with SCR and followed by an ammonia slip catalyst. The central utility plant at the site used a cogeneration design based on a 13.5 MW Solar Turbines Titan gas turbine generator and a heat recovery generator that produced about 58,000 pounds per hour (lb/hr) of steam unfired and 120,000 lb/hr with a duct burner. The produced steam was 230 to 240 pounds per square inch gage, slightly superheated, and was fed to a condensing steam turbine, which drives a 5 MW generator. According to the manual, in typical operation the gas turbine tracks the facility electrical load. The steam chiller is operated when steam is not needed for space heating, and the turbine generator would be continuously modulated to maintain the steam header pressure. The tracking of steam demand is done manually by the operators in an effort to avoid exporting power to the grid.

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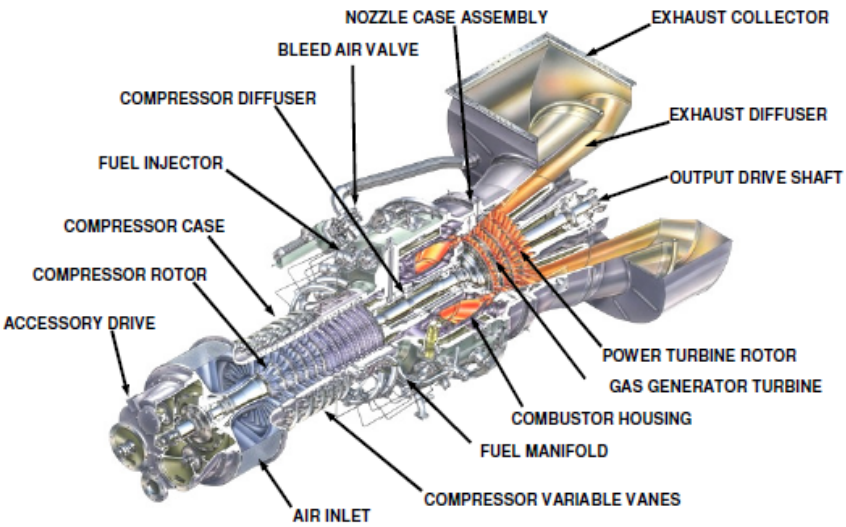
6 For information on the Solar Turbines Titan 130,
see http://mysolar.cat.com/cda/layout?m=41108&x=7.

Typically, the Solar Turbines Model Titan™ 130 gas turbine two-shaft for compressor and mechanical drive applications shown in Figure 3-8 is designed to deliver a simple-cycle thermal efficiency of 36 percent.

Figure 3-8: Schematic of a Titan 130 Mechanical Drive Package



The turbine at the test site was a combined cycle gas turbine with a Deltak Heat Recovery Steam Generator (HRSG). The turbine utilizes a low-NO_x combustion technology, the SoLoNOx Combustion System**,** capable of achieving NO_x and CO emissions of 10 ppmv and 20 ppmv, respectively. To further reduce NO_x and CO emissions from the turbine, SCR technology and CO catalysts are included as exhaust treatment. The SCR and CO catalysts are considered best available control technology (BACT), and are reliable, proven technology that reduces NO_x and CO emissions to 2 ppmv and 3 ppmv, respectively. Selective catalytic reduction relies upon injection of ammonia vapor (NH_3) into the flue gases and the subsequent reaction on a downstream catalyst to reduce NO_x to elemental nitrogen and water. Ammonia emissions are limited to 5 ppmv, based upon the SCAQMD Permit to Operate.

3.2.3 Test Setup for the Solar Turbines Turbine with SCR

Setup for this test required mounting equipment on a testing platform about 50 feet above the ground. All the hydrocarbon methods were located on the platform, including, EPA 25A (FID), SCAQMD 25.3, and EPA TO-12. Instruments for measurements of NOx, CO, CO_2, and particle diameter were located on the ground level. In addition, data loggers for collecting the data during the tests were located on the ground level (See Figure 3-9).

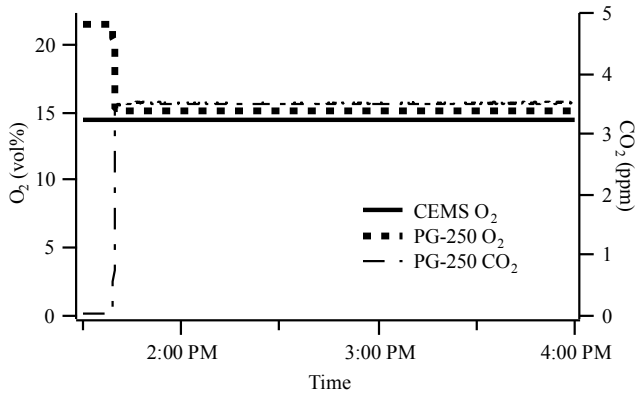
Figure 3-9: Test Setup Showing the Locations for the Measurement Sites

3.2.4 Measuring O2, NOx, CO, and CO_2 with Method 100 and Ambient Instruments

Instruments on the ground level measured NOx, CO, and CO_2 using both ARB Method 100 and ambient instruments. Properties of these instruments were shown earlier in Table 2-2 and Table 3-2. Figure 3-10 shows the comparison between the O_2 measured by the PG-250 portable device with a zirconium oxide sensor and the CEMS7 . Agreement is quite good. Figure 3-10 also shows the CO_2 emissions over the test period. The near steady-state nature for the turbine was particularly helpful in interpreting a resultant high COV value, as was the case for the microturbine.

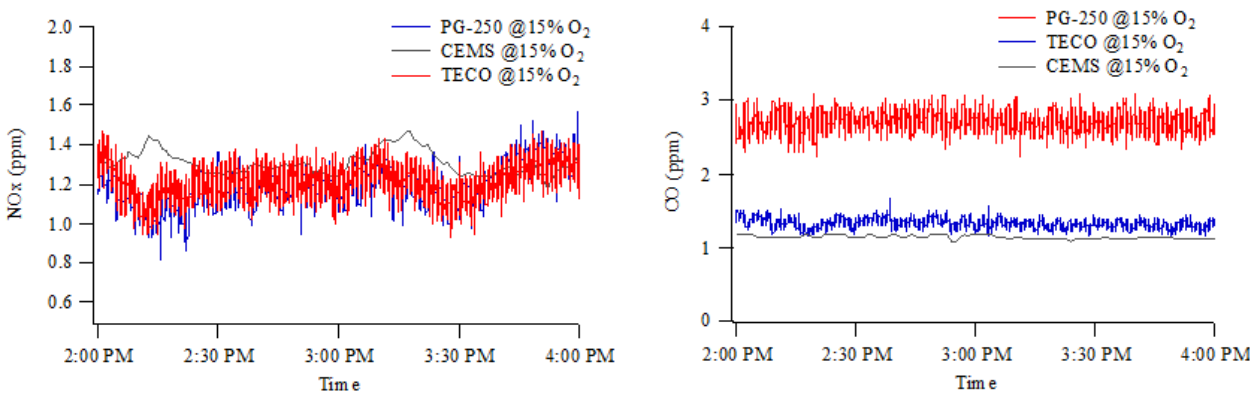
7 *CEMS* is the continuous emissions monitoring system used for reporting compliance of the turbine for CO, NOx, and oxygen, providing an additional and independent check on the concentration levels of our measurements

Figure 3-10: Left Axis Shows Oxygen: PG-250 vs. CEMs; Right Axis Shows CO_2 by PG-250.



Simultaneous measurements for NOx and CO with ARB Method 100 using the PG-250, ambient level instruments using the TECO, and the site's CEMS instruments are shown in Figure 3-11. Clearly, NOx and CO levels at ~1 ppmv are very low. First looking at the NOx data, we see all three instruments are about the same level and all closely track the transient nature of the emissions from the turbine. Further, even though the generally accepted useable level for an analyzer is 20 percent of its range (or for the NOx analyzer, 20 percent of 25 or 5 ppm), it is clear that the value measured with M-100 was quite accurate, since it agreed with the CEMs and ambient instruments.

Figure 3-11: Comparing NOx and CO Measured by: Method 100 (PG-250), Ambient (TECO); CEMS Instruments



In the case of the CO level, the Method 100 instrument is biased high, as compared with UCR's ambient instrument and the site's CEM, which are quite close. This deviation is not surprising as the lowest range on the instrument is 0–200, which suggests that the generally lowest usable limit is 20 percent of 200, or 40 ppm. Clearly the accuracy of the instrument so far below the usable level is below that needed for such low concentrations. Overall results for the two instruments are shown in Table 3-11. Note the low COV values.

Table 3-11: Comparison of Method 100 and Ambient Instruments

	Method 100 Instruments			Ambient Instruments	
	NOx	**CO**	**CO_2**	**NOx**	**CO**
Range	0–25 ppm	0–200 ppm	0–5%	0–5,000 ppb	0–5 ppm
Ave	1.209	2.642	3.510	1.214	1.284
STDEV	0.099	0.125	0.007	0.077	0.051
COV	8.2%	4.7%	0.2%	6.4%	3.9%

3.2.5 Measurement of Hydrocarbons by SCAQMD 25.3, EPA TO-12, and EPA 25a

As mentioned earlier, the measurement of low levels of hydrocarbons was a known challenge. Triplicate source samples and one ambient sample following SCAQMD Method 25.3 were collected during the test period and results are shown in Table 3-12. For the exhaust samples, the TGNMO of 6.8 ± 4 seemed high, and the COV was 58 percent (=4/6.8), a very high value indicating that parameters controlling the measurement were "out of control." Values for CH_4 and CO_2 in the ambient air seemed reasonable.

Table 3-12: Analysis of Exhaust by SCAQMD Method 25.3, Both Canister and Impinger

	Canister				Impinger	
Measurements	Methane (ppm)	Ethane (ppm)	TGNMO (ppm)	CO_2 (ppm)	ppmC	Volume (ml)
1/Ambient	1.64	<1	11.19	422	0.86	2.57
	1.77	<1	5.57	428	0.54	2.79
1/Source	1.49	<1	4.72	33600	0.29	2.89
	1.21	<1	10.56	35200	0.4	2.78
2/Source	1.31	<1	3.76	32900	<0.2	2.64
	1.32	<1	13.03	32100	0.21	2.48
3/Source	1.39	<1	3.72	33200	0.45	2.79
Summa 165(UCR28)	1.33	<1	5.13	33500	0.59	2.78
Source (Average±STDEV)	1.3 ± 0.1	<1	6.8 ± 4.	33,416.7 ± 1026.5	0.4 ± 0.1	2.7 ± .1
Ambient (Average±STDEV)	1.7 ± 0.1	<1	8.4 ± 4.	425. ± 4.2	0.7 ± 0.2	2.7 ± .2

ppmC = parts per million carbon

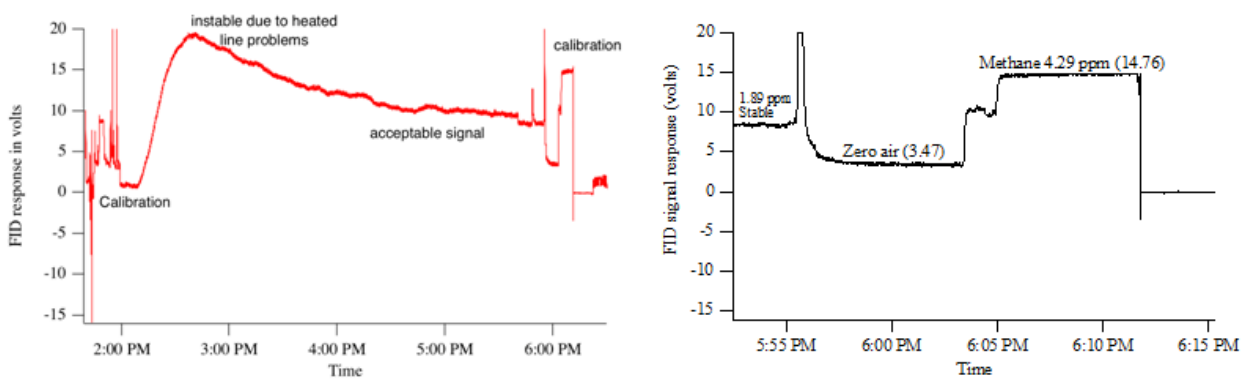
A second set of canisters were collected and analyzed by EPA TO-12 and the Fixed Gas by EPA 3c. Results for those samples are shown in Table 3-13. Results for the oxygen seem close to the CEM levels. In addition, the TGNMO values are much lower than those from SCAQMD 25.3 and close to the values observed for the Capstone microturbine.

Table 3-13: Analysis of Exhaust for TGNMO by EPA TO-12 and Fixed Gases by EPA 3c.

	Canisters		Fixed gas analysis	
Test ID	Canister ID	TGNMO(ppmv)	Nitrogen (%v)	Oxygen (%v)
1/Ambient	Summa 294	1.94	78.2	20.7
1/Source	Summa 157	2.55	80.1	14.5
2/Source	Summa 399	1.69	81.1	14.3
3/Source	Summa 330	1.08	80.8	14.6
Source (Average±STDEV)		1.8 ± 0.7	80.7 ± 0.5	14.5 ± 0.2
Ambient(Average±STDEV)		1.94	78.2	20.7

Analysis was also carried out following EPA Method 25A: determination of total gaseous organic concentration using a flame ionization analyzer. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon. As the method requires, the calibration gases were added through the sample tip to ensure that the errors associated with the sampling line were properly accounted. The results, shown in Figure 3-12, unfortunately show there was drift in the system of about 10 ppmv during the sampling process. Calibration at the end of the test provided an accurate measure of the total hydrocarbons. Figure 3-12 shows that the THC levels are 1.89 ppm, as measured by EPA Method 25A.

Figure 3-12: Data for EPA 25A Showing: (a) Systematic Drift and (b) Final Calibration



3.2.6 Measurement for Carbonyl and Trace Light Hydrocarbons

Selected trace hydrocarbon species were measured using special sorption materials, as in the earlier test with the Capstone microturbine. Results for the carbonyls are presented in Table 3-14. Comparing these values to those of the Capstone unit indicate that the formaldehyde levels are significantly lower in both the source and ambient samples. In any case, the values are in the ppb levels and do not account for the amount of TGNMO found in the canisters.

Table 3-14: Analysis for Aldehydes and Ketones Using DNPH Cartridges (ppbv)

Sample ID	Formaldehyde	Acetaldehyde	Acetone	Crotonaldehyde	Benzaldehyde
1-Ambient	2.13	1.84	6.24	0.00	1.15
2-Source	2.20	0.93	1.47	1.09	0.00
3-Source	4.58	3.36	2.48	1.70	0.00
Source	3.4 ±1.7	2.1 ±1.7	2.0 ±0.7	1.4 ±0.4	0.0 ±0.0

Notes: No propionaldehyde, Methyl ethyl ketone, methacrolein, butyraldehyde, n-valeraldehyde, n-tolualdehyde, and hexaldehyde were found.
Numbers are reported in parts per billion by volume (ppbv).
1-Source was not analyzable due to contamination.

Exhaust and ambient samples were collected on thermal desorption tubes (TDS) and analyzed in a Gerstel/GC/FID (gas chromatography and flame ionization detector) analytical train. Results are in Table 3-15. As with the Capstone unit, hydrocarbon concentrations are very low and could not account for a fraction of the TGNMO.

Table 3-15: Analysis for Selected Trace Hydrocarbons Using TDS Tubes (pptv)

	1*3-Butadiene	Benzene	Toluene	m&p-xylene	Ethyl-benzene	o-Xylene	Naphthalene
Ambient	61.3	354.0	96.9	50.1	28.1	62.2	15.3
Source 1	230.7	2416.9	227.7	122.9	48.8	72.9	22.9
Source 2	349.1	1449.7	113.7	55.5	25.8	58.5	79.5
Source 3	148.6	723.2	135.5	72.3	42.3	74.1	102.6
Source	242.8 ±100.8	1,529.9 ±849.7	159.0 ±60.5	83.6 ±35.1	39.0 ±11.8	68.5 ±8.7	68.3 ±41.0

Note: Numbers are reported in parts per trillion (pptv).

3.2.7 Flow Measurement

Flow rate in the exhaust was determined by two methods: ARB Methods 1–4 and by the ISO 8178 Carbon Balance Method. Given that the stack was 84 inches in diameter, a special sampling assembly was needed to span the cross section. Data from the traverse of the exhaust is shown in Table 3-16. Using the equations listed in Table 3-9, the dry standard volumetric flow rate (Q_{std}) was 4.76 mmSCFH.

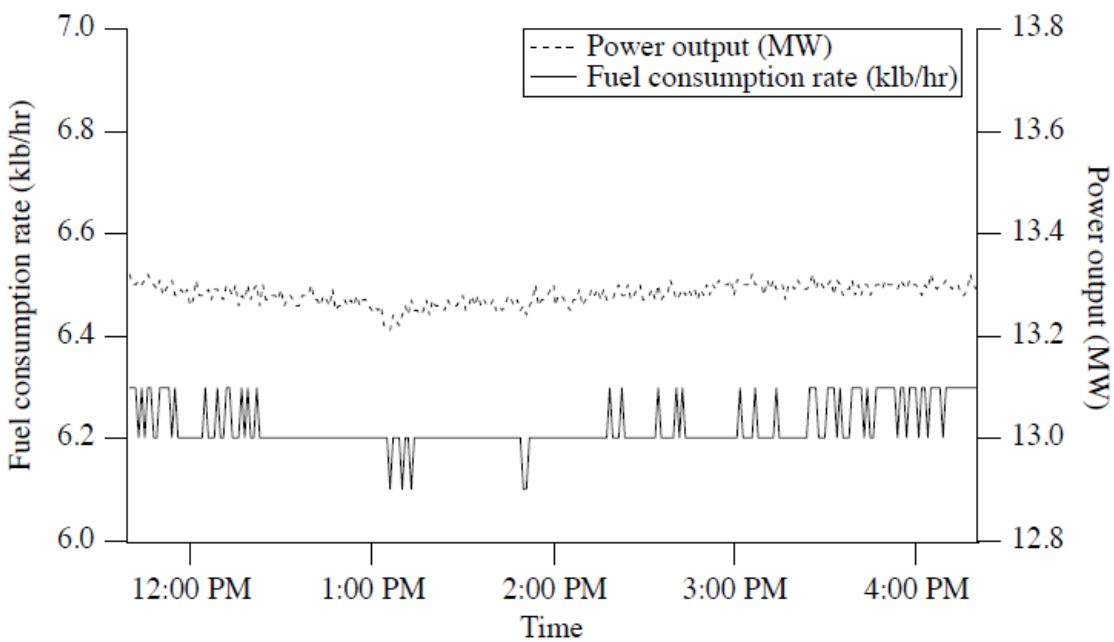
Table 3-16: Stagnation Pressure and Temperature of Stack Gas at a Point

Point	% Distance	ΔP_{south} (in H_2O)	T_{south} (°C)	ΔP_{west} (in H_2O)	T_{west} (°C)
1	14.7	0.54	155	0.65	155
2	20.8	0.64	156	0.68	156
3	28.3	0.66	157	0.65	157
4	39.1	0.66	157	0.67	157

Point	% Distance	ΔP_{south} (in H_2O)	T_{south} (°C)	ΔP_{west} (in H_2O)	T_{west} (°C)
5	68.9	0.63	156	0.64	156
6	79.7	0.64	154	0.75	154
7	87.1	0.65	155	0.64	155
8	93.3	0.64	146	0.60	146

Flow was also calculated based on the Carbon Balance Method using plant readings of the natural gas flow and assuming the gas was 100 percent methane. Gas flow was very stable during the test, as shown in Figure 3-13, and the control room data showed a flow of 146.9 kSCFH. Using these data lead to a calculated flow of 4.63 mmSCFH, a value 1.7 percent less than the value measured using Methods 1–4.

Figure 3-13: Plant Data for Fuel Consumption and Power Rate



Charts show the steady-state nature of the combustion and power processes. Fuel flow rates from the control panel were viewed as highly accurate, since the customer calibrates them and they were used in the ISO calculation (See Table 3-17).

Table 3-17: Results of Carbon Balance Method for Determining Flow

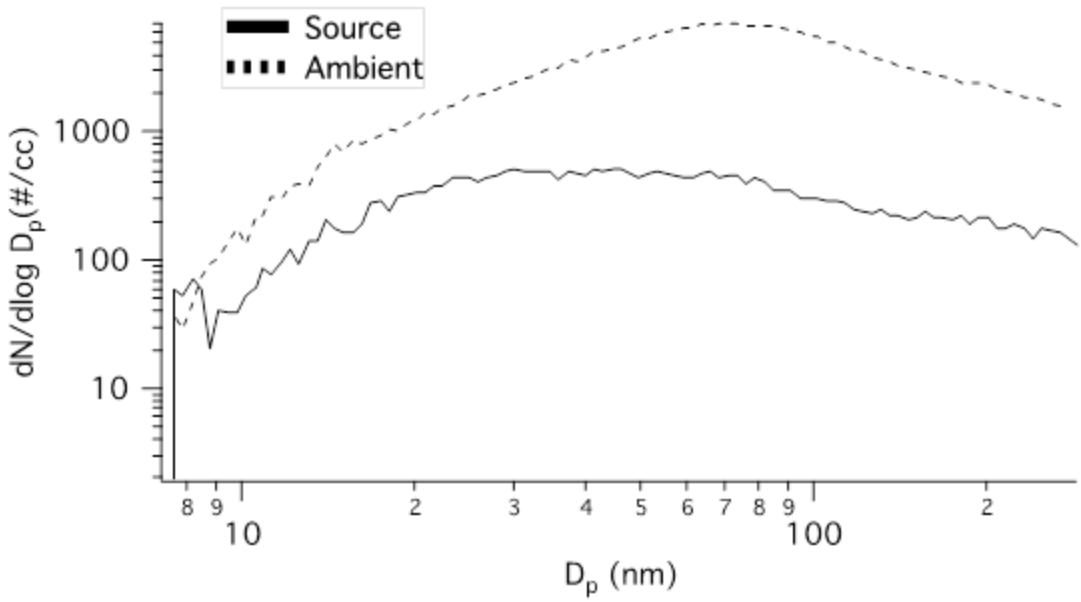
Parameter	Value	Unit
ARB Method		
Stack diameter	84	inch
Stack exhaust temperature	310.1	°F
Stack exhaust Velocity	64.7	ft/sec

Parameter	Value	Unit
Stack Volumetric Flow rate (dry basis)	4.76	mmSCFH
ISO Carbon Balance Method		
Natural gas volumetric flow rate	146.9	kSCFH
CO_2 concentration	3.34	vol%
Calculated flow rate	4.63	mmSCFH

3.2.8 PM Measurements

As mentioned earlier, UCR characterized PM using a SMPS (Scanning Mobility Particle Sizer) instrument. One of the challenges for the site with the Solar Turbines turbine was getting a sample from the exhaust platform about 50 feet in the air to the SMPS unit on the ground level. At this site a sample line made from oil-free refrigeration copper tubing served as the conduit for moving the sample from the platform to the ground level. While there may be questions about PM losses in such a long line, we expected that sampling over long periods would allow the samples of exhaust and ambient air to be at equilibrium. During the testing, the SMPS data were very constant. A typical plot is provided in Figure 3-14. The small particles are coming from the turbine exhaust. Particle number concentration averaged over a period of time provided an average value of 456 ± 102 number of PM particles per cubic centimeters (#/cc) which is orders of magnitude less than measured for the Capstone microturbine (see Figure 3-14).

Figure 3-14: SMPS Data for the Solar Turbines Turbine Showing Ambient and Source Particle Concentrations



3.3 Interim Analysis Identifies Issues with Hydrocarbon Data

Analysis of data from the first two tests with the Capstone and Solar Turbine turbines indicated that when testing concentrations of NOx and CO at ~1 ppm, the commercial instruments designed for ambient levels provided the needed analysis and accurate values. However, results with various methods for measuring ~1 ppm hydrocarbon were problematic. There were several problems:

1. EPA Method 25A had drift exceeding the value allowed by U.S. EPA.
2. Values for TGNMO of ambient air from the EPA TO-12 and SCAQMD 25.3 methods did not agree.
3. Values for exhaust samples of TGNMO from the EPA TO-12 and SCAQMD 25.3 did not agree.
4. Values for the TGNMOC source by SCAQMD 25.3 were higher than could be explained from the EPA TO-12 and the EPA 25A data.

A systemic plan was developed to analyze the available data and resolve each of the problems with EPA Method 25A, SCAQMD 25.3, and EPA TO-12 that were associated with the sampling and analysis of very low hydrocarbon levels.

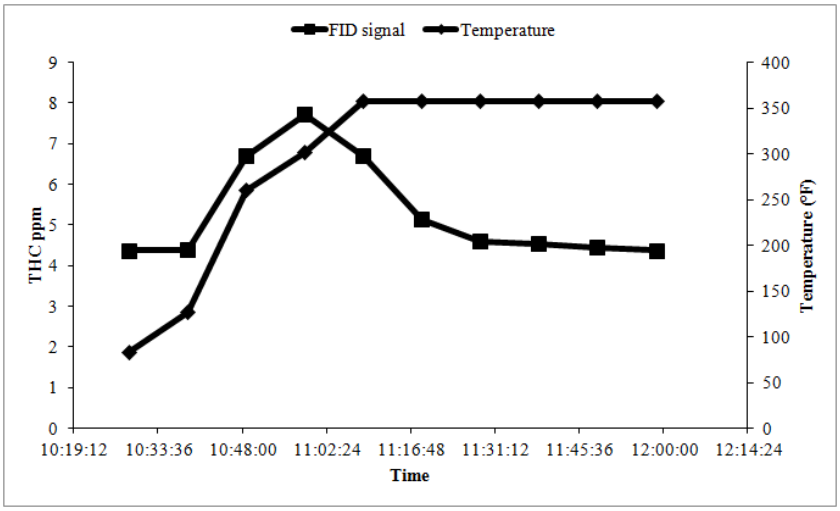
3.3.1 EPA Method 25A: Fixing the Drift Problem

Review of the THC data from the first two tests with the Capstone and Solar Turbines turbines indicated the new heated line, which was sold as HC-free, had a problem with HC elution and created a drift that exceeded the U.S. EPA standard. This hypothesis was tested by operating UCR's THC analyzer for a day while measuring the THC concentration in ambient air, a value

of about 4 ppm in the UCR area. Over a day of operation, results showed the analyzer met the 1 percent stability specification of the instrument so the drift had to be attributed to the new sample line. Repeating the sampling of ambient air, except this time through the new heated line showed unacceptable drift levels similar to that seen in testing the Solar Turbines turbine. The results confirmed the hypothesis that the problem was with the heated line.

To fix the drift in the new sample line, we baked the heated transfer line at 350°F (177°C) for two days with a nitrogen purge. Subsequent laboratory tests showed the heated line/FID combination was stable at low levels (< 10 ppmv), and the FID maintained its calibration within the specification for the instrument (see Figure 3-15). Preliminary analysis of data from this test showed the FID output was steady at values near 1 ppmv after about one hour, a time that experience had shown was needed to bring the unit to equilibrium. Another perspective showed that it took about 20 minutes to reach equilibrium after the line was heated to the operating temperature. Further, the THC level increase during heating of the transfer line was a maximum of 3 ppm, not 20 ppm as seen earlier in Figure 3-12.

Figure 3-15: Data Showing Stability of Heated Line/FID Unit with Ambient Air (~4 ppm)



3.3.2 Resolving the Differences Between SCAQMD 25.3 and EPA TO-12

Reviewing the data for NMNEOC from the tests with the Capstone and Solar Turbines turbines indicated significant differences between the two methods for measuring hydrocarbons and the emissions using SCAQMD 25.3 was always higher, as can be seen in Table 3-18. The finding that values for SCAQMD 25.3 were higher than those measured using the EPA TO-12 method was similar to what other source testers had observed.

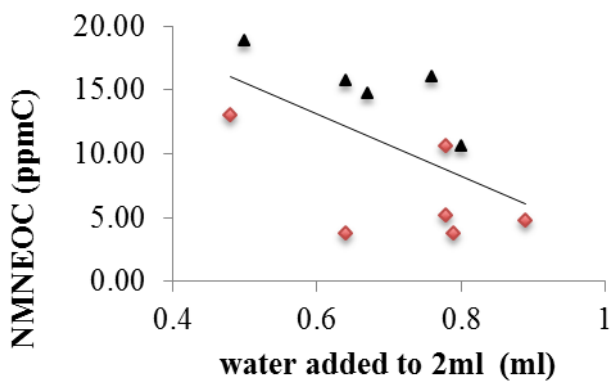
Table 3-18: Comparison of EPA TO-12 and SCAQMD 25.3 HC Values for Ambient and Source Concentrations

	Methane		TGNMO		
	AQMD25.3		25.3-Can	25.3-Imgr	TO-12
Ambient-1	2.05		7.04	2.4	1.6
Source-1	<1		14	1.1	1.5
Ambient-2	1.7		8.4	0.7	1.94
Source-2	1.3		6.8	0.4	1.8

Looking deeper at values measured in this project and other projects, we concluded the methane values seemed accurate, so then the focus shifted to the canister and the impinger values. Discussions with experienced source testers indicated that the impinger numbers were about correct at ~1 ppm, so only the canister values were in question. Deeper analysis of the results of the duplicate canister sampling for NMNEOC showed results deviated more than 20 percent from the average of the two values; thus the data did not meet the precision criteria of the SCAQMD 25.3. Since experienced source testers were used, testing experience was another parameter that was ruled out.

Another interesting plot was created from the first two tests by plotting the amount of water added to the impinger during the sample collection against the NMNEOC in the canister. Results are shown in Figure 3-16. There was an apparent relation between the amount of added water to the small vials due to condensation of water vapor and the measured amount of NMNEOC in the cans. While the correlation coefficient is small, there is still a trend shown on the graph. It was an unexpected and unexplained result.

Figure 3-16: Canister NMNEOC vs. Water Added to Impinger



3.3.3 Conclusions After Reviewing Methods for Measuring Hydrocarbons

Review of the methods revealed the following:

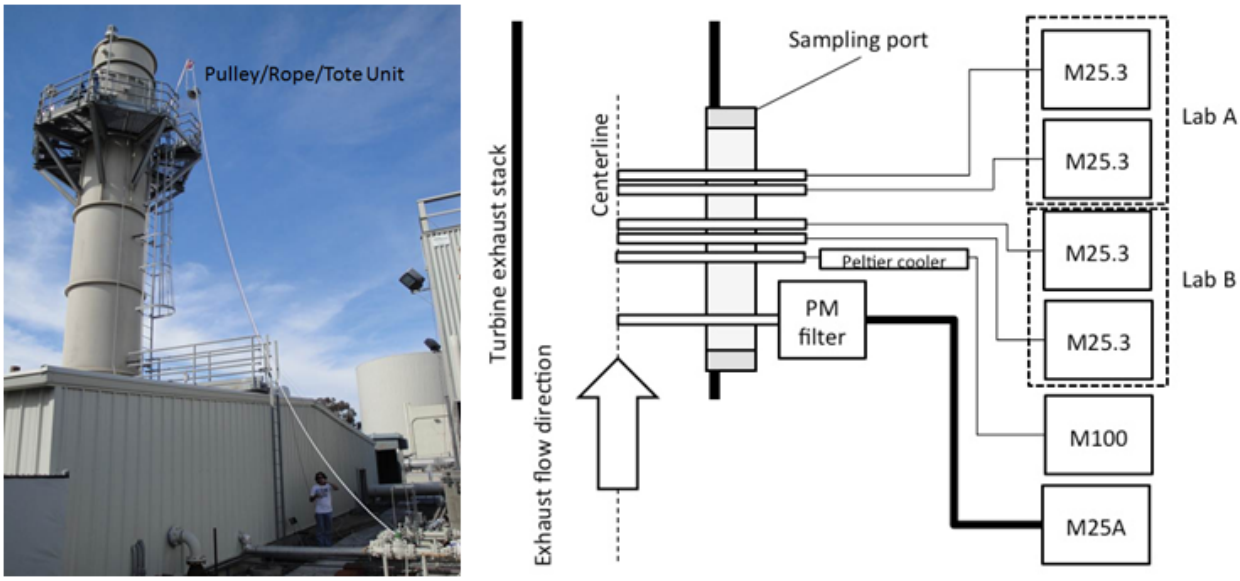
1. The problem with the heated line for EPA Method 25A was resolved, so the test rig meets the U.S. EPA drift specification, even at the 0–10 ppm range.
2. The NMHC in the SCAQMD 25.3 was higher than could be explained.
3. Ambient values for EPA TO-12 seemed about right when compared with other data.

Since we were less confident in the accuracy of the SCAQMD Method 25.3 results, we decided to: (1) have a mini-round robin with another SCAQMD-approved testing company making the same measurements, and (2) inject the canisters with U.S. EPA certification gases and have the lab analyze them. We also told the current lab about the number of failures to the 20 percent rule for SCAQMD 25.3 and that the NMHC values from the canisters seemed high, as they were expected to be at about ambient levels. The lab tried to dissuade us from using SCAQMD Method 25.3 for measurement of the NMHC at near-ambient levels.

3.4 Retest Solar Turbines Titan™ 130 Turbine with SCR; with a Focus on Hydrocarbons

On April 5, 2011, the Solar Turbines turbine was retested, right after the turbine had undergone a major maintenance cycle to replace the turbine and replace the post-SCR catalyst. (See Figure 3-17 for the test setup and turbine.) The new post-SCR catalyst was reported to be platinum-based and more active than the catalyst used during our earlier measurements. The turbine was placed into operation about a week before we arrived and was operating normally.

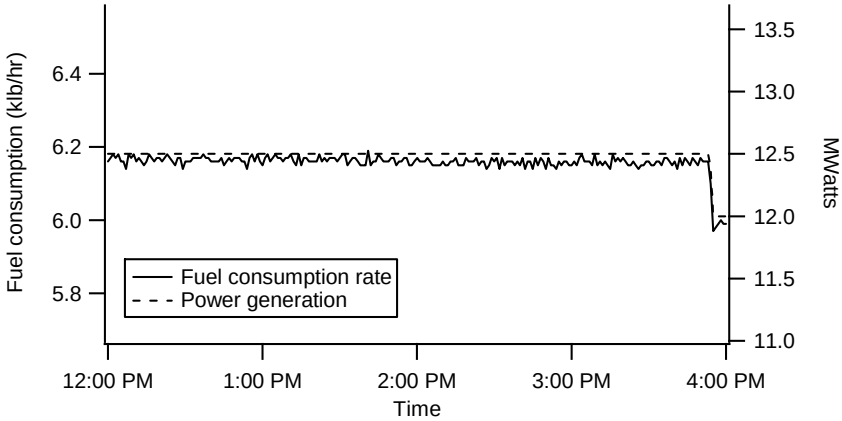
Figure 3-17: (a) Test Platform and Pulley to Raise Equipment, and (b) Schematic of the Sampling System



3.4.1 Measuring CO, CO_2, and NOx with Method 100

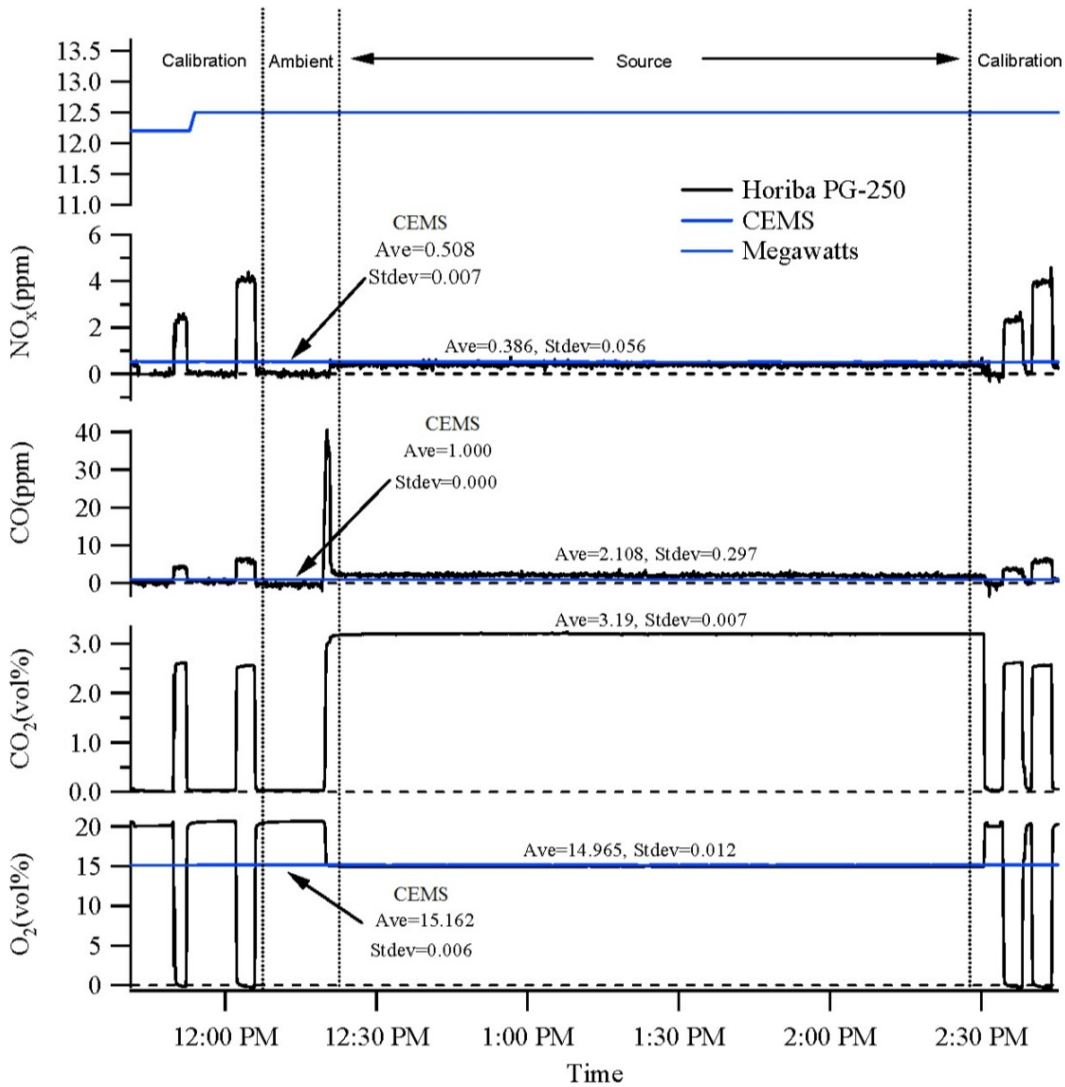
Because the repeat testing of the Solar Turbines unit was focusing on the problem of hydrocarbon measurement at low levels, the ARB M-100 instruments were used to measure the concentrations of CO, CO_2, and NOx. As before, the records and continuous charts were obtained from the plant operators for fuel, power, and CEM recordings. Figure 3-18 shows that the plant ran at steady state during the testing.

Figure 3-18: Power and Fuel Consumption Rates of Solar Turbines Turbine (13 MW)



As indicated in the chart below, the gas concentrations were steady over the test period. Furthermore, agreement was good for the measurement of NOx and CO between the CEMs and the ARB Method 100 instruments, even though the concentration levels were lower than the last time they were measured. Note the very low COV for measuring oxygen and CO_2 concentrations as the process was near steady state and the instruments were operating within the span of that range (See Figure 3-19).

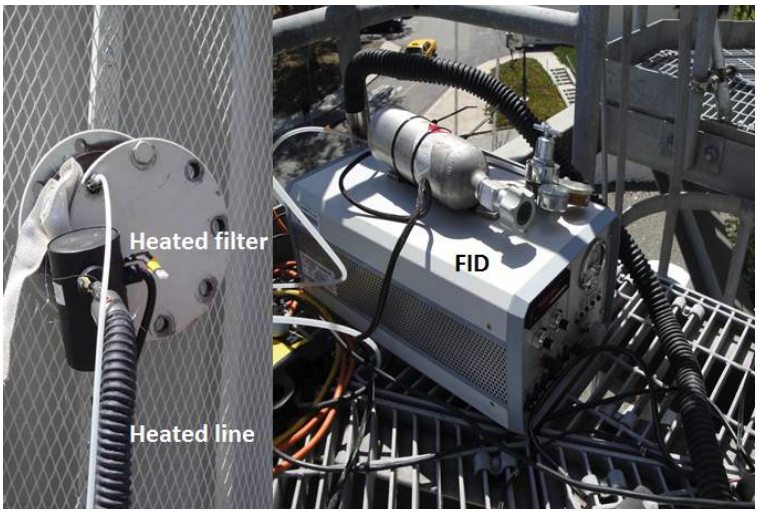
Figure 3-19: Concentrations for O_2, CO_2, CO, and NOx from CEMS and M-100



3.4.2 Measurement of Hydrocarbons by EPA Method 25A

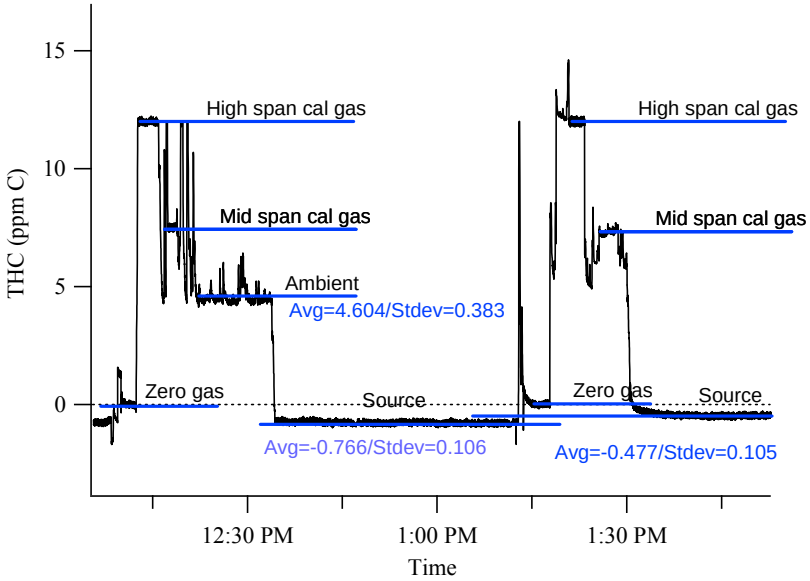
One of the key standard methods examined for this project was EPA Method 25A, as it is useful for measuring low hydrocarbon levels at the time of testing, as compared with canister methods that require off-line analysis and weeks of waiting for the final results. Clearly one benefit of EPA M25A in the field is that the testing parties know immediately if the unit is meeting specifications. The EPA M25A equipment was hoisted to the sampling deck and warmed up for at least an hour before data acquisition. See Figure 3-20.

Figure 3-20: Setup for EPA Method 25A on the Test Platform



Calibrations were carried out by flowing calibration gases through the probe tip as required in EPA M25A and shown in Figure 3-21. Since the catalyst was new and had enhanced activity, the exhaust had only about 0.77 ppm of hydrocarbons. By contrast, the ambient measurement was about 4 ppm, a value typical for that area.

Figure 3-21: FID Response to the Exhaust HC Concentrations and Calibration Gases

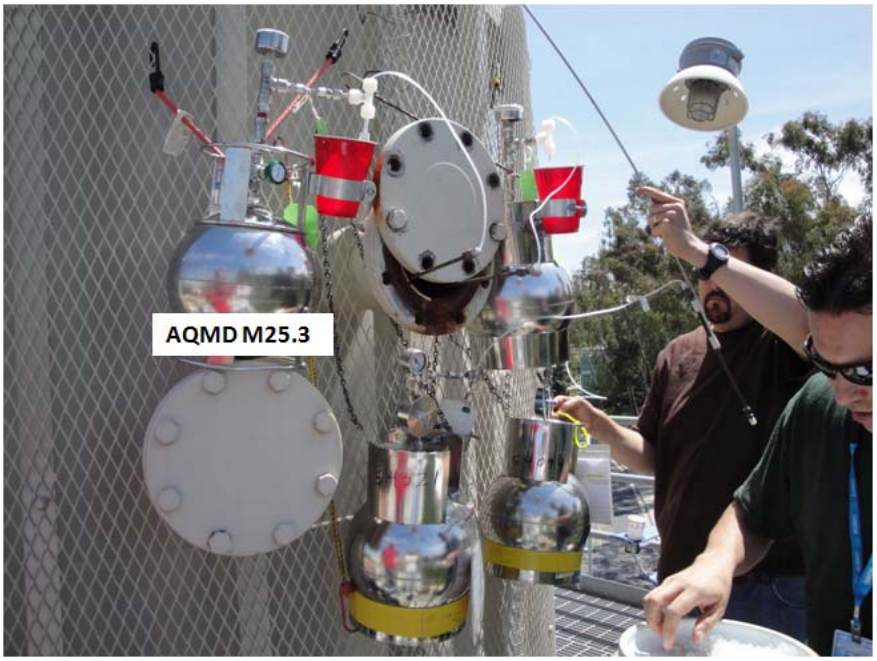


3.4.3 Measurement of Hydrocarbons by Two Labs Using SCAQMD 25.3

A key element of the retest was a mini-cross lab study for SCAQMD 25.3, involving two groups of testers and two labs on the SCAQMD approved list. Both groups worked on the sample platform and took ambient and exhaust samples following SCAQMD 25.3 protocols, as shown in Figure 3-22. Testing for both groups went well, although the other group lost a couple of samples when the sample flow regulator malfunctioned and flow to the canister stopped.

Previously UCR had lost samples as the canisters simply stopped collecting sample, a frustrating aspect of this test.

Figure 3-22: Canister Testing with SCAQMD 25.3 on the Platform



The UCR results from the SCAQMD 25.3 sampling are shown in Table 3-19. For this test all samples easily met the 20 percent precision criteria for the method, even though hydrocarbon levels were very low right after the SCR catalyst change. One change in the methodology that helped improve the precision and accuracy of the method was filling the canister all the way to 5 inches of vacuum instead of stopping at 15 inches. This approach meant there was less dilution gas added at the lab, so the error due to dilution was reduced. In addition to the exhaust and ambient air samples, a zero-gas certification sample was submitted to gauge the lower detection limit.

Table 3-19: UCR's (Lab A) Results for SCAQMD 25.3

Test	Methane (ppm)	Ethane (ppm)	TGNMO (ppmC)	Impinger Carbon (ppmC)	CO_2 (vol%)	O_2 (vol%)
Source 1	<1	<1	5.25	0.67	2.95	14.8
	<1	<1	5.22	1.49	2.98	15.3
		Ave ± σ:	***5.23 ± 0.02***	***1.08 ± 0.58***	***2.97 ± 0.02***	***15.05 ± 0.35***
Source 2	<1	<1	3.05	1.06	2.99	14.9
	1.39	<1	3.25	0.89	3.02	14.8
		Ave ± σ:	***3.15 ± 0.14***	***0.98 ± 0.12***	***3.01 ± 0.02***	***14.85 ± 0.07***
Ambient	1.55	<1	1.42	1.03	0.042	20.4

Test	Methane (ppm)	Ethane (ppm)	TGNMO (ppmC)	Impinger Carbon (ppmC)	CO_2 (vol%)	O_2 (vol%)
	<1	<1	1.37	0.74	0.040	20.6
		Ave ± σ:	***1.40 ± 0.04***	***0.89 ± 0.21***	***0.04 ± 0.00***	***20.50 ± 0.14***
Zero Gas Sample	<1	<1	2.92	0.44	97.2	19.4

Looking at the data for the exhaust samples indicates that values < 5 ppm were a problem, as the zero gas registered a TGNMO value of 2.92, and the companion impinger is 0.44. These values probably are indicative of the lower detection level for this method.

Comparing results for SCAQMD 25.3 between the two labs for the sample source shows some differences at these low THC levels. The UCR samples went to Lab A; while Lab B sampled and analyzed their own samples (see Table 3-20).

Table 3-20: Lab B's Measured Values for SCAQMD 25.3

	H_2 ppm	O_2 vol%	N_2 vol%	TOC ppmC	CO ppm	CH_4 ppm	CO_2 ppm	Ethane ppmC	NMNEOC ppmC
Source 1/A	<0.2	15.2	79.5	4	<2	<2	32400	<2	<2
Source 1/B	<0.2	15.2	79.1	4	<2	<2	31200	<2	<2
Source 2/A	<0.2	15.1	78.5	12	<2	<2	31300	<2	<2
Source 2/B	<0.2	15.1	78.5	5	<2	<2	31100	<2	<2
Ambient 1/A	<0.2	20.7	77.2	3	<2	<2	433	<2	<2
Ambient 1/B	<0.2	20.7	77.2	2	<2	<2	446	<2	<2
Source		**15.15 ± 0.06**	**78.90 ± 0.49**	**6.2 ± 3.8**	**<2**	**<2**	**31500 ± 605**	**<2**	**<2**
Ambient		**20.70 ± 0.00**	**77.20 ± 0.00**	**2.5 ± 0.7**	**<2**	**<2**	**439 ± 9**	**<2**	**<2**

Looking at Fixed Gases, there is excellent agreement between the various lab data.

Looking at the NMEOC values, Lab A values range from 3.2 to 5.2, with an average of 4.19 versus an average of < 2 by Lab B (see Table 3-21). On the other hand, the TOC values from Lab B were 6.2 versus 1.0 for Lab A, so there are significant differences. Ambient air samples were about 0.9 for Lab A and < 2 for Lab B; so the values were about equal at such low concentrations. For comparison, EPA Method 25A for THC was about 2 ppm; much less than the ~8 and ~5 ppm measured with the SCAQMD 25.3 canister method. Another result of interest was the value for the zero calibration gas submitted to Lab A. As is evident, Lab A measured about 2.9 ppm in the canister and 0.44 in the impinger. This "zero" provides an indication of the lower detection level for Lab A.

Table 3-21: Comparison of Fixed Gas and SCAQMD 25.3 Analyses

Fixed Gas	**Lab B**	**Lab A**
O_2, vol %	15.15	15.16
CO, ppm	<2	1.00
CO_2, vol%	3.15	***3.15***
SCAQMD 25.3		
Exhaust. TOC	6.2	***1.03***
Exhaust. NMEOC	<2	***4.19***
Ambient. TOC	2.5	***0.89***
Ambient. NMEOC	<2	***1.40***

3.5 Third Test: Solar Turbines Titan™ 130 Turbine with SCONOx Emission Controls

The third unit tested was on June 9, 2011, at a site with combined heat and power (CHP) operation. The site operated two 13.5 MW Solar Turbines Titan 130 gas-powered turbine generators with a 3 MW Dresser-Rand steam-powered "bottoming cycle" turbine-generator (See Figure 3-23). The Solar Turbines units include three-stage, axial flow turbines with rotational speeds of up to 11,200 revolutions per minute (RPM), coupled with three-phase, wye-connected, synchronous, brushless generator units. Waste heat from the gas turbine is used to generate steam for various uses. The first use of steam is for cooling a steam-driven centrifugal chiller. The second use is to produce domestic hot water for buildings located near the central plant. The third use is to run a 3 MW Dresser-Rand steam turbine for additional electricity production. Reportedly, their CHP system achieves about 66 percent gross thermal efficiency and was installed for about $27 million, or about $1,000 per kilowatt. To address emission concerns in California, the Solar Turbines Titan 130 installation included the SoLoNOx™ system as part of the pollution system, with a guarantee of 25 ppm exhaust emissions.

Figure 3-23: The Stacks from Solar Turbines Titan 130

To further reduce the NOx emissions, the site added EmeraChem's SCONOx exhaust treatment system (http://emerachem.com) to reduce NOx to 2.5 ppm without added NH_3. SCONOx is a proprietary catalytic oxidation and absorption technology for the removal of NOx, CO, and VOC. The platinum-based catalyst is very susceptible to fouling by sulfur in the exhaust gas, but this can be minimized by use of a sulfur absorption SCOSOx catalyst. In normal use the SCONOx simultaneously oxidizes NO, CO, and VOCs and absorbs NO_2 on a potassium carbonate sorbent as nitrates. The absorbent is a monolith design and requires regeneration in an oxygen-free environment about every 15 minutes. Regeneration gases are produced in an external reformer and then passed over the sorbent beds during regeneration. The absorption operating range is 300°F to 700°F (150°C to 370°C), and regeneration takes place at > 450°F (230°C). When the catalyst reaches the end of its service life, it is recycled to recover the precious metal. We were told the catalyst/sorbent beds in the SCONOx process attached to the unit being tested were at end of life and being changed within a week of the testing.

3.5.1 Plant Operation During Testing

During the test, the plant burned natural gas, and operation was at steady state, as seen in Figure 3-24 and Figure 3-25. A metric indicative of the steadiness of operation is the coefficient of variation, which was ~0.3 percent during the testing.

Figure 3-24: Concentration of Carbon Dioxide (CO_2) in vol% During the Test Period

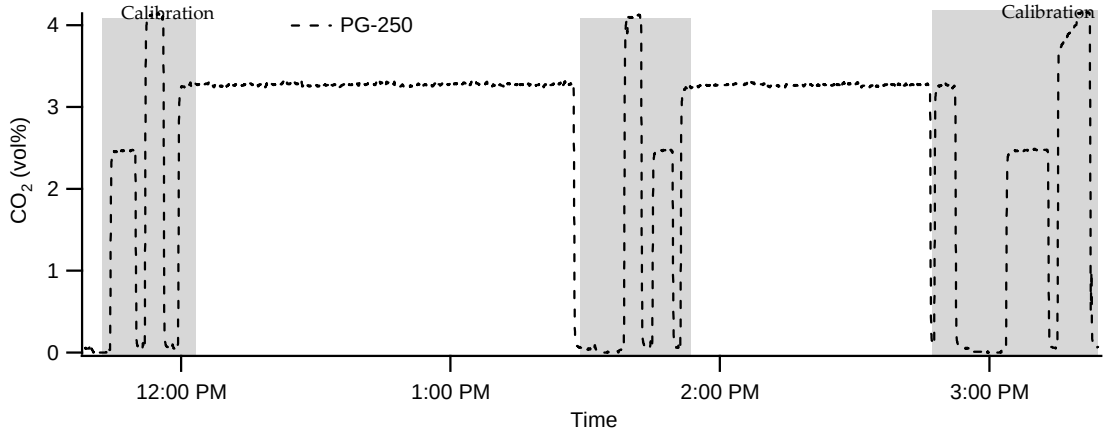
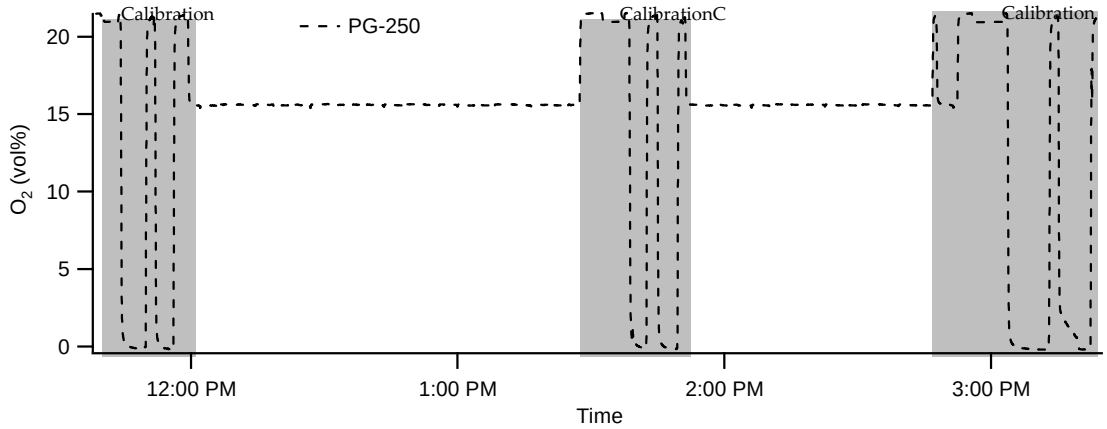


Figure 3-25: Concentration of Oxygen (O_2) in vol% During the Test Period



As the test was in the San Diego area, the feed gas was analyzed, as some NG in that area comes from off-shore to a liquefied natural gas plant in Mexico with a NG composition that is not typical of California NG. One consequence is that the off-shore gas has different calorific properties. Grab samples of the feed gas were collected using Tedlar bags on the low-pressure side of a boiler, since the pressure at the turbines was too high to safely sample. Analysis of the bag is shown in Table 3-22, and the results showed that the NG was representative of normal pipeline gas.

Table 3-22: Analysis of Tedlar Samples for Gas Composition

Species	ppmC	# C Atoms	ppm	vol%
Methane	191,309	1.0	191,309	96.94
Ethane	8,113	2.0	4,056	2.06
Ethene	2,008	2.0	1,004	0.51
Propane	2,005	3.0	668	0.34
Propene	455	3.0	152	0.08
Butane	451	4.0	113	0.06
2*2-DM-Propane	6	5.0	1	0.00
2M-Butane	177	6.0	30	0.01
Propyne	0	3.0	0	0.00
Pentane	118	5.0	24	0.01
		Sum:	197,356	

3.5.2 ARB Method 100 Measurements for CO and NOx

Data collection was uneventful. A picture of the setup is shown in Figure 3-26, and a data summary is shown in Table 3-23. In addition to the calibration gas checks, and as part of our Quality Assurance Project Plan (QAPP), the values from ARB Method 100 were monitored using the PG-250 and compared with the CEM values for NOx at the test site.

Figure 3-26: Gaseous and PM Instruments (SMPS) were at Ground Level for this Site

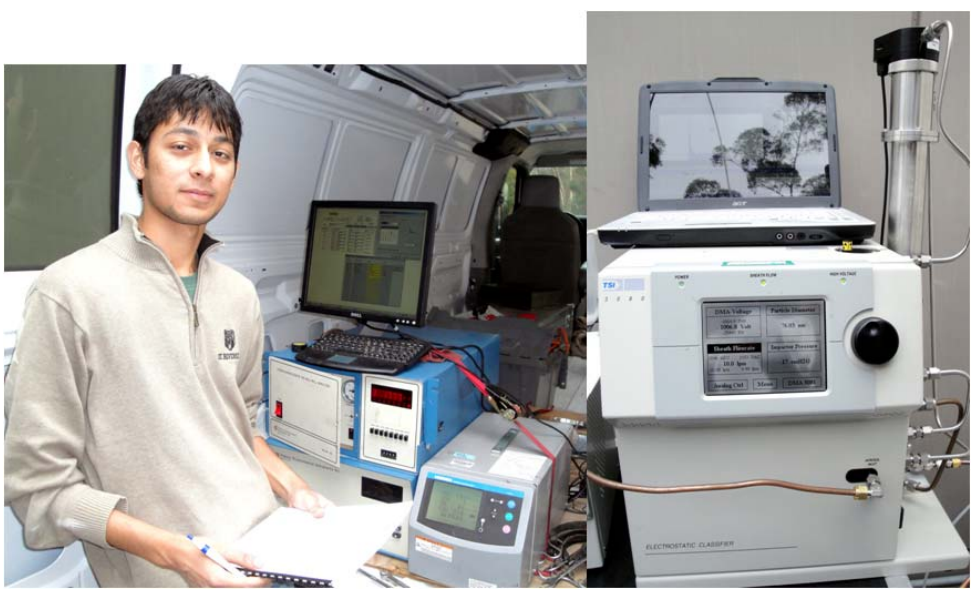


Table 3-23: Summary of Statistical Values for NOx, CO, CO_2, O_2, and HCs

	NOx	NOx	CO	CO	HCs	O_2	CO_2
Instrument Unit	PG-250 ppm	TECO ppm	PG-250 ppm	Ambient ppm	FID ppm	PG-250 vol%	PG-250 vol%
Mean (m)	0.87	1.15	2.55	0.63	6.89	15.60	3.27
STDEV (σ)	0.32	0.46	0.51	0.59	3.56	0.03	0.01
COV, %	37	40	20	93	52	0.2	0.3
Min	0.18	0.43	1.76	0.00	3.42	15.38	3.24
Max	1.79	1.98	7.01	2.13	31.66	15.66	3.32

One observation from the results in the table is that in this test the COV values for O2 and CO2 were very low, representative of a combustion process near steady state. However, it is clear from the range of recorded values and high values for the COV for NOx, CO, and THC emissions that the process emissions were highly transient, due to the transient nature of the SCONOx control process. An obvious view at the transient nature of these processes is seen in Figure 3-27 and Figure 3-28. For example, the NOx ranges from about 0.2 to 2.0 ppm, with a mean value of about 1.0 ppm. The NOx by ARB Method 100 using the PG-250 was about 75 percent of the value measured by the ambient analyzer and had considerable more noise, as indicated in Figure 3-27. One aspect of this test site is that previously, a careful mapping of the interior of the stack showed that the concentration was dependent on the location of the sample point so a specially prepared sampling rake with multiple sampling points was used for the CEM. We did not expect to get the same value as the rake with multi-sampling points.

Figure 3-27: Concentration of NO_x at 15% O_2 by M-100, On-site CEMs and an Ambient Instrument

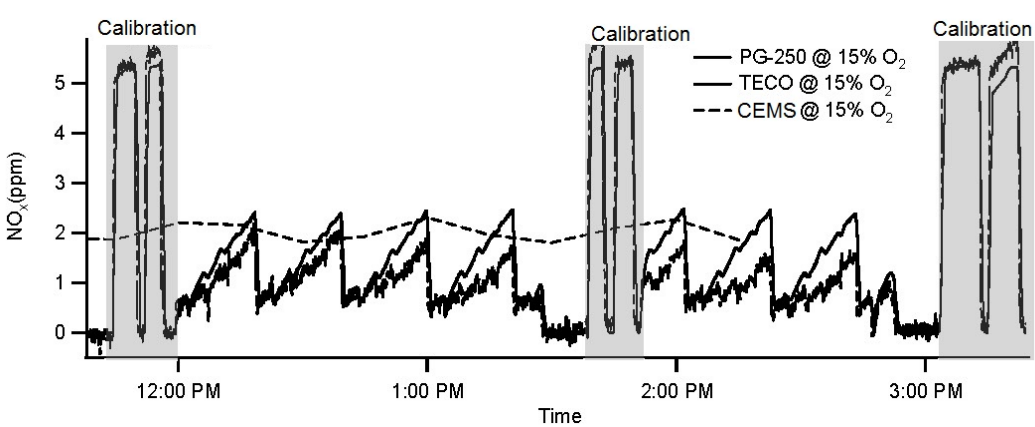
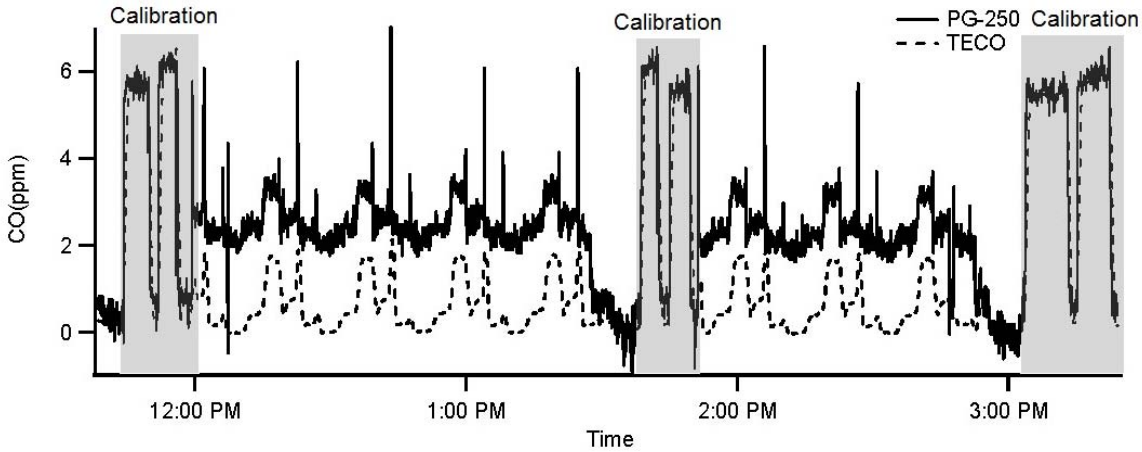


Figure 3-28: Concentration of CO by ARB Method100 and an Ambient Instrument



The concentration of CO as measured by the more accurate TECO ambient instrument was < 1 ppm, as claimed in EmeraChem's SCONOx brochure. Also the CO measured by M-100 was 400 percent higher than the value recorded with the ambient instrument, similar to the earlier finding on the other Solar Turbines test unit.

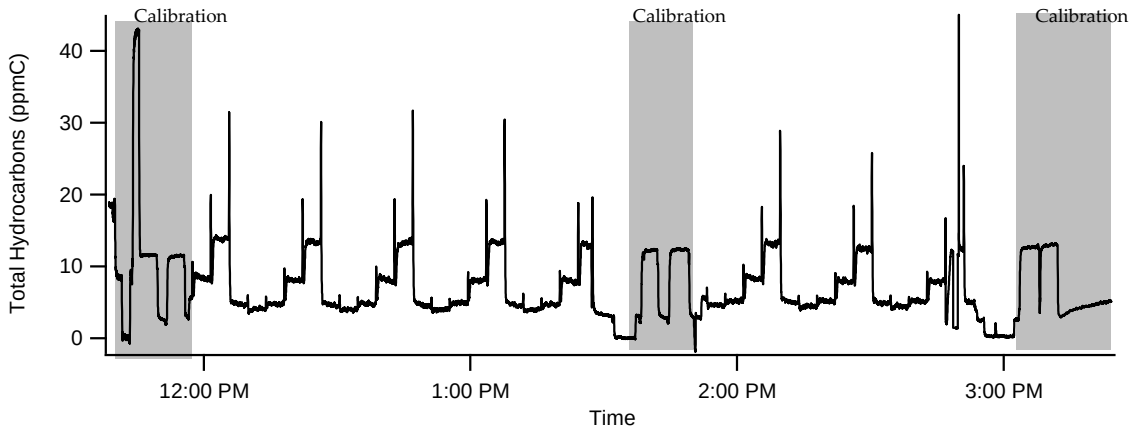
3.5.3 Measurement of Hydrocarbons

Past measurement campaigns had problems with hydrocarbons at low levels (< 10 ppm) but recent work resolved issues (see Figure 3-29). For the SCAQMD 25.3 method, UCR changed to Lab C, another lab on the SCAQMD approved list. This decision was based on the mini-round robin of two labs, the analysis of the zero gas, and discussion with other source testers.

Figure 3-29: Hydrocarbon Sampling and Testing Was on the Platform Level

Testing for hydrocarbons with EPA M25A showed the transient nature of the emissions, as hydrocarbon levels ranged from 3.4 to 31.6, with a mean value of 6.89 ppm. For part of the sampling, the instrument was run in the non-methane total hydrocarbon (NMTHC) mode from 2:48 PM to 2:51 PM, and the methane concentration was measured as about 1.43 ppmC. Right before switching the instrument from the THC to the NMTHC modes, the THC level was about 12 ppmC. Given the highly transient nature of the THC levels, UCR probably should have taken multiple measurements in the NMTHC mode. The transient nature of the emissions can be seen in Figure 3-30. The SCONOx technology has sorbent elements that become spent after about 15 minutes and then are regenerated. Each time the SCONOx technology regenerates a sorbent module, there is a burst of HC emissions from the regeneration gases.

Figure 3-30: Continuous Concentration of THC by EPA Method 25A



Canister samples of ambient air and exhaust were collected from the stack following the technique learned in the last test. Namely, the canister was filled to near 5 inches of vacuum rather than stopping at 15 inches of vacuum, so as to reduce the errors introduced when the canister was repressurized. Fixed gas analysis for CO_2 indicated near steady-state operation of the turbine, as the COV was about 3 percent; however, it was apparent that the hydrocarbon levels were highly transient due to the switching of sorbent beds in the SCONOx emission control process. Even though the hydrocarbon levels were very low, the repeatability between simultaneous samples from the canisters was very good—the best we had seen in the test program. Some of the success we believed should be attributed to the new laboratory. In the end, the total of impinger and canister NMNEOC was 3.0 ppm. Given the low levels of NMNEOC versus that measured using the EPA 25A method, the results suggest that the majority of the HC is methane and ethane (See Table 3-24).

Table 3-24: Analysis of Ambient and Source Canisters and Impinger Vials by SCAQMD 25.3

Test No.	Fix Gases EPA 3C			Canister NMNEOC (ppmC)	Impinger NMNEOC (ppmC)	Total NMNEOC (ppmC)
	O_2 (vol%)	CO (ppm)	CO_2 (vol%)			
1/Ambient-A	21.70	<1	0.04	0.9	2.2	3.5
1/Ambient-B	20.40	<1	0.04	1.0	2.2	3.1
1/Source-A	16.10	<1	3.7	1.1	2.1	2.1
1/Source-B	16.30	<1	3.6	1.2	1.4	1.4
2/Source-A	16.10	<1	3.4	1.3	2.2	3.8
2/Source-B	16.20	<1	3.6	1.5	1.5	3.3
3/Source-A	16.40	<1	3.5	1.6	2.0	3.9
3/Source-B	15.90	<1	3.5	1.2	1.7	3.2
Source (m ± σ)	16.2 ± 0.2	<1	3.6 ± 0.1	1.3 ± 0.2	1.8 ± 0.3	3.0 ± 1.0

Canisters of ambient and source samples were analyzed by EPA TO-12, and results are shown in Table 3-25. One concern is the differences in the levels of CO_2. For example, CO_2 is about 4.7 percent in the EPA TO-12 canisters, versus 3.6 percent in the SCAQMD 25.3 canisters and 3.32 percent when using the ARB M-100 method. The value for CO_2 in the EPA TO-12 seems significantly high; however, the value for CO is < 1 ppm as measured with the ambient instrument. The measured oxygen was the same as that measured with the M-100 instrument.

Table 3-25: Analysis of Ambient and Source Canisters by EPA TO-12; Fixed Gases by EPA 3C

Test No.	**Fixed Gas**					**EPA Modified TO-12**	
	O_2 (vol%)	N_2 (vol%)	CO (ppm)	CH_4 (ppm)	CO_2 (vol%)	Total PAMs (ppbC)	TNMHC (ppbC)
1/Ambient	21.8	77.2	<1	<1	0.04	32.8	1180
1/Source	15.6	79.7	<1	<1	4.7	175	326
2/Source	15.6	79.6	<1	<1	4.8	157	248
3/Source	15.6	79.8	<1	<1	4.5	135	345
Source (m ± σ)	15.6 ± 0.	79.7 ± .1	<1	<1	4.7 ± 0.2	155.7 ± 20.0	306.3 ± 51.4

From earlier work it was clear that the trace hydrocarbons being measured, namely aldehydes and selected organics like benzene, were at the part per billion levels and could not account for the part per million levels of the NMNEOC in the canisters. Accordingly for this test the samples were subjected to a complete hydrocarbon analysis starting with C_1 to C_{12}. Table 3-26 presents the results for measureable compounds, and Table 3-27 presents the list of other compounds that were undetected.

Table 3-26: Analysis by Modified EPA TO-12 for C_1-C_{12} Hydrocarbons in ppb

Species	Ambient	Source 1	Source 2	Source 3
ethylene	2.6 ppb	7.1 ppb	7.3 ppb	6.2 ppb
acetylene	<dl	<dl	<dl	<dl
ethane	6.4 ppb	165.0 ppb	145.0 ppb	127.0 ppb
propylene	1.6 ppb	<dl	<dl	<dl
propane	2.7 ppb	2.7 ppb	2.9 ppb	2.2 ppb
2-M pentane	2.0 ppb	<dl	<dl	<dl
3-M pentane	3.7 ppb	<dl	<dl	<dl
1-hexane	<dl	<dl	<dl	<dl

Species	Ambient	Source 1	Source 2	Source 3
n-hexane	5.2 ppb	<dl	<dl	<dl
M-cyclopentane	2.3 ppb	<dl	<dl	<dl
toluene	6.4 ppb	<dl	1.7 ppb	<dl
Total PAMS	32.8 ppb	175.0 ppb	157.0 ppb	135.0 ppb
TNMHC	180.0 ppb	326.0 ppb	248.0 ppb	345.0 ppb

dl = detection limit

Note, the term PAMS stands for "Photochemical Assessment Monitoring Stations." This test method is one of those included in the U.S. EPA's ozone precursors monitoring program started in 1994, and it deals with the measurement of various C_2–C_{12} hydrocarbons responsible for photochemical activity in the lower atmosphere and leading to the smog/ozone formation.

Table 3-27: Table of Other Analytes Less Than the Detection Level

Species	Ambient	Source 1	Source 2	Source 3
isobutane	<dl	<dl	<dl	<dl
1-butane	<dl	<dl	<dl	<dl
n-butane	<dl	<dl	<dl	<dl
trans-2-butane	<dl	<dl	<dl	<dl
cis-2-butane	<dl	<dl	<dl	<dl
isopentane	<dl	<dl	<dl	<dl
1-pentene	<dl	<dl	<dl	<dl
n-pentane	<dl	<dl	<dl	<dl
isoprene	<dl	<dl	<dl	<dl
trans-2-pentene	<dl	<dl	<dl	<dl
cis-2-pentene	<dl	<dl	<dl	<dl
2,2-DM butane	<dl	<dl	<dl	<dl
cyclopentane	<dl	<dl	<dl	<dl
2,3-DM butane	<dl	<dl	<dl	<dl
2,4-Dmpentane	<dl	<dl	<dl	<dl
Benzene	<dl	<dl	<dl	<dl
cyclohexane	<dl	<dl	<dl	<dl
2-M hexane	<dl	<dl	<dl	<dl
2,3-DM pentane	<dl	<dl	<dl	<dl
3-M hexane	<dl	<dl	<dl	<dl
2,2,4- 3M pentane	<dl	<dl	<dl	<dl
n-heptane	<dl	<dl	<dl	<dl

Species	Ambient	Source 1	Source 2	Source 3
M-cyclohexane	<dl	<dl	<dl	<dl
2,3,4-3M pentane	<dl	<dl	<dl	<dl
2-methyleheptane	<dl	<dl	<dl	<dl
3-methylheptane	<dl	<dl	<dl	<dl
n-octane	<dl	<dl	<dl	<dl
ethylebenzene	<dl	<dl	<dl	<dl
m/p-xylenes	<dl	<dl	<dl	<dl
styrene	<dl	<dl	<dl	<dl
o-xylene	<dl	<dl	<dl	<dl
nonane	<dl	<dl	<dl	<dl
isopropylbenzene	<dl	<dl	<dl	<dl
n-propylbenzene	<dl	<dl	<dl	<dl
m-ethyltoluene	<dl	<dl	<dl	<dl
p-ethyltoluene	<dl	<dl	<dl	<dl
1,3,5-3M benzene	<dl	<dl	<dl	<dl
o-ethyltoluene	<dl	<dl	<dl	<dl
1,2,4-3M benzene	<dl	<dl	<dl	<dl
n-decane	<dl	<dl	<dl	<dl
1,2,3-3M benzene	<dl	<dl	<dl	<dl
m-diethylbenzene	<dl	<dl	<dl	<dl
n-undecane	<dl	<dl	<dl	<dl
n-dodecane	<dl	<dl	<dl	<dl

A comparison of all the measured hydrocarbon data is shown in Table 3-28.

Table 3-28: Comparison of HCs: EPA TO-12, SCAQMD 25.3, EPA M25A, and Tedlar Bag

HC and Method of Measurement	Ambient	Source 1	Source 2	Source 3
Methane (**Fixed gases**)	<1.5 ppm	<1.6 ppm	<1.7 ppm	<1.5 ppm
Cans **M25.3** / NMNEOC	0.95 ppm	1.15 ppm	1.40 ppm	1.40 ppm
Vials **M25.3** / NMNEOC	2.20 ppm	1.75 ppm	1.85 ppm	1.85 ppm
M25.3 Total NMNEOC	3.30 ppm	1.75 ppm	3.55 ppm	3.55 ppm
EPA TO-12 TNMOC	0.18 ppm	0.33 ppm	0.25 ppm	0.35 ppm
Tedlar bag - Methane	4.34 ppm			
Tedlar bag - Ethane	0.06 ppm			

HC and Method of Measurement	Ambient	Source 1	Source 2	Source 3
Tedlar bag - Ethene	0.01 ppm			
FID-THC (average)				6.89 ppm
FID-Methane. 1 measure				1.43 ppm

3.5.4 Flow Measurements

The total flow in the exhaust was determined using ARB Methods 1–4. Values for the traverse in the 84-inch stack are provided in Table 3-29. From these values we determined the flow was 5.23 mmSCFH. Flow was also calculated from the Carbon Balance Method outlined in ISO 8178-1 using data from the control room in Table 3-30 and Table 3-31 and the measured CO_2 concentration. The ISO calculated value was 5.01 mmSCFH and within 4.4 percent of the ARB Methods 1–4 value of 5.25. Interestingly for both Solar Turbines units, the ISO approach resulted in a lower flow value, and both were within the existing method and 5 percent quality goal set for the project. Some discussion indicated that the ARB method is usually higher, because it assumes a higher flow near the walls of the stack.

Table 3-29: Stagnation Pressure and Temperature of Stack Gas at a Point

Point	% Distance	ΔP_{south} (in H_2O)	T_{south} (ºC)	T_{south} (ºF)
1	14.7	0.75	177.5	351.5
2	20.8	0.95	177.8	352.1
3	28.3	1.00	178.3	352.9
4	39.1	1.00	177.8	352.1
5	68.9	0.95	177.5	351.5
6	79.7	0.90	177.2	351.0
7	87.1	0.85	176.7	350.0
8	93.3	0.80	172.2	342.0

Flow rates from this Solar Turbines unit were compared with those of the earlier Solar turbine, and we learned that the flow measured on this unit of 4.41 mmSCFH was about 10 percent higher than the 4.76 mmSCFH found at the earlier site. Presumably the difference was due to design and planned operational targets.

Table 3-30: Control Room Values for NOx, O_2, and Fuel Consumption Rates

Time	NOx (lb/hr)	NOx (ppm)	O_2 (vol%)	Fuel (MMBtu/hr)	Fuel consumption (klb/hr)
10:00:00 AM	1.03	1.88	15.2	143.71	6.15
10:15:00 AM	1.23	2.25	15.2	143.71	6.15
10:30:00 AM	1.08	1.97	15.2	143.83	6.15
10:45:00 AM	0.95	1.74	15.2	143.55	6.14
11:00:00 AM	1.09	2.00	15.2	142.86	6.11

Time	NOx (lb/hr)	NOx (ppm)	O_2 (vol%)	Fuel (MMBtu/hr)	Fuel consumption (klb/hr)
11:15:00 AM	1.20	2.2	15.2	143.30	6.13
11:30:00 AM	0.99	1.82	15.2	143.50	6.14
11:45:00 AM	1.00	1.81	15.2	144.25	6.17
12:00:00 PM	1.17	2.13	15.2	144.16	6.16
12:15:00 PM	1.14	2.09	15.2	143.83	6.15
12:30:00 PM	0.97	1.76	15.2	144.46	6.18
12:45:00 PM	1.03	1.87	15.2	144.58	6.18
1:00:00 PM	1.23	2.23	15.2	144.25	6.17
1:15:00 PM	1.04	1.89	15.2	143.80	6.15
1:30:00 PM	0.96	1.75	15.2	144.07	6.16
1:45:00 PM	1.11	2.02	15.2	144.02	6.16
2:00:00 PM	1.21	2.19	15.2	144.15	6.16
2:15:00 PM	0.99	1.80	15.2	144.69	6.19

Table 3-31: Results of ARB M1-4 and ISO Carbon Balance Method for Flow

Parameter	Value	Unit
ARB Method		
Stack diameter	84	inch
Stack exhaust temperature	350.4	°F
Stack exhaust Velocity	78.3	ft/sec
Stack Volumetric Flow rate (dry basis)	5.23	mmSCFH
ISO Carbon Balance Method		
Natural gas volumetric flow rate	153.0	kSCFH
CO_2 concentration	3.22	vol%
Calculated flow rate	5.01	mmSCFH

3.5.5 Particulate Matter

As agreed to with the Advisory committee, the exhaust was sampled and the properties of the particles measured with an SMPS analyzer. Data indicated that the particle number concentration was 13,500 ± 4100 #/cc, and the particle size distribution is shown in Figure 3-31. Clearly the particles from the turbine are smaller and have less mass than those in the ambient air, as the 100 nm peak is much higher for the ambient air.

Comparing the PM particle size distribution from the two Solar Turbines turbines in Figure 3-31 and Figure 3-32 is interesting, as they used the same Solar turbine but had different exhaust control systems.

Figure 3-31: Particle Size Distribution for Ambient and Exhaust of Solar Turbines Turbine with SCONOx

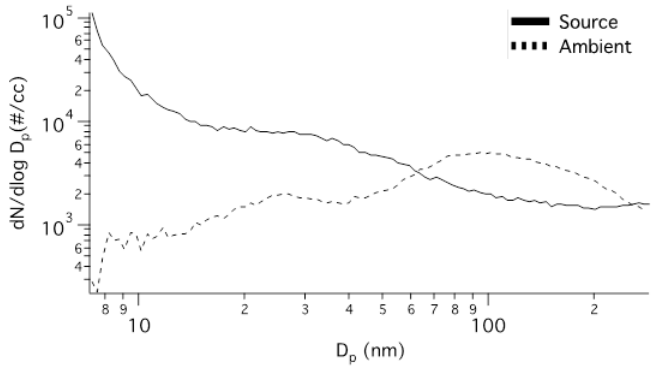
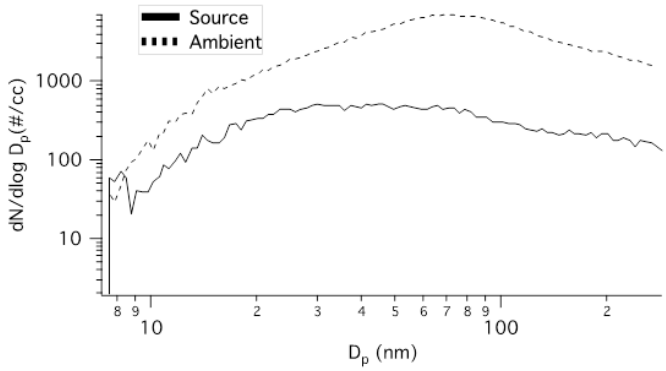


Figure 3-32: Particle Size Distribution for Ambient and Exhaust for Solar Turbines Turbine with SCR



The figures show that the ambient air properties were similar; however, data for the SCONOx-treated exhaust showed several orders of magnitude higher number of smaller particles when compared with the unit with a SCR. This indicates that the SCR is much more effective at removing ultrafine (< 10 nanometer) particles than the SCONOx system.

3.6 Tests of FuelCell Energy's DFC300MA Fuel Cell (300 kW)

One of the DG sources of interest to the Advisory Committee was testing a DFC300MA fuel cell, as it is designated for ultra-low emissions and is certified to the California Air Resources Board 2007 (ARB 07) Distributed Generation emissions limitations. From the company brochure, the DFC300MA is a commercial-grade power plant capable of providing high-quality baseload electric power using natural gas or anaerobic digester gas as fuel. The brochure provides example concentrations of gaseous constituents of the fuel cell cathode exhaust, as shown in Table 3-32. One outstanding feature is the extremely low levels of NOx emissions.

Table 3-32: Features of the DFC300MA Fuel Cell

Constituent	Concentration
Oxygen (O_2)	8%–10% by volume

Constituent	Concentration
Carbon Dioxide (CO_2)	4%–5% by volume
Water Vapor (H_2O)	12%–20% by volume
Nitrogen (N_2)	Balance
Carbon Monoxide (CO)	< 10 ppmv
Oxides of Nitrogen (NOx)	< 0.5 ppmv
Sulfur Dioxide (SO_2)	< 0.05 ppmv
Flow	3,950 lb/h
Temperature	700°F ± 50F

3.6.1 Description of the DFC300MA Fuel Cell Test Unit

Fuel Cell Energy's DFC300 system is a self-contained electrical power generation system capable of providing high-quality baseload power up to 300 kW, with 47 percent electrical efficiency. Featuring ultra-low emissions, low operating noise, and a small footprint (600 square feet), the DFC300 is suitable for on-site power generation and combined heat and power (CHP). Unlike other fuel cell products, these DFCs internally reform readily available fuels, such as natural gas and anaerobic digester gas, into the hydrogen gas required to power the fuel cell system. This internal reformation process is the key to the DFC's ability to operate at such high electrical efficiency.

Figure 3-33 provides a schematic of the main operating section of Fuel Cell Energy's DFC300. The supply of natural/digester gas is cleaned of sulfur and other impurities while the water is purified to specification. The cleansed fuel gas and purified water are then simultaneously injected into the fuel humidifier, where the fuel gas is heated and humidified. The fuel gas is then routed to the pre-converter vessel where higher hydrocarbons are converted to methane to avoid depositing carbon on the fuel cell stacks. The pre-converter outlet gas is routed to the internal reformer and fuel cell electrodes, where the chemical energy of the hydrocarbons in the fuel gas is converted into DC power and heat. Note that feed/product heat exchangers are used to recover the energy and boost efficiency of the plant. The plant that tested for this study was a CHP plant, as the exhaust went to the heat exchanger for heating water that was directed to the biomass plant.

Figure 3-33: Schematic Diagram of Fuel Cell Energy's DFC300

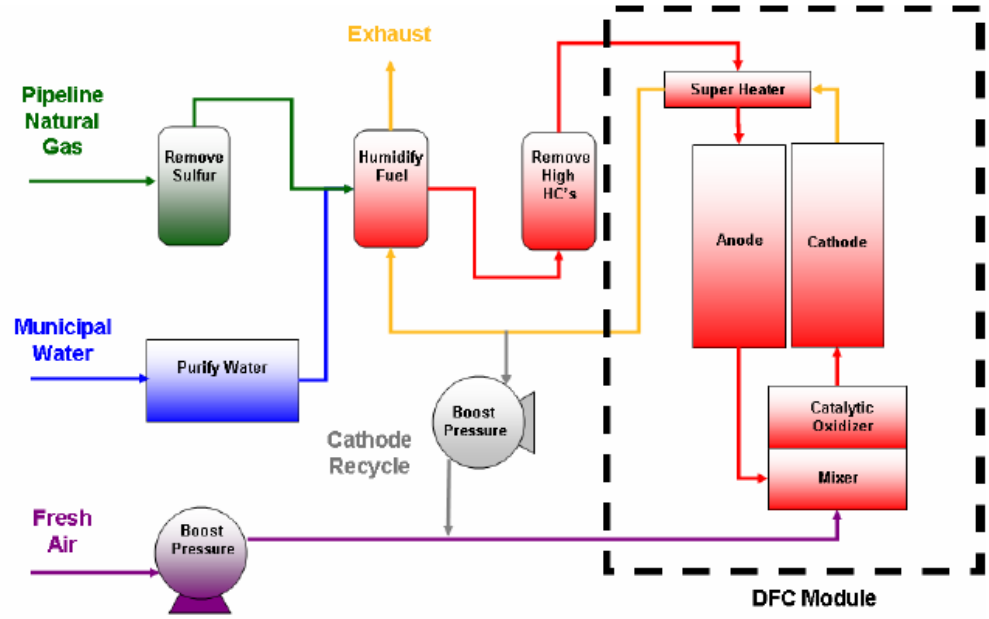


Figure 3-34 provides a schematic of the fuel cell module. Fuel Cell Energy's DFC300 uses carbonate fuel cell technology, operates at high temperatures, and allows natural gas/digester gas to be used with an internal reforming system according to the reaction below.

Internal reformer: $CH_4 + 2H_2O \rightarrow 4\,H_2 + CO_2$

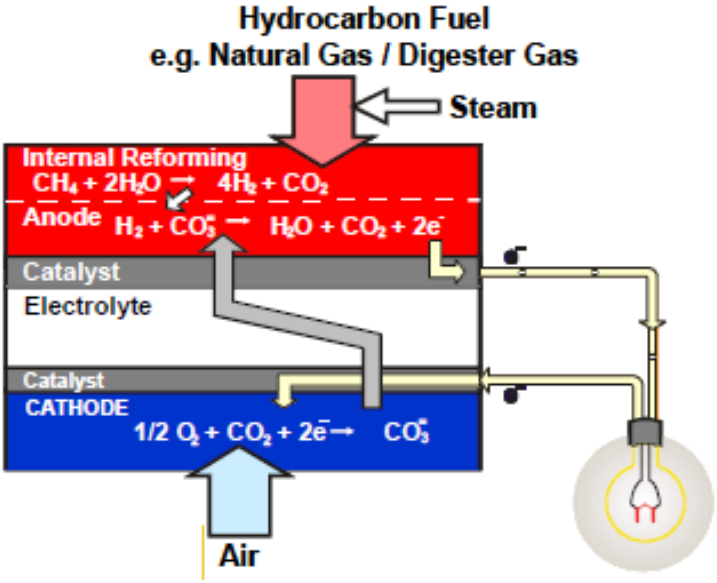
The hydrogen generated by the internal reforming process is consumed immediately, as it reacts with carbonate ions in the fuel cells. The anode exhaust gas is then combined with fresh air and oxidized in a catalytic oxidizer on route to the cathodes.

Anode: $H_2 + CO_3^- \rightarrow 4\,H_2O + CO_2 + 2e^-$

In the fuel cell cathodes, oxygen, carbon dioxide, and electrons are consumed as they react to form carbonate ions. These carbonate ions migrate through the carbonate electrolyte to the anode side of the fuel cells, replacing the carbonate ions consumed by the anode half of the fuel cell process. Hot exhaust gases leave the cathode side of the fuel cell stack modules and are utilized to heat the incoming natural gas, and possibly to generate combined heat and power, before being vented to the atmosphere.

Cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^-$

Figure 3-34: Detailed Chemistry Associated with Internal Reforming and a Direct Fuel Cell



According to the brochure, the fuel cell module contains a stack of approximately 420 individual fuel cells clamped together with manifolds inside insulated carbon steel container electrochemical cells that produce DC power. Molten carbonate fuel cells (MCFCs) use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminum oxide ($LiAlO_2$) matrix. Because they operate at extremely high temperatures of ~650°C (roughly 1,200°F), non-precious metals can be used as catalysts at the anode and cathode, reducing costs.

3.6.2 Testing Fuel Cell Energy's DFC300; First Test (February 11, 2011)

One of the difficulties in testing a fuel cell was finding a unit to test. Following safety training at one site, UCR was allowed access on February 4, 2011, to their molten salt fuel cell made by Fuel Cell Energy. The unit was a 300 kW fuel cell, Model No. DFC300MA. Before testing the fuel cell was serviced by Fuel Cell Energy as part of normal maintenance. For our testing the fuel was switched from biogas to natural gas, to assure uniformity of fuel properties during the day of testing. We also redirected the exhaust flow so the heat exchanger tubes in the exhaust for waste heat recovery were by-passed, to allow a direct collection of the PM from the fuel cells.

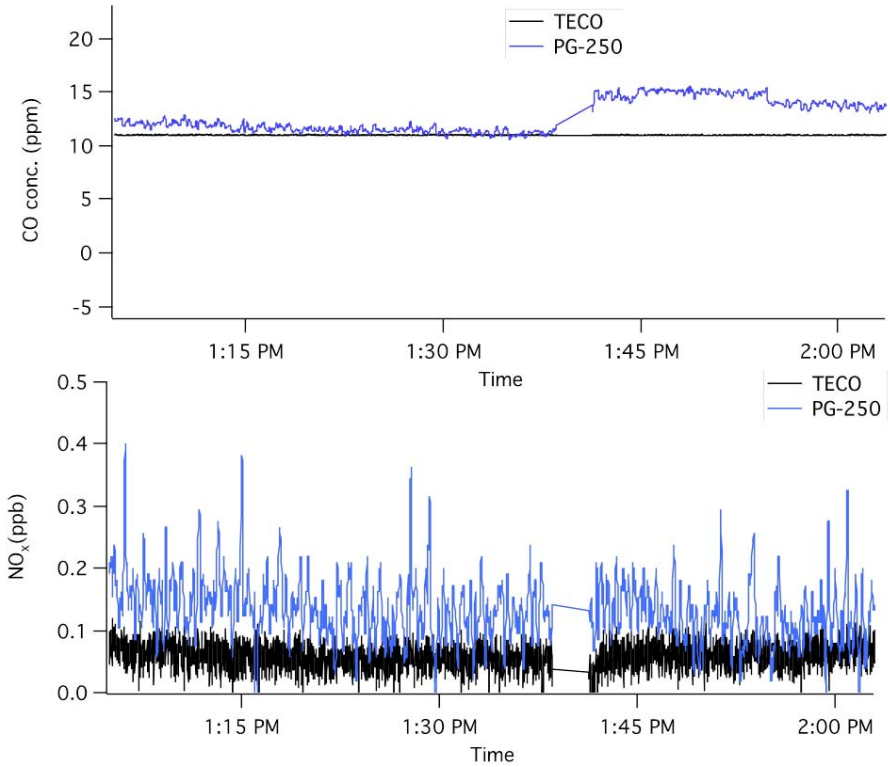
As before, the gases were sampled following ARB M-100 for CO_2, CO, O_2, and NOx, and using commercial ambient instruments for CO and NOx because of the expected concentration levels being ~1 ppm. The exhaust of the fuel cell and the background air were sampled using SCAQMD Method 25.3; EPA Method TO-12, DNPH cartridges for aldehydes, and thermal desorption tubes for light VOCs, as in prior field measurements. A field gas chromatograph with a FID was set up to monitor total hydrocarbons. Moreover, size distribution of fresh exhaust particulate matter was measured using an SMPS. Because of the very high moisture content in the exhaust (12 to 20 percent), we installed a Peltier Thermoelectric cooler to condense and remove water from the exhaust flow before directing the streams to the gaseous instruments. In addition, a dilution tunnel was used to reduce the humidity of the exhaust

sample being directed to the SMPS instrument (Figure 3-35). The power generated and natural gas consumed by the fuel cell were recorded during the testing.

Figure 3-35: Set-up to Sample the Fuel Cell Exhaust

Results from the unit, shown in Figure 3-36, showed that the emission levels of NOx were close to expected values; however, the emission of CO was much higher than expected. Results from the testing are shown in the figures and tables below. Clearly the NOx from the fuel cells is the lowest value measured of all the DG units in the project and was repeated between the two test dates.

Figure 3-36: Concentrations of CO and NOx; Data from February 11, 2011



Results were averaged over a portion of the test period. They are presented in Table 3-33. Note that NOx measured by the M-100 instrument is about 250 percent higher than the values measured with the ambient instrument (TECO). Also, the values for COV are relatively high for NOx, indicative of a process with wide variations or fluctuations.

Table 3-33: ARB Method 100 Results for CO and NOx during a 1-hr test (February 11, 2001)

Measurements	Instrument	Average (η)	Stdev (σ)	COV, %
CO (ppm)	PG-250	12.695	1.495	12
	TECO	>10 ppm, off scale	-	-
NO_x (ppm)	PG-250	134.1 ppb	51.66	39
	TECO	54.65 ppb	21.45	39
CO_2 (ppm)	PG-250	5.42 vol%	0.032	16

Comparative Data. As part of the data analysis, the measured emission factors of the fuel cell were compared with the certification values. The comparison is shown in Table 3-34. No surprise, the NOx emission factor is well below the standard. However, even at 12 ppm, the CO emissions are slightly above the standard.

Table 3-34: Concentration and Emission Factors of NOx and CO

Species	Concentration	Emission Factor (lb/MWh)	DG standards lb/MWh
NO_x	43.34 ppb	0.001	0.07
CO	12.52 ppm	0.149	0.10

Flow Measurement. Flow was measured following ARB Methods 1-4, based on velocity and pressure measurements as the probe traversed the conduit, and compared with the ISO Carbon Balance Method. Results are presented in Table 3-35. As the ISO method is based on mass balances, you must include both the mass of carbon and added water for the Fuel Cell (see Figure 3-40) in order to get the accurate flow rate. Measured and calculated ISO are within 2 percent.

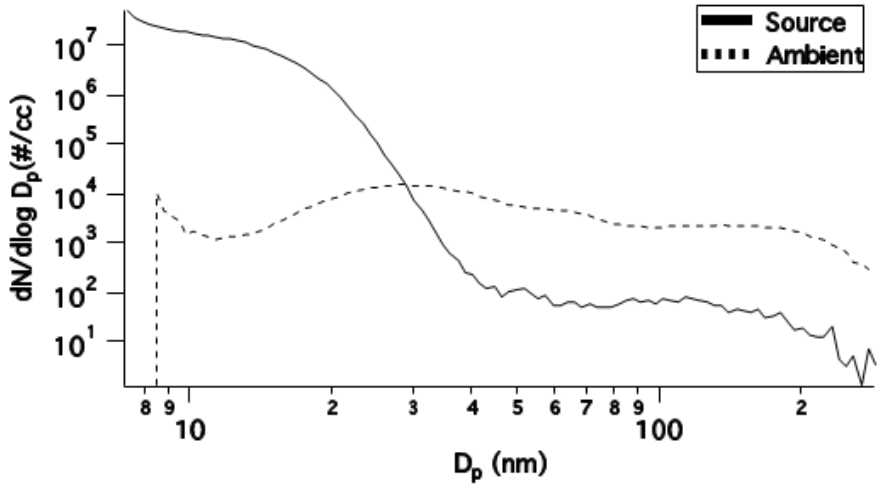
Table 3-35: ARB Methods 1–4 and ISO 8178 Flow Values

Parameter	Value	Unit
ARB Method		
Stack diameter	8	inch
Stack exhaust temperature	727.3	°F
Stack exhaust velocity	125.9	ft/sec
Stack volumetric flow rate (dry basis)	49.03	kdSCFH
ISO Carbon Balance Method		
Natural gas volumetric flow rate	39	SCFM
CO_2 concentration	4.52	vol%
Calculated flow rate	49.91	kdSCFH

kdSCFH = thousand dry standard cubic feet per hour

Particle Size Distribution. Using an SMPS, the particles were counted based on their size, as shown in Figure 3-37. Results in Figure 3-37 indicate that on the order of 10^3 more small particles were present in the exhaust than in the ambient air. At sizes greater than about 40 nm the source had considerably fewer number of particles than in ambient air, so it is likely that the ambient air had a greater overall mass emission factor.

Figure 3-37: Particle Size Distribution of the Emissions from Fuel Cell



3.6.3 Testing Fuel Cell Energy's DFC300; Second Test (February 13, 2011)

Unable to collect all the data on February 11, the test team returned to the same site on Sunday, February 13, to continue testing with a focus on the NOx and CO levels and some measurements of THC (see Figure 3-38). On the restart, the data showed that CO levels had increased to > 50 ppm (see Table 3-36). The NOx values remained at the lowest values measured in this project.

Figure 3-38: Concentration of CO and NO_x Measured 02/13/11

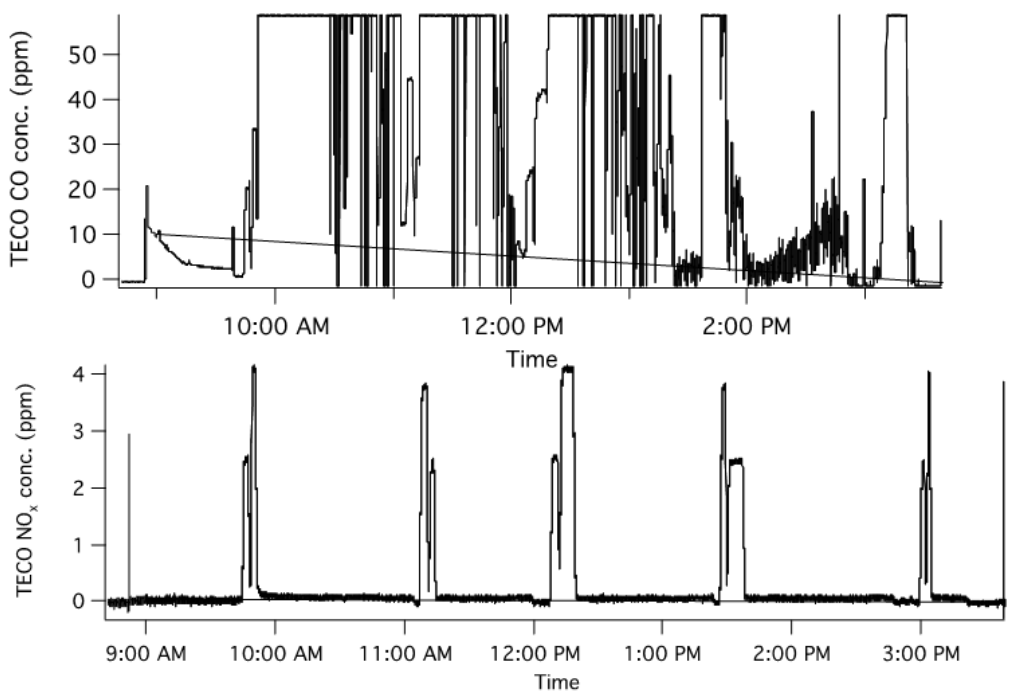
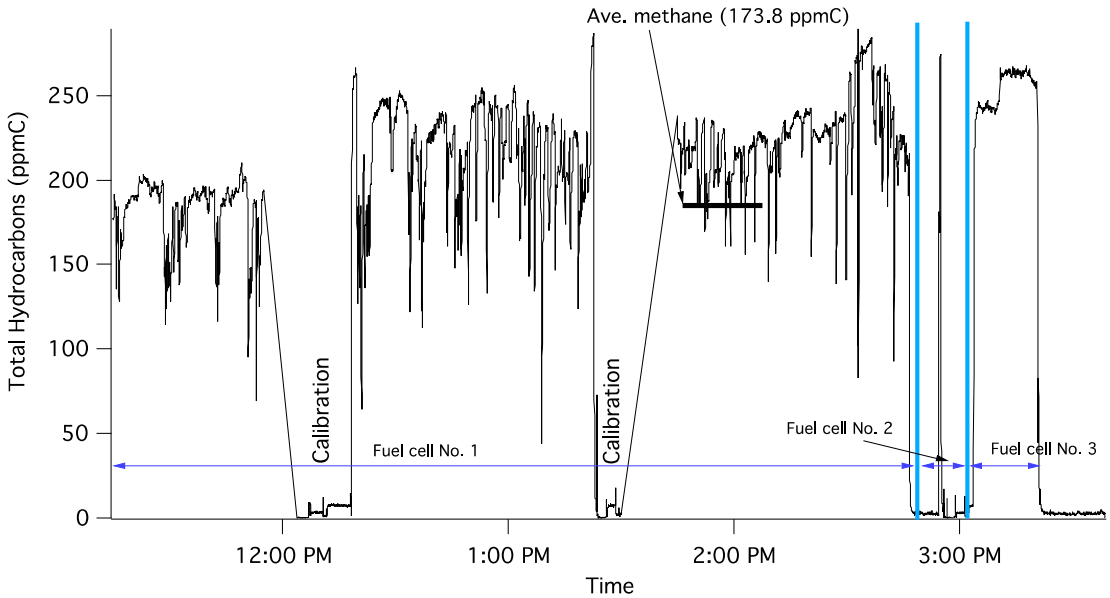


Table 3-36: Ambient Instrument Results for CO and NOx During a 1-Hr Test (February 13, 2001)

Measurements	Instrument	Average (η)	Stdev (σ)	COV (%)
CO (ppm)	TECO	> 50 ppm	-	-
NO_x (ppm)	TECO	69.69 ppb	23.61	34

Concentrations of NOx, CO, and total hydrocarbons were all expected to be ~1 ppm. The FID results in Figure 3-39 showed levels higher than UCR expected but perhaps nearer to what was realistic for a MCFC. Because the hydrocarbon was > 50 set for SCAQMD 25.3, we did not collect or analyze canisters by either EPA TO-12 or SCAQMD 25.3. As the site had three fuel cell units, we moved the sample line to the other two cells and measured the hydrocarbon levels. All three cells had levels of hydrocarbon much higher than the 10 ppm that was expected (perhaps wrongly so). Note that the average hydrocarbon is about 200 ppm, of which about 175 ppm (87 percent) is methane.

Figure 3-39: Concentration of Hydrocarbons on Three Different Units (February 13, 2011)



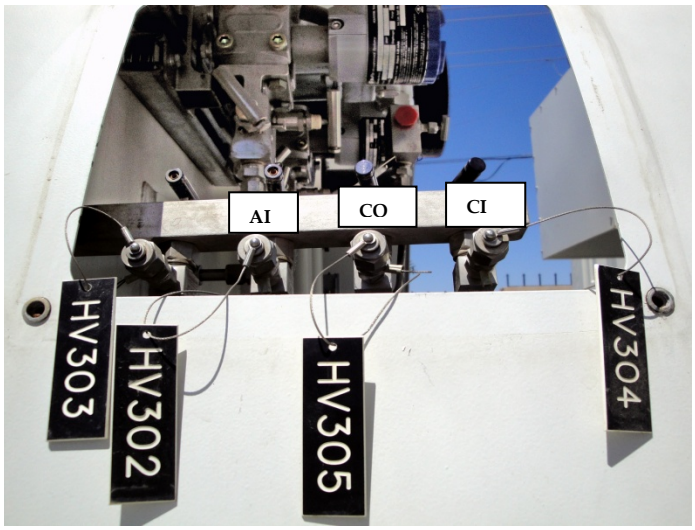
During the testing on February 13, we learned from a representative of Fuel Cell Energy Company there was a possibility of a leak in the feed gas/exhaust gas heat exchanger (see Figure 3-41) that led to the high THC concentrations in the exhaust. For future testing, they suggested sampling the cathode output of the fuel cell and showed us where that sample port was located. Sampling there would eliminate any confusion caused by a leaking exchanger.

3.6.4 Testing Fuel Cell Energy's DFC300; Third Test (May 2011)

On May 26, 2011, we set up for a re-test of a test molten salt fuel cell, Model DFC300MA, running on natural gas. For this test, we directly sampled the exhaust gas from the cathode output rather than from the exhaust (see Figure 3-40). Due to the very high moisture content in the exhaust (up to 20 percent), we added a chiller impinger before the Peltier Thermoelectric

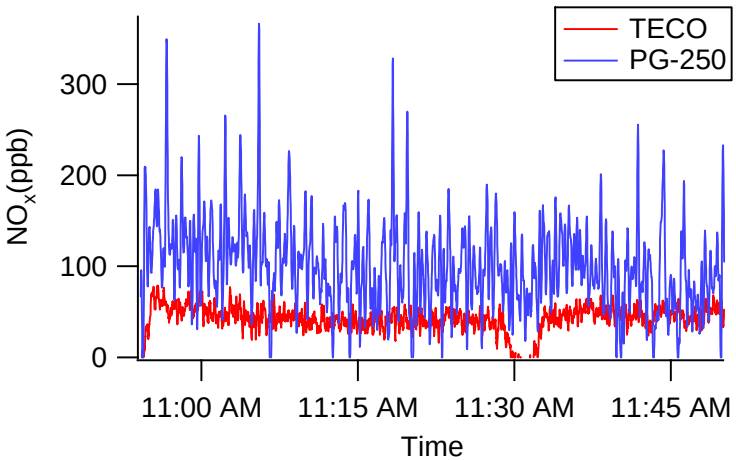
cooler to condense and remove water from the exhaust before directing the gases to the instruments. As before, gases were sampled and analyzed following ARB M-100 protocols for CO_2, CO, O_2, and NO_x, and using ambient instruments for CO and NO_x because of the expected low concentration levels. The exhaust and background air were to be sampled and analyzed for hydrocarbons with SCAQMD Method 25.3; EPA Method TO-12, TDS tubes for VOCs, and DNPH cartridges for aldehydes.

Figure 3-40: Ports from Fuel Cell Electrodes; Cathode Out (CO) is HV305.



Oxides of nitrogen measured with the ambient instrument were very low, about 50 ppb, and similar to concentrations measured in February. Values were significantly higher with the M-100 instrument and highly variable, as shown in Figure 3-41 below; not surprising, as the values were close to the lower detection limit.

Figure 3-41: NOx Concentrations Measured by Ambient and M-100 Instruments



Measured values of THCs remained in the hundreds of parts per million, and CO was ~75 ppm in the first unit. While there, the CO concentration was measured at the cathode output of the other two cells located at that site, and they were even higher; respectively, 125 and 175 ppmv

of CO. Subsequently, we learned from the operating staff that the CO values were highest for the plants with more operating hours on the fuel cell. Because those units had more operating hours, it was not surprising that the emissions in those units would be higher.

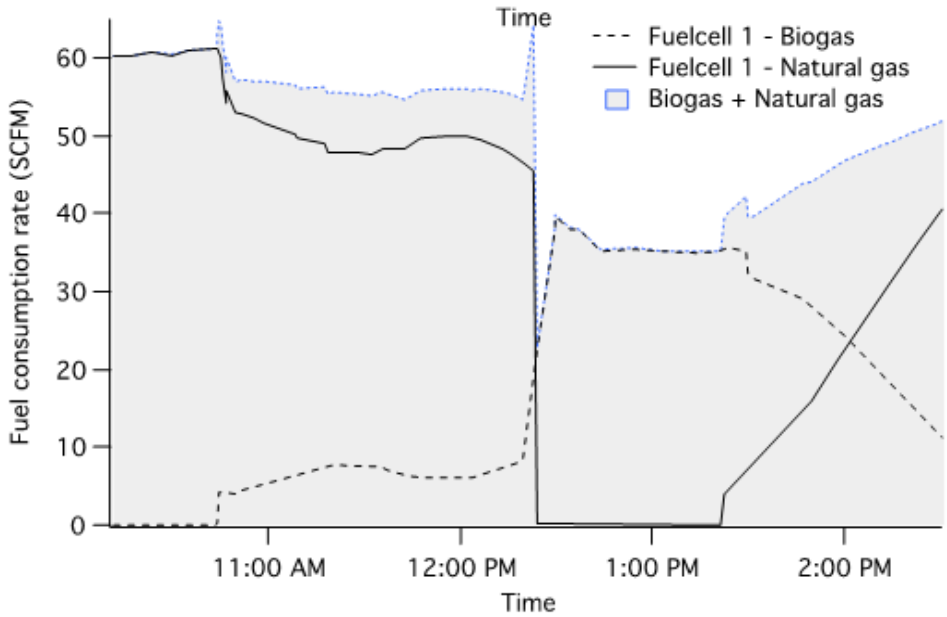
Alternative Site Tested. The testing of a molten fuel cell with low emissions did not seem to be working out at the first site; a second site was selected for testing. At this site the fuel cell module had fewer operating hours than the earlier site, and when it operated on natural gas, the values for CO and THC were lower than at the other site, as seen in Figure 3-42. Note that the 0.1 ppm for NOx and the THC analyzer is on Range #2, so the THC value is 27 ppmC. We did not collect canisters here.

Figure 3-42: Data from Method 100 Instruments at Site 2, Fuel Cell #1

3.6.5 Testing Fuel Cell Energy's DFC300; Fourth and Fifth tests (September 2011)

On September 9, 2011, we returned to the second test site and set up to sample and analyze gases, but not PM as we had measured it earlier. After all the equipment was set up at Unit #1, some instruments did not work reliably due to the high ambient temperature (~110°F, or ~177°C). Thus we put off the test until cooler conditions prevailed. On September 27 we returned to the site and same fuel cell. During the test, the biogas plant had some problems, leading to wide variations in the quality of the fuel cell gas as it ranged from near pure biogas to pure natural gas. The unit is designed to hold load so it will automatically shift from biogas to natural gas and vice versa when the biogas flow fails to maintain the planned output. The wide variation in the composition of the gas going to the fuel cell during UCR's testing is evident in Figure 3-43.

Figure 3-43: Fuel Cell Natural Gas/Biogas Consumption Rates (SCFM) for Units 1 and 3



Fuel Composition. Samples of fuel cell feed gases were taken in Tedlar bags after passing the gases through a mini-impinger, and were submitted for subsequent off-line analyses. Results are listed in Table 3-37. As discussed earlier, the outside lab was expert with portable emissions measurement systems (PEMS) analysis and even though PEMS is normally used for identifying ozone precursors, the method provided this project with a measurement of various C_2–C_{12} hydrocarbons. Once we learned that light VOCs and aldehydes were < 1 percent of the non-methane hydrocarbons, we needed to identify the other hydrocarbons, and PEMS enabled that learning.

As this was the fifth test of a project funded for one test, we took the in-use data, as it was likely the last chance to collect any data before the project ended. Data taken before noon was mainly on natural gas.

Table 3-37: Analysis of biogas and Natural Gas Fuels, September 29, 2011

Analyte	Biogas sample	Mainly Natural Gas sample	Unit
EPA 3C and 25C			
H_2	< 1.0	< 1.0	vol%
O_2	1.10	1.30	vol%
N_2	71.30	86.00	vol%
CO	< 0.1	< 0.1	vol%
CO_2	9.70	0.14	vol%
CH_4	18.00	12.40	vol%
Ethane	< 0.1	0.13	vol%

Analyte	Biogas sample	Mainly Natural Gas sample	Unit
TNMNEOC	< 2.8	673.00	ppmv
Composition of fuels			
CH_4	62.5%	89.6%	mol/mol
CO_2	33.7%	1.0%	mol/mol
Ethane	< 0.3%	0.9%	mol/mol
O_2	3.8%	9.4%	mol/mol
C_2–C_{12} Speciated			
Ethyelene	8.9	2,060.00	ppbC
2-Methylheptane	< SRL	935.00	ppbC
3-Methylheptane	< SRL	< SRL	ppbC
n-Octane	< SRL	1460	ppbC
Ethylbenzene	< SRL	< SRL	ppbC
m/p-Xylenes	< SRL	811	ppbC
Styrene	< SRL	< SRL	ppbC
o-Xylene	< SRL	897	ppbC
Nonane	< SRL	< SRL	ppbC
Isopropylbenzene	< SRL	< SRL	ppbC
n-Propylbenzene	< SRL	< SRL	ppbC
m-Ethyltoluene	< SRL	< SRL	ppbC
p-Ethyltoluene	< SRL	< SRL	ppbC
1,2,5-Methylbenzene	< SRL	< SRL	ppbC
o-Ethyltoluene	< SRL	< SRL	ppbC
1,2,4-Trimethylbenzene	< SRL	< SRL	ppbC
n-Decane	< SRL	< SRL	ppbC
1,2,3-Trimethylbenzene	< SRL	< SRL	ppbC
Total PAMs (ppbC)	811	2,940,000	ppbC
TNMHC	1,100	3,440,000	ppbC

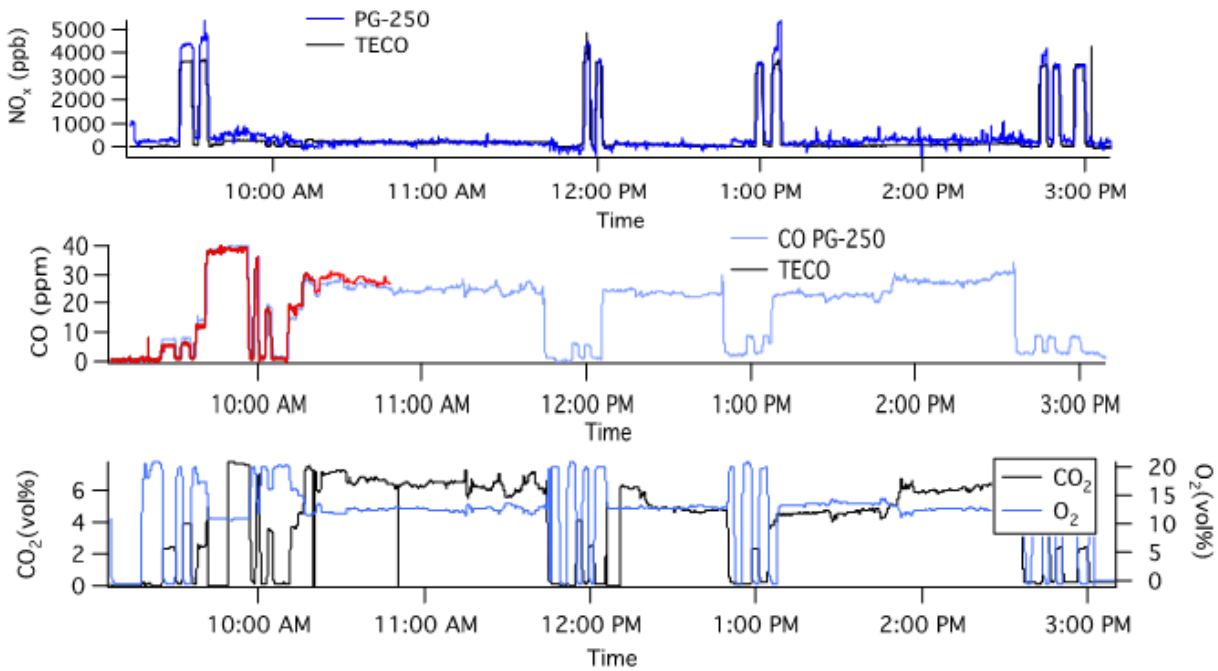
TNMNEOC = Total Non-Methane Non-Ethane Organic Carbon

PAMs = Photochemical Assessment Monitoring Stations compounds

SRL = sample reporting limit

Gases (CO_2, CO, O_2, and NO_x) were sampled following ARB Method 100, and CO and NO_x were also measured using ambient TECO instruments because of the expected low concentration levels(see Figure 3-44). All sampling modifications to handle the high water content worked as planned, including an additional in-line, chilled impinger prior to the Peltier cooler and larger impingers in the SCAQMD 25.3 samplers.

Figure 3-44: Concentrations of CO, CO_2, NOx, O_2 using Ambient and M-100 Instruments



Values from M-100 instruments and from commercial ambient concentration instruments were averaged and are presented in Table 3-38.

Table 3-38: Results for CO and NOx Averaged Over a 1-Hr Interval

Measurements	Instrument	Average (η)	Stdev (σ)	COV,%
CO (ppm)	PG-250	26.35	1.28	5
	TECO	28.23	1.45	5
NO_x (ppb)	PG-250	200.39	91.29	45
	TECO	198.87	55.90	28
CO_2 (vol%)	PG-250	6.52	0.52	8
THC (ppm)	JUM FID	890.21	107.38	12

Hydrocarbon Sampling. Although the hydrocarbon levels by EPA M25A were very high, as indicated in Figure 3-45, we decided to take canister samples to get information on the compounds and the concentration levels in the gas from the cathode outlet. The setup is shown in Figure 3-46 and Figure 3-47. Because of the high water content of the exhaust gas, 20 milliliter (ml) vials initially filled with 5 ml water were used in place of the earlier 5 ml vials with 2 ml of water. During the fuel cell tests, the final volume was ~8–9 ml after filing the canisters to about 10 inches of vacuum.

Figure 3-45: Hydrocarbon Emission Measurements by EPA 25A

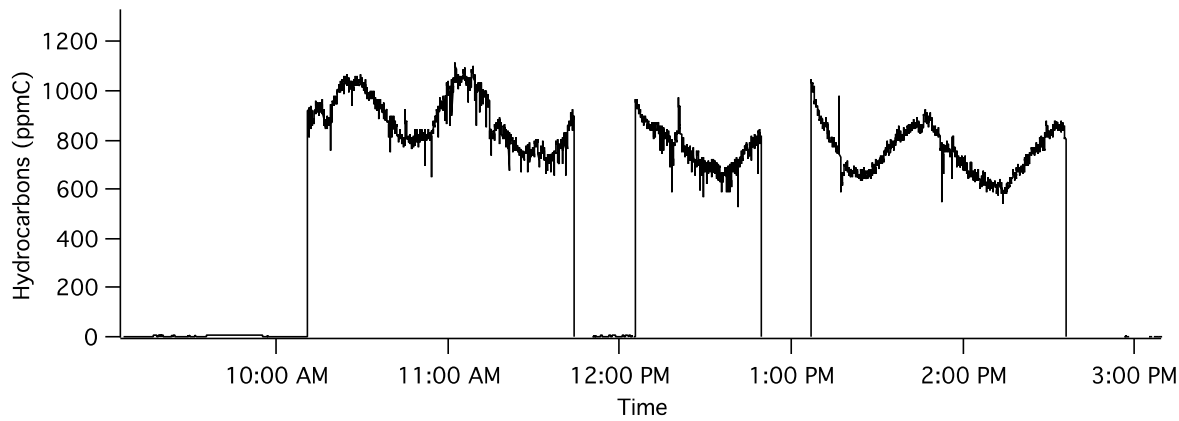


Figure 3-46: Sampling Manifold, Heated Line and Heated Filter Setup

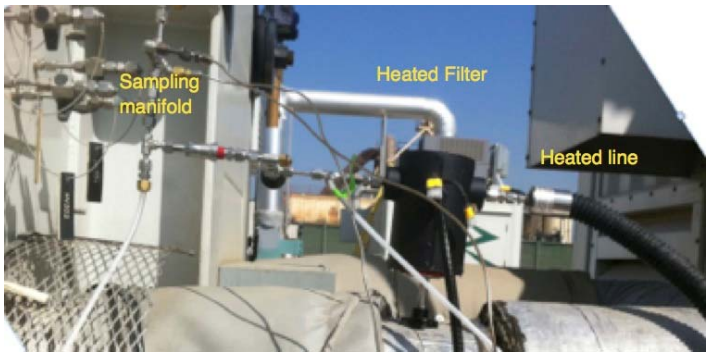


Figure 3-47: SCAQMD Method 25.3 Sampling Setup

Data from EPA Method 25A in Figure 3-45 shows a very high level of hydrocarbons in the exhaust, and it did not seem to matter whether the feed gas was methane or biogas. One observation is that the high levels of methane will reduce the overall fuel cell efficiency.

The term PAMS stands for "Photochemical Assessment Monitoring Stations." See earlier explanation how the measurement of various C_2–C_{12} hydrocarbons helped this project to understand better the total nature of the hydrocarbons emissions (Table 3-39).

Table 3-39: Repeat Analysis from Site for EPA 3C and EPA TO-12

Analyte	Ambient	Source 1	Source 2	Source 3	Ave ± σ	Units
EPA 3C Fixed Gas						
O_2	20.9	15.1	15.1	14.2	14.8 ± 0.5	vol%
N_2	78	77.8	79.1	78	78.3 ± 0.7	vol%
CO	-	-	-	-	-	vol%
CH_4	-	0.11	0.09	0.13	0.1 ± 0.0	vol%
CO_2	0.041	6.9	5.8	7.7	6.8 ± 1.0	vol%
EPA TO-12						
Ethylene	12	36.3	138	83.5	85.9 ± 50.9	ppbC
Acethylene	12.4	2.7	-	-	2.7	ppbC
Ethane	8.5	334	755	598	562.3 ± 212.8	ppbC
Propylene	6.7	6.4	14.8	12.2	11.1 ± 4.3	ppbC
Propane	24.3	16.2	35.8	20.4	24.1 ± 10.3	ppbC
Isobutane	3	2.1	6.6	3.1	3.9 ± 2.4	ppbC
1-Butane	-	2.1	7.1	9.9	6.4 ± 4.0	ppbC
n-Butane	5.4	3.4	7	5.3	5.2 ± 1.8	ppbC
trans-2-Butane	-	-	-	-	-	ppbC
cis-2-Butane	-	-	-	-	-	ppbC
Isopentane	9.9	-	-	-	-	ppbC
1-Pentane	-	-	-	-	-	ppbC
n-Pentane	3.9	-	3.7	-	3.7	ppbC
Isoprene	-	-	-	-	-	ppbC
trans-2-Pentene	-	-	-	-	-	ppbC
cis-2-Pentene	-	-	-	-	-	ppbC
2,2-Dimethylbutane	-	-	-	-	-	ppbC
Cyclopentene	-	-	-	-	-	ppbC
2,3-Dimethylbutane	-	-	-	-	-	ppbC
2-Methylpentane	4.7	-	-	-	-	ppbC
3-Methylpentane	2.3	-	-	-	-	ppbC
1-Hexane	-	-	-	-	-	ppbC
n-Hexane	2.4	-	8.1	-	8.1	ppbC

Analyte	Ambient	Source 1	Source 2	Source 3	Ave ± σ	Units
Methylcyclopentane	2.2	-	-	-	-	ppbC
2,4-Dimethylpentane	2.4	-	-	-	-	ppbC
Benzene	4.9	-	140	56	98.0 ± 59.4	ppbC
Cyclohexane	-	-	-	-	-	ppbC
2-Methylhexane	-	-	-	-	-	ppbC
2,3-Dimethylpentane	4	-	-	-	-	ppbC
3-Methylhexane	2.9	-	-	-	-	ppbC
2,2,4-Trimethylpentane	8.2	-	-	-	-	ppbC
n-Heptane	-	-	-	3.3	3.3	ppbC
Methylcyclohexane	5.2	-	-	-	-	ppbC
2,3,4-Trimethylpentane	2.3	-	-	-	-	ppbC
Toluene	23.5	27.8	56.1	25.4	36.4 ± 17.1	ppbC
2-Methylheptane	-	-	-	-	-	ppbC
3-Methylheptane	-	-	-	-	-	ppbC
n-Octane	-	-	-	-	-	ppbC
Ethylbenzene	3.2	5.3	10.6	4.1	6.7 ± 3.5	ppbC
m/p-Xylene	18.2	9.4	17.3	7.2	11.3 ± 5.3	ppbC
Styrene	6.9	53.8	82.9	105	80.6 ± 25.7	ppbC
o-Xylene	4.9	4	7.7	2.9	4.9 ± 2.5	ppbC
Nonane	-	-	-	-	-	ppbC
Isopropylbenzene	-	-	-	-	-	ppbC
n-Propylbenzene	-	-	-	-	-	ppbC
m-Ethyltoluene	2.8	-	-	-	-	ppbC
p-Ethyltoluene	-	-	-	-	-	ppbC
1,3,5-Trimethylbenzene	4	-	-	-	-	ppbC
Methyltoluene	-	-	-	-	-	ppbC
1,2,4-Trimethylbenzene	4.6	7	12.5	5.2	8.2 ± 3.8	ppbC
n-Decane	-	4.4	9.5	3.9	5.9 ± 3.1	ppbC
1,2,3-Trimethylbenzene	-	-	-	-	-	ppbC

Analyte	Ambient	Source 1	Source 2	Source 3	Ave ± σ	Units
m-Diethylbenzene	-	-	-	-	-	ppbC
p-Diethylbenzene	-	-	-	-	-	ppbC
n-Undecane	-	6.7	11.9	4.8	7.8 ± 3.7	ppbC
n-Dodecane	-	6.6	9.8	5.5	7.3 ± 2.2	ppbC
Total PAMs	**195**	**640**	**1340**	**956**	**978.7 ± 350.6**	**ppbC**
TNMHC	**341**	**3820**	**6530**	**3350**	**4566.7 ± 1716.5**	**ppbC**

One observation from the data in Table 3-40 is the good agreement in the paired SCAQMD 25.3 canisters and that even at low level the results met the quality criteria for the test method.

Table 3-40: Results of Triplicate Analysis of SCAQMD 25.3 Canisters and Water Vials

	EPA 3C Fixed Gases				Tank	Impinger	Total
Sample	O_2 (vol%)	CO (ppm)	CH_4 (vol%)	CO_2 (vol%)	NMNEOC(ppmC)	Carbon (ppmC)	NMNEOC (ppmC)
Ambient air A	21.3	< PQL	< PQL	0.039	1.90	2	4.20
Ambient air B	21.2	< PQL	< PQL	0.039	2.40	1.4	4.10
Source 1A	13.1	< PQL	0.15	8.3	1.80	2.8	5.00
Source 1B	13.1	< PQL	0.14	8.1	1.30	3.7	5.40
Source 2A	13.7	< PQL	0.11	6.8	1.90	5.8	8.30
Source 2B	14.1	< PQL	0.12	6.3	1.30	6.9	9.00
Source 3A	13.6	< PQL	0.12	7.3	2.10	5.2	7.90
Source 3B	14	< PQL	0.11	7.0	2.40	5	8.10
Source (Average±STDEV)	13.6 ± 0.4	< PQL	0.13 ± 0.02	7.30 ± 0.77	1.8 ± .4	4.9 ± 1.5	7.28 ± 1.66
Ambient(Average±STDEV)	21.3 ± 0.1	< PQL	< PQL	0.039 ± 0.000	2.2 ± .4	1.7 ± 0.4	4.15 ± 0.07

PQL = practical quantitation limit

3.7 Test of Large, 50 MW, GE LM6000 Turbine

The test unit selected was a GE LM6000 turbine with installed SCR control technology in the SCAQMD. Meetings with some power companies revealed these "peaker" plants were only operated when ISO requests power; otherwise they are too costly. Another constraint was the limited hours of operation allowed by the operating permit. However, we did find one plant that needed its annual Relative Accuracy Test Audits (RATA) and were able to work out an agreement for testing the plant.

3.7.1 Background on GE's LM6000 Gas Turbines

According to the literature, the General Electric LM6000 is a turbo-shaft gas turbine derived from the CF6-80C2 aircraft turbofan and is modified depending on application. For example, the turbine section can be expanded to convert thrust into shaft power and the control package reworked for power generation, such as peaking power plants. The LM6000 provides 54,610 shaft horsepower (40,700 kW) from either end of the low-pressure rotor system, which rotates at

3,600 rpm. This twin-spool design with the low-pressure turbine operating at 60 hertz (Hz), a common electrical frequency, eliminates the need for a conventional power turbine.

General Electric offers several options for industrial LM6000s, including *SPRINT* (SPRay INTercooling), water injection (widely known as "NOx water"), and Spray Mist Evaporative Cooling (SMEC). The SPRINT and SMEC options are designed to increase efficiency and power of the turbine, and the water injection is for reducing emissions. The SMEC system is a water fogger system that sprays a fine mist of water into the inlet air before the air filters. This system is high maintenance and may be replaced by chillers in newer units. The SPRINT system used in the turbine tested in this project injects demineralized water into the engine either upstream of the low-pressure compressor or between the low-pressure and high-pressure compressors. The GE LM6000 PC is rated to provide more than 43 MW with a thermal efficiency of around 42 percent LHV at ISO conditions. Today, with options, this can be increased to above 50 MW rated power.8

3.7.2 Description of Test Unit

The peaking plant tested in this project used a LM6000 in simple-cycle mode of operation and was built to exclusively serve a local area (see Figure 3-48, Table 3-41). Nitrogen oxide emissions were restricted to 2.5 ppm dry and attained by using water injection in series with a catalyst system from Express Integrated Technologies. A 3,200 ton chiller from Turbine Air Systems was part of the installed unit and is used about 80 percent of the time that the plant is on-load. The site is sized for additional machines of similar size. A flow schematic of the plant is provided in Figure 3-49.

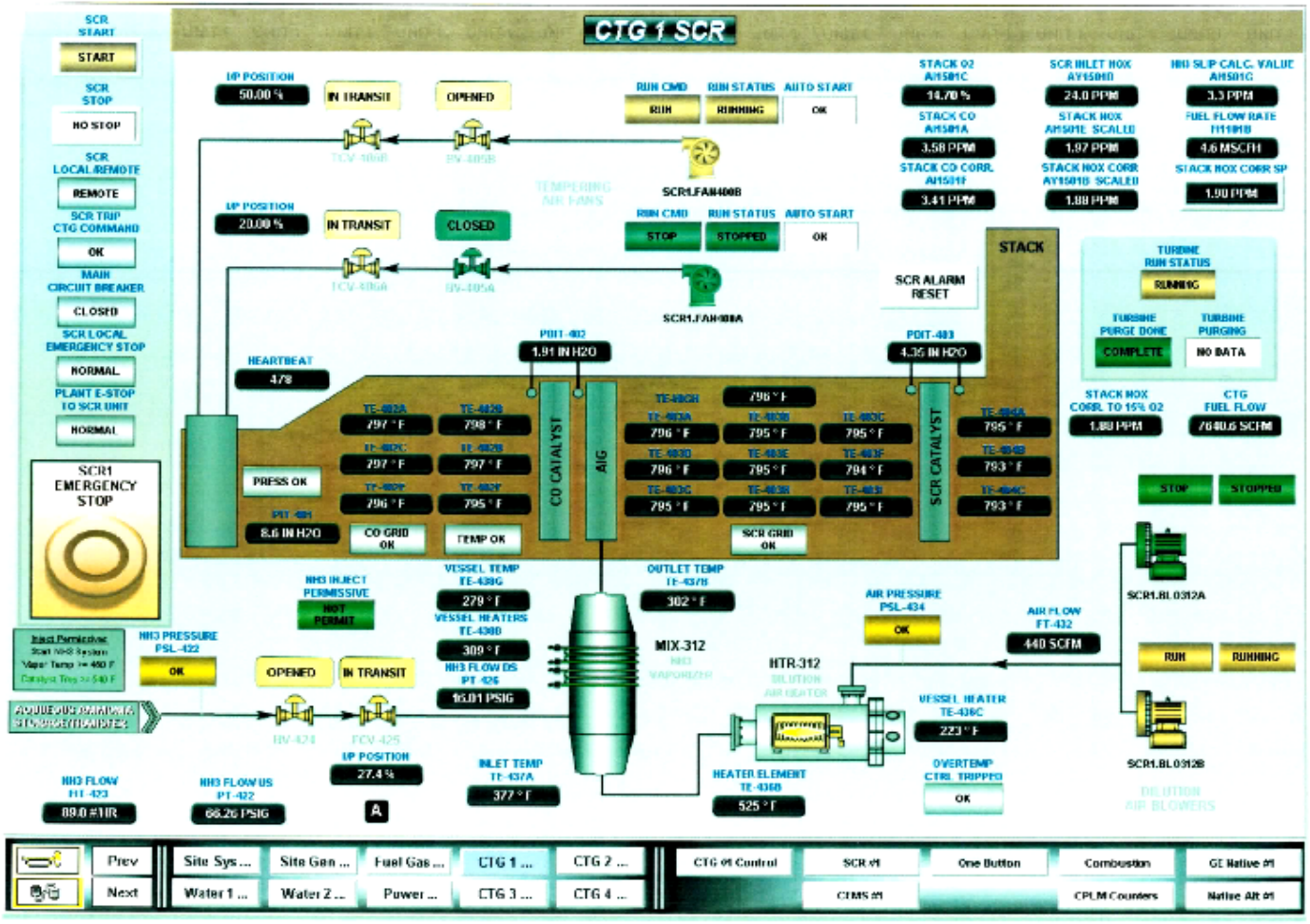
Figure 3-48: A 50-MW, Peaker Power Plant Using GE's LM6000 Turbine with SCR

8 See http://www.ge-energy.com/products_and_services/products/gas_turbines_aeroderivative/lm6000_ph.jsp.

Table 3-41: Operating Parameters for the Tested LM6000 Unit

Configuration	2 X 48-MW LM6000 Sprint NxGen gas turbines
In operation	2006
Fuel	Natural gas
T/G supplier	GE

Figure 3-49: Schematic of the Process Flow for the Tested Unit

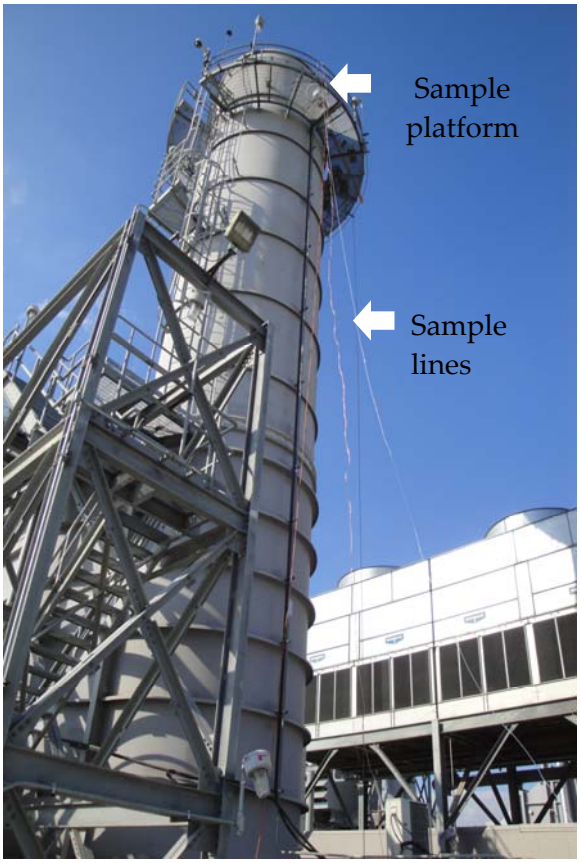


3.7.3 Method 100 and Ambient Instrument Measurements

Gas measurements were made on the sample platform and on the ground level. Gaseous measurements of NOx, CO, and CO_2 were made at the ground level by arranging for sample lines to carry the gases to a truck with the M-100 and ambient monitors (See Figure 3-50). An additional oil-free copper line was used to transport a continuous stream of exhaust from the platform to the ground for connection with the SMPS, in order to monitor the particle size distribution. As the system was at steady state, there was no concern with the transient time for the signal to reach the analyzers. Sample data for the CO, CO_2, and NOx are provided in Figure 3-51.

The measurement of the hydrocarbons was carried out on the sample platform levels. These measurements included the EPA Method 25A, EPA TO-12, and SCAQMD 25.3.

Figure 3-50: Sample Lines from the Platform Coming to Ground Level



Looking at the CO data in Figure 3-51 shows that with the M-100 instrument, there was a transient behavior not seen in the ambient instrument or in the CO_2 values. As all gaseous samples came from the same sample line, we do not believe the transient is accurate and have no explanation for the observed results. Notice just after 9AM that all instruments show a transient, so it is not clear why the M-100 instruments shows the later transients. Taking the average of the high population for the CO values shows an average of 3.69 ± 0.31 ppm with a COV of 8 percent, a rather low value. Looking at the NOx data shows the same unsteady behavior of the M-100 instrument, as compared with the ambient instrument (see Table 3-42). The NOx value of 2.32 ± 2.7 ppm was with a COV of 12 percent.

Figure 3-51: Emission Concentration of CO, NO_x, and CO_2 Following ARB Method 100

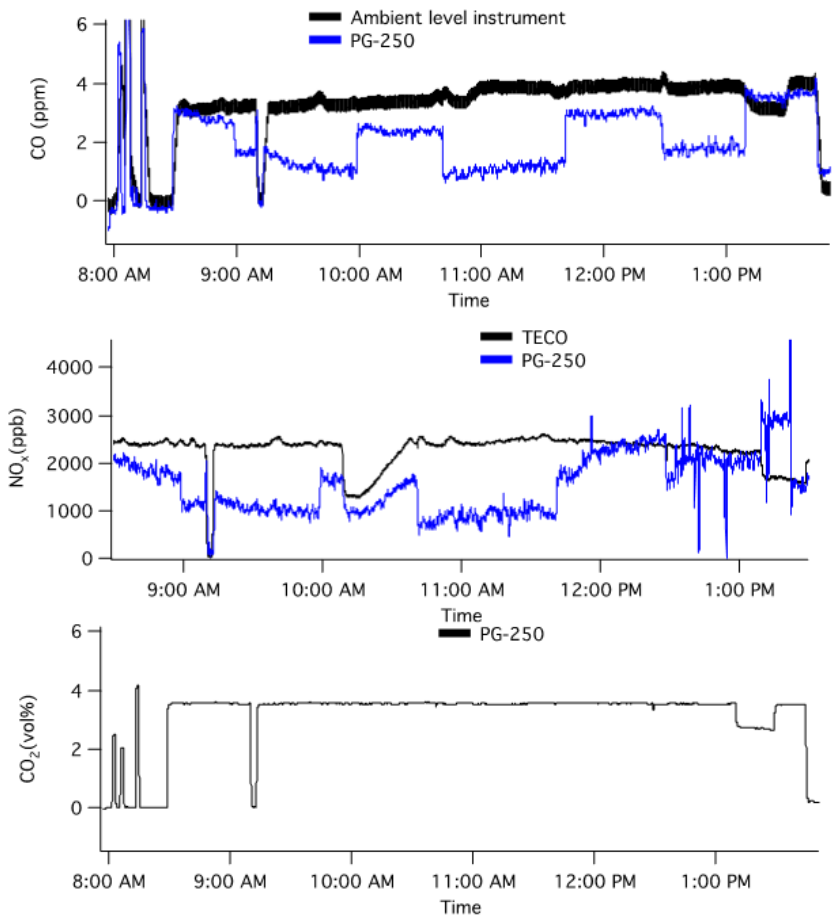


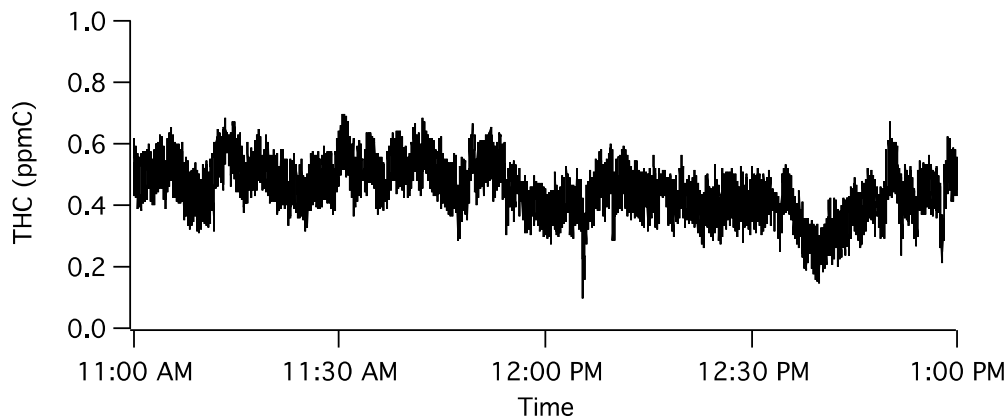
Table 3-42: Concentration of Measured Gases by ARB M-100 and Ambient Instruments

Measurements	Method	Average (η)	Stdev (σ)	COV, %
CO (ppm)	M-100	1.850	0.75	41
	Ambient	3.689	0.31	8
	CEM	3.58		
NO_x (ppb)	M-100	1,459.18	594.10	41
	Ambient	2,319.07	271.50	12
	CEM	1.97		
CO_2 (vol%)	M-100	3.552	0.020	0.5
THC (ppm)	M25A	0.459	0.092	20

3.7.4 Measurement of Hydrocarbons, EPA Method 25A

All hydrocarbon measurements and sampling were made on the platform level, about 75 feet in the air. Hydrocarbons were continuously measured by EPA Method 25A and from canisters supplied from two independent laboratories. By EPA M25A, the total hydrocarbons were extremely low, at about 0.5 ppm, as indicated in Figure 3-52. Furthermore, the values were relatively steady during the run, as evidenced in the narrow range of the concentration, from 0.4 to 0.6 ppm. The THC analyzer was on its 0 to 10 ppm scale, so it was near its lower detection limit.

Figure 3-52: Total Hydrocarbons (ppm) from the LM6000 Gas Turbine (EPA M25A)



3.7.5 Measurement of Hydrocarbons, Canisters SCAQMD 25.3

Looking at the values from Lab C in Table 3-43, we see the total NMNEOC hydrocarbons are about 1.5 ppmC; a value that is greater than the 0.5 ppm found from Method 25A. As will be evident in the EPA TO-12 values, the TNMHC average was 102 ppb, a value closer to that measured with EPA 25A.

Table 3-43: Hydrocarbon Analysis by SCAQMD 25.3 and Fixed Gases by EPA 3C, from Lab C

	Fix Gases (EPA 3C)				Canister	Impinger	Total
Test No.	**O_2 (vol%)**	**CO (ppm)**	**CH_4**	**CO_2(vol%)**	**NMNEOC (ppmC)**	**NMNEOC (ppmC)**	**NMNEOC (ppmC)**
1/Ambient-A	20.7	< PQL	< PQL	0.0357	1.09	0.98	2.07
1/Ambient-B	20.7	< PQL	< PQL	0.0352	0.98	1.74	2.72
1/Source-A	15.8	< PQL	< PQL	4.6	0.87	1.09	1.96
1/Source-B	15	< PQL	< PQL	4.9	0.33	1.41	1.74
2/Source-A	14.9	< PQL	< PQL	5.1	0.65	0.65	1.3
2/Source-B	14.9	< PQL	< PQL	5.1	0.43	0.98	1.41
3/Source-A	14.9	< PQL	< PQL	5.5	0.33	1.09	1.42
3/Source-B	15.6	< PQL	< PQL	4.6	0.43	0.98	1.41
Source (m ± σ)	**15.18 ± 0.41**	**< PQL**	**< PQL**	**4.97 ± 0.34**	**0.51 ± 0.21**	**1.03 ± 0.25**	**1.54 ± 0.25**
Ambient (m ± σ)	**20.70 ± 0.00**	**< PQL**	**< PQL**	**0.04 ± 0.00**	**1.04 ± 0.08**	**1.36 ± 0.54**	**2.40 ± 0.46**

Values for the CO_2 analysis seem about right for the ambient sample, at ~400 ppm, but on the high side (4.97 percent) for the source samples when compared with value of 3.55 percent measured

with M-100. Other comparative analyses in this project suggested that the measured values for source samples at Lab C might be biased high, and this was reported to the lab.

3.7.6 Measurement of Hydrocarbons, Canisters EPA TO-12

Table 3-44 provides data on the measurement of various C_2–C_{12} hydrocarbon species using the standard PAMS methods. Note the total NMHC gases are about 100 ppb, a very low value and similar to those found with the EPA M25A.

Table 3-44: Hydrocarbons in ppb for Canister and Tedlar Bag by EPA TO-12, from Lab C

Species	Ambient	Source 1	Source 2	Source 3	Tedlar Bag	Zero Gas	4.13 ppm propane cal-gas
ethylene	2.3	7.3	9	10.6	5	<dl	<dl
acetylene	<dl	1.6	<dl	1.9	1.4	<dl	<dl
ethane	8.1	4.2	6.3	6.8	3.9	3.0	<dl
propylene	<dl	<dl	<dl	<dl	<dl	<dl	<dl
propane	6.5	<dl	6.5	2.2	1.7	2.8	12,000
isobutane	<dl	<dl	<dl	<dl	<dl	<dl	9.0
1-butane	<dl	<dl	<dl	<dl	<dl	<dl	<dl
n-butane	2.5	<dl	2.5	<dl	<dl	<dl	<dl
trans-2-butane	<dl	<dl	<dl	<dl		<dl	<dl
cis-2-butane	<dl	<dl	<dl	<dl		<dl	<dl
isopentane	<dl	<dl	<dl	<dl	<dl	<dl	<dl
1-pentene	<dl	<dl	<dl	<dl	<dl	<dl	<dl
n-pentane	<dl	<dl	<dl	<dl	<dl	<dl	<dl
isoprene	<dl	<dl	<dl	<dl	<dl	<dl	<dl
trans-2-pentene	<dl	<dl	<dl	<dl		<dl	<dl
cis-2-pentene	<dl	<dl	<dl	<dl		<dl	<dl
2,2-DM butane	<dl	<dl	<dl	<dl		<dl	<dl
cyclopentane	<dl	<dl	<dl	<dl		<dl	<dl
2,3-DM butane	<dl	<dl	<dl	<dl		<dl	<dl
2-M pentane	2.1	<dl	2.2	2.0		<dl	<dl
3-M pentane	<dl	<dl	<dl	<dl		<dl	<dl
1-hexane	<dl	<dl	<dl	<dl	<dl	<dl	<dl
n-hexane	<dl	<dl	<dl	<dl	<dl	3.2	11.9
M-cyclopentane	<dl	<dl	<dl	<dl		<dl	<dl
2,4-Dmpentane	<dl	<dl	<dl	<dl		<dl	<dl
Benzene	<dl	<dl	<dl	17.4	<dl	<dl	<dl
cyclohexane	<dl	<dl	<dl	<dl		<dl	<dl

Species	Ambient	Source 1	Source 2	Source 3	Tedlar Bag	Zero Gas	4.13 ppm propane cal-gas
2-M hexane	<dl	<dl	<dl	<dl		<dl	<dl
2,3-DM pentane	<dl	<dl	<dl	<dl		<dl	<dl
3-M hexane	<dl	<dl	<dl	<dl		<dl	<dl
2,2,4- 3M pentane	<dl	<dl	<dl	<dl		<dl	<dl
n-heptane	<dl	<dl	<dl	<dl	<dl	<dl	<dl
M-cyclohexane	<dl	<dl	<dl	<dl		<dl	<dl
2,3,4-3M pentane	<dl	<dl	<dl	<dl		<dl	<dl
toluene	4.3	<dl	1.9	13.8	2.7	<dl	3.6
2-methyleheptane	<dl	<dl	<dl	<dl		<dl	<dl
3-methylheptane	<dl	<dl	<dl	<dl		<dl	<dl
n-octane	<dl	<dl	<dl	<dl	<dl	<dl	<dl
ethylebenzene	<dl	<dl	<dl	<dl		<dl	<dl
m/p-xylenes	<dl	<dl	<dl	<dl		2.6	<dl
styrene	<dl	<dl	<dl	6.4	<dl	<dl	<dl
o-xylene	<dl	<dl	<dl	1.9	<dl	<dl	<dl
nonane	<dl	<dl	<dl	<dl	<dl	<dl	<dl
isopropylbenzene	<dl	<dl	<dl	<dl		<dl	<dl
n-propylbenzene	<dl	<dl	<dl	<dl		<dl	<dl
m-ethyltoluene	<dl	<dl	<dl	<dl		<dl	<dl
p-ethyltoluene	<dl	<dl	<dl	<dl		<dl	<dl
1,3,5-3M benzene	<dl	<dl	<dl	<dl		<dl	<dl
o-ethyltoluene	<dl	<dl	<dl	<dl		<dl	<dl
1,2,4-3M benzene	<dl	<dl	<dl	<dl		<dl	<dl
n-decane	<dl	<dl	<dl	<dl	2.6	<dl	<dl
1,2,3-3M benzene	<dl	<dl	<dl	<dl		<dl	<dl
m-diethylbenzene	<dl	<dl	<dl	<dl		<dl	<dl
n-undecane	<dl	<dl	<dl	<dl		<dl	<dl
n-dodecane	<dl	<dl	<dl	<dl		<dl	<dl
Total PAMS	25.8	14.9	19.3	60.7	20	20	12,100
TNMHC	139	67.9	103	135	140	69.6	12,500

The source sample measurement of CO_2 at ~5 percent (Table 3-45) is again on the high side for Lab C, versus the 3.55 percent found in the M-100 test. Also, as the propane calibration gas had 4.12 percent CO_2, and the lab reported 5.9 percent, the CO_2 values are biased high.

Table 3-45: Fixed Gas Analysis of EPA TO-12 Canister and Tedlar Bag by EPA 3C, in ppb, from Lab C

	EPA 3C Fixed Gas Results						
Species	**Ambient**	**Source 1**	**Source 2**	**Source 3**	**Tedlar Bag**	**Zero Gas**	**4.13 ppm propane cal-gas**
O_2 (vol%)	21.1	15.0	14.8	14.9	15.6	21.3	0.3
N_2 (vol%)	77.9	80.1	80.1	80.2	80.1	77.6	93.8
CO (ppm)	<dl	<dl	<dl	<dl	<dl	<dl	<dl
CH_4 (ppm)	<dl	<dl	<dl	<dl	<dl	<dl	<dl
CO_2 (vol%)	<dl	5.0	5.1	5.0	4.3	<dl	5.9

From Lab D, Table 3-46 provides the average values for the NMNEOC are about 0.3 ppmC; much lower than the 1.5 ppmC measured by SCAQMD 25.3. When compared with the NMNEOC values from Lab C of about 0.1 ppmC, there is a much better agreement, considering the very low values being measured. Further, the value measured with EPA 25A was about 0.5 ppmC, so all these values seem to be within the error of measurement accuracy.

Table 3-46: Triplicate Analysis of Fixed Gas and EPA TO-12 from Lab D

	O_2 (vol%)	N_2 (vol%)	CH_4 (ppm)	CO (vol%)	CO_2 (vol%)	Ethane (vol%)	Ethane (vol%)	NMNEOC (ppmC)
Ambient	22	78	2.4	N.D.	0.039	N.D.	N.D.	0.31
Source 1	16	81	N.D.	N.D.	2.9	N.D.	N.D.	0.20
Source 2	16	81	N.D.	N.D.	3.4	N.D.	N.D.	0.39
Source 3	15	82	N.D.	N.D.	3.4	N.D.	N.D.	0.28
Zero	22	78	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Calibration gas 4.13 ppm C_3H_8	N.D.	96	N.D.	N.D.	4.3	N.D.	N.D.	20.3
Lab Blank	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.11

N.D. = non detect

Note the average CO_2 value of 3.2 percent for the source measured by Lab D was closer to the 3.55 percent value measured by M-100 than the value from Lab C. Furthermore, the calibration gas with 4.12 percent CO_2 was close to the 4.3 value measured by Lab D; again, closer than the value from Lab C. While Lab D is accurate for hydrocarbons in the zero gas and for CO_2 in the cal gas, the reported value of 20.3 ppmC is very high for a cal gas with 12.4 ppmC.

3.7.7 Summary Results for Analysis of the Calibration Standards for All Test Sites

During the course of the project, a number of calibration standards were submitted to the various certified labs to learn more about their accuracy, especially at the very low hydrocarbon levels. Analytical results of the calibration samples are listed in Table 3-47. As is evident, some of the values were difficult for the labs to accurately measure. We were especially interested in measurement of the hydrocarbon samples, as this was the most challenging.

Table 3-47: Summary of Data for Calibration Standards

Species	Zero air	Lab A	Lab C	Lab C	Lab D	Cal. gas	Lab C	Lab D
THC (ppmC)	**0**	2.92	0.9	0.07	N.D.	**13.08**	12.5	20.3
O_2 (vol%)	**21**	19.4	20.4	21.3	22	**0**	0.3	<dl
N_2 (vol%)	**78**	n.a.	n.a.	77.6	78	**Filler gas**	93.8	96.0
CO (ppm)	**0**	n.a.	<dl	<dl	<dl	**5.81**	<dl	<dl
CH_4 (ppm)	**0**	<1.0	n.a.	<dl	<dl	**0**	<dl	<dl
CO_2 (vol%)	**0**	0.00972	n.d.	<dl	<dl	**4.12**	5.9	4.3

3.7.8 Flow Measurements

Given that the stack was 156 inches in diameter, a special sampling assembly was needed to span the cross section, and flow had to be measured in the stack using ARB Methods 1–4 across four diameters. Data are shown in Table 3-48. Using the equations outlined earlier in Table 3-9 leads to the dry standard stack volumetric flow rate (Q_{std}) of 14.02 mmSCFH.

Table 3-48: Stagnation Pressure and Temperature of Stack Gas at a Point

Point #	ΔP (in H_2O)	T (°F)
1	1.4	792
2	1.3	793
3	1.2	794
4	0.9	792
5	1.4	793
6	1.1	793
7	0.8	792
8	0.8	793
9	1.2	790
10	1.0	790
11	0.8	790
12	0.7	789
13	1.6	793
14	1.4	792
15	1.3	792
16	1.1	792
Average:	1.13	791.9

Table 3-49 shows the result of the carbon mass balance method following ISO 8178-1. The calculated stack gas flow is 13.90 mmSCFH, about 2.0 percent less than the value of 14.02 mmSCFH from the M1–4 measurements. Again, it was within the 5 percent accuracy method that ARB had specified as their goal.

Table 3-49: Results of ARB M1-4 and ISO Carbon Balance Method for Flow

Parameter	Value	Unit
ARB Method		
Stack diameter	156	inch
Stack exhaust temperature	791.9	°F
Stack exhaust Velocity	90.33	ft/sec
Stack Volumetric Flow rate (dry basis)	14.03	mmSCFH
ISO Carbon Balance Method		
Natural gas volumetric flow rate	464.2	kSCFH
CO_2 concentration	3.52	vol%
Calculated flow rate	13.90	mmSCFH

3.7.9 Particle Size Distribution

The exhaust was sampled and the properties of the particles measured with a SMPS analyzer. Data indicated that the particle number concentration was 1,127 ± 1,223 #/cc, and the particle size distribution is shown in Figure 3-53. The data in the figure indicates the particles in the turbine exhaust have less mass than particles in the ambient air.

Figure 3-53: Particle Size Distribution for the LM6000 Plant with SCR

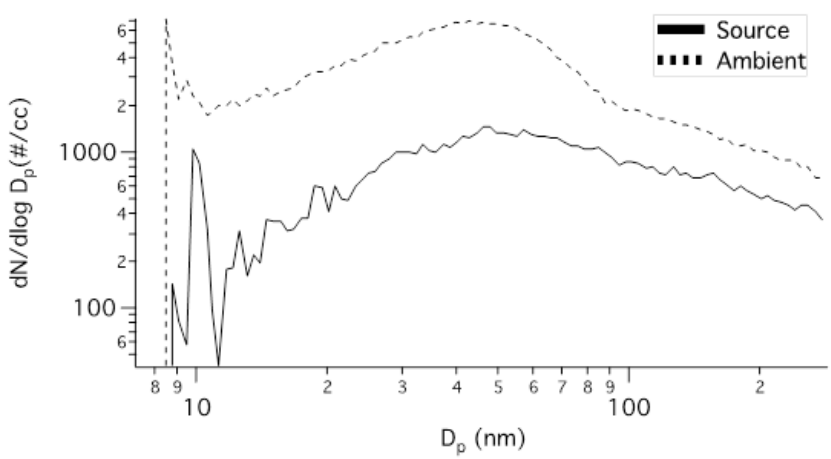
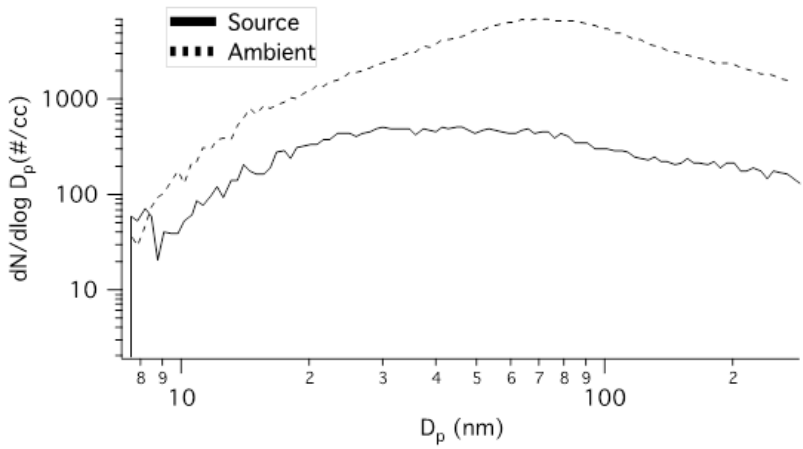


Figure 3-54 shows the data from the Solar Turbines turbine, fired on natural gas with an SCR treating the exhaust. In comparison with the data in Figure 3-60, the ambient air sample looks

about the same. However, the exhaust source sample was about a factor of ten times lower on the exhaust from the Solar Turbines plant.

Figure 3-54: Particle Size Distribution for Ambient and Exhaust for the Solar Turbines Turbine with SCR



CHAPTER 4: Discussion

This project's goal was to determine if current ARB methods for measuring gaseous concentrations and flow rates were accurate enough for the current generation of DG sources, as the technology in these units has lowered the exhaust concentrations of CO, NOx, and hydrocarbons to < 10 ppm. Furthermore, if ARB Method 100 instruments were operating below their lower detection limits and inaccurate at the low levels, the project sought to identify new methods.

The project's approach was to measure exhaust emissions from a variety of commercial, real-world DG sources rather than mixing gases and carrying out laboratory tests. Measurements were made with instruments meeting current regulations and some commercial products capable of measuring the lower concentration levels of modern DG units. Flow rate accuracy was investigated as well, since the contribution of the source emissions to the local inventory is determined by multiplying the concentration and the flow rate. For this project, flow rate was determined by two independent methods, both widely accepted as standards. One method followed the ARB Methods 1–4 and is based on Bernoulli's principle. The other, from the International Standards Organization, is based on the principle of mass balances.

4.1 Findings

4.1.1 Measurements of CO and NOx

The project showed that measuring the concentrations of gases in exhaust gas at the very low levels of modern DG units is challenging and prone to inaccurate results. Basically, instruments currently specified in ARB M-100 do not have the range and span to cover the operating range of the current DGs. For example, even if the NOx instrument were run at the lowest range of 0 to 25 ppm; a value of 1 ppm would be outside the guidance in CFR Part 60, which recommends a measurement range of 10 to 90 percent of the span, or from 2.5 to 22.5 ppm. Interestingly, data collected in this project showed the NOx values at 1 ppm were very close to those measured with the appropriate instrument and had about the same precision; however, with fuel cell values near 0.1 ppm, the NOx values with the M-100 instrument were nearly 100 percent inaccurate. By comparison, using an instrument with a range of 0 to 5,000 ppb of NOx showed a very good agreement with the data reported from the continuous emission monitors (CEMs). Thus the recommended instrument for the NOx at very low levels is outside of the current M-100 limits, and available instruments for ambient levels should be used.

The results from the M-100 instrument proved even more inaccurate for CO than for NOx. The range of the M-100 instrument was 0 to 200 ppm, so using the 10 to 90 percent recommendation suggests an operating range of 20 to 180 ppm. Clearly, with CO concentration values of < 5 ppm the instrument was not recommended for this measurement. Results showed that the CO measured with Method 100 was biased higher than the value measured with an instrument with the appropriate range, as it repeatedly read higher than an instrument with the appropriate range.

4.1.2 Measurement of Hydrocarbons

Hydrocarbons were the most challenging gas to measure, especially at values of < 10 ppm. Method 100 is good for measurements of > 50 ppm but measuring at low concentrations proved very difficult in the past and lead to the adoption of SCAQMD 25.3. For this project, a number of methods were selected to measure the low HC concentrations:

1. Selective sorbents and measurement of hydrocarbons, EPA TO-18
2. Selective sorbents and measurement of carbonyls, EPA TO-11
3. Field method using GC-FID, EPA Method 25A
4. Canisters based on EPA TO-12 and SCAQMD 25.3
5. Collection of Tedlar bags with EPA TO-12

Conclusions were reached during the project regarding hydrocarbon results:

1. Levels of carbonyls and volatile light hydrocarbons were in the ppb levels, so they did not contribute measurably to the ppm levels of hydrocarbons found in the exhaust. These species are at trace levels and are not an important contribution to the exhaust hydrocarbon levels.
2. Hydrocarbon concentrations at values < 5 ppm are extremely challenging to measure accurately and with precision. Even when using SCAQMD 25.3, and when the certified labs carefully follow the method, from cleaning the canisters to running the samples, the resultant values are imprecise.
3. Results showed that a U.S. EPA protocol calibration "zero-gas" should be used for establishing a laboratory's minimum detection limit and confidence limits.
4. Using qualified labs listed on an air district web page does not mean that the results from the various labs will be the same when hydrocarbon levels are very low, < 10 ppm. Four qualified labs were used in this project, and results differed for EPA protocol gases.
5. Even if the purchased transfer lines for the EPA Method 25A are new and claimed to be oil-free, they must be checked to ensure they do not bleed hydrocarbons and introduce a systematic drift into the data.
6. EPA 25A or EPA TO-12 values are numerically close and always much less than values measured with SCAQMD 25.3. Detailed carbon analysis of the TO-12 samples does not provide insight into the cause of the greater levels found in the SCAQMD Method, either in the impinger or in the canister.
7. For SCAQMD 25.3, it is possible to have acceptable repeatability at very low (< 10 ppm) hydrocarbon levels, and the changes are improved if 25 of the 30 inches of vacuum in the canister are filled with sample, in order to minimize the error caused by pressurizing the sample. The method shows a fill to 15 inches, but data were clearly more repeatable and precise with the canisters filled to nearer 25 inches.

8. The volume of the impinger with SCAQMD 25.3 needs to be adjusted to accommodate the levels of moisture in the exhaust. As indicated in this report, impinger volumes up to 20 ml are required for fuel cell exhaust with its high moisture levels.

4.1.3 Measurement of Exhaust Flow

The summary of the flow measurements by two independent methods in Table 4-1 shows that the values for exhaust flow agree to within 5 percent of ARB's goal. Some care must be taken when applying the ISO 8178 methods, in that they are based on mass balances, so all added streams must be summed. For example, with the fuel cell, water is added to the system, so both the fuel and water flow must be accounted for in the balance.

Table 4-1: Summary Table of the Comparative Flow Rates

No.	DG Unit	Methods 1–4	ISO8178-1	Diff. (%)
1	Microturbine (65 kW)	57.27 kSCFH	57.41 kSCFH	0.3
2	Turbine (13 MW) + SCR	4.76 mmSCFH	4.63 mmSCFH	1.7
3	Turbine (13 MW) + SCONOx	5.25 mmSCFH	5.01 mmSCFH	4.4
4	Fuel cell, 300 kW	4108 klb/h	4022.5 klb/h	1.8
5	~50 MW turbine + SCR	14.02 mmSCFH	13.90 mmSCFH	2.0

One advisor observed that the project values measured with ISO 8178 for the Solar Turbines and GE turbines were less that those measured by ARB Methods 1–4. He commented that the equipment manufacturers often have felt the flow measured with ARB Methods 1–4 was a bit higher than their values, which they believed were truer. The results might suggest that there are wall effects with ARB Methods 1–4, resulting in a higher overall velocity and a higher exhaust flow rate. Accounting for this apparent bias is an issue needing further investigation.

4.1.4 Measurements of Particulate Matter (PM)

The continuous Scanning Mobility Particle Sizer (SMPS) provided a quick and easy setup measure of the particle size distribution of the source and ambient air. With this technical approach, the results quickly showed that:

1. Pre-filers on the Capstone DG were not effective in removing small particles.
2. Water-based condensation particle counters (CPCs) measure the same as the butanol-based CPC for ambient air but only 1/100 of the particles found in the exhaust as the exhaust particles appear to be too small to be wetted by the water-based system.
3. SMPS data for turbines with SCRs suggest that exhaust air from the combustion process has less mass than the ambient air. For the 50 MW unit, both the number and mass of the exhaust was less than the PM found in ambient air. In general, air is cleaner coming from the gas turbine than going into the turbine.

4. SMPS data for the SCONOx and FuelCell plants show high levels of very small (< 5 nm) particles but low mass amounts.

4.2 Recommendations

Based on the findings in this project; there are several recommendations.

1. Instruments for ARB Method 100 for measuring CO, CO_2, NOx, and THC should be specified to operate between 10 to 90 percent of their range.
2. For measuring the hydrocarbons, U.S. EPA Method 25A should be considered as a replacement for the canister samples methods in the field. This approach would: (1) allow a field determination of whether the exhaust is within compliance values, like currently done for NOx and CO, and (2) provide a more precise method that proved capable of measuring samples as low as 1 ppm.
3. If canister methods (EPA TO-12 and SCAQMD 25.3) are continued, then for exhaust values < 10 ppm, the samples sent to the lab should include a zero-gas sample and a sample with a certification gas near the expected levels in the exhaust.
4. Current exhaust flow methods meet ARB's 5 percent criteria; however, as part of a quality assurance program, some exhaust flow rates should be checked with ISO 8178 method, an independent method based on mass balance.
5. There is a question of ARB Methods 1–4 showing a bias of a slightly (< 5 percent) exhaust flow from turbines that should be investigated.

GLOSSARY

AP-42	U.S. EPA's Compilation of Air Pollutant Emission Factors
AQMD	Air Quality Management District
ARB	California Air Resources Board
BACT	best available control technology
BC	black carbon
Btu	British thermal units
C_2H_6	ethane
CCR	California Code of Regulations
CE-CERT	University of California, Riverside, Bourns College of Engineering—Center for Environmental Research and Technology
CEM	continuous emissions monitor
CH_4	methane
CHP	combined heat and power
CO	carbon monoxide
CO_2	carbon dioxide
COV	coefficient of variation
CPC	Condensation Particle Counter
DG	distributed generation
Dh	hydraulic diameter
DMA	Differential Mobility Analyzer
DNPH	2,4-Dinitrophenylhydrazine
EC/OC	elemental carbon and organic carbon
EI	emission indices
FID	Flame Ionization Detector
F.S.	full scale
GC	Gas chromatography
H_2	hydrogen
HC	hydrocarbon
HCLD	Heated Chemiluminescence Detector
HFID	hydrogen flame ionization detector
Hg	mercury
HHV	higher heating value
HRSG	Heat Recovery Steam Generator
ISO	International Standards Organization

K	kelvin
kg	kilogram
kSCFH	1,000 standard cubic feet per hour
kW	kilowatt
kWh	kilowatt-hour
LHV	lower heating value
MCFC	molten carbonate fuel cell
ml	milliliter
mm	millimeter
MMBtu	1 million Btu
mmSCFH	million standard cubic feet per hour
mol	mole
MST	Manufacturer's Stability Test
MW	megawatt
N_2	nitrogen
NDIR	Non-dispersive Infrared Absorption
NG	natural gas
NH_3	ammonia vapor
NMNEOC	non-methane, non-ethane, organic carbon
NMTHC	Non-methane total hydrocarbons
NOx	Nitrogen oxide
O_2	oxygen
O_3	ozone
PAM	Photochemical Assessment Monitoring Stations
PEMS	portable emissions measurement systems
PIER	Public Interest Energy Research
PM	particulate matter
ppb	parts per billion
ppbv	parts per billion, volume
ppm	parts per million
ppmC	parts per million carbon
ppmv	parts per million, volume
pptv	parts per trillion, volume
PQL	practical quantitation limit
psi	pounds per square inch

PTFE	polytetrafluoroethylene
QAPP	Quality Assurance Project Plan
RATA	Relative Accuracy Test Audits
RPM	revolutions per minute
SAE	Society of Automotive Engineers
SB	Senate Bill
SCAQMD	South Coast Air Quality Management District
SCC	Source Classification Codes
SCONOX	A catalytic reduction technology for natural gas-fired turbines
SCR	selective catalytic reduction
SMEC	Spray Mist Evaporative Cooling
SMPS	Scanning Mobility Particle Sizer
SO_2	sulfur dioxide
SPRINT	SPRay INTercooling
SRL	sample reporting limit
STEDV	standard deviation
TDS	thermal desorption tubes
TGNMO	total gas non-methane organics
THC	total hydrocarbons
TOC	total organic compounds
UCR	University of California, Riverside
UHC	unburned hydrocarbon
U.S. EPA	United States Environmental Protection Agency
VOC	volatile organic compounds

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APPENDIX A:
Literature Review

A literature review was carried out during the project with a focus on similar projects that:
(1) investigated measuring low levels of gaseous emissions from combustion units, and
(2) researched aircraft turbine engines, as many stationary gas turbines and aircraft engines have the same design principles. In fact, for some cases, the same aircraft turbine engine is used as stationary gas turbine.

A.1 Literature Review on Measuring Low Concentrations of Gases

A review of prior literature on the measurement of low concentration levels in exhaust gases lead to reports about the U.S. EPA's development of Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure) using a continuous analyzer. One feature of 7E is the design to provide high-quality data for determining compliance with federal and state emission standards and for the relative accuracy testing of continuous emissions monitors (CEMS). The method uses an instrument with a calibration span of 20 ppm NO_X or lower and includes interference checks that are an issue with low concentrations.

Basically the approach used in this research called for the adaption of instruments capable of measuring much lower concentrations than allowed in the ARB Method 100. Portions of the U.S. EPA's work related to Interference Checks for compounds other than those of interest. The concern is the level of the analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream that is not adequately accounted for in the calibration procedure. Such compounds may cause measurement bias. Another concern was the need for a Section 3.12 Low-Concentration Analyzer. This is any analyzer used to routinely measure low NO_X concentrations, and it must pass a Manufacturer's Stability Test (MST). An MST subjects the analyzer to a range of line voltages and temperatures that reflect potential field.

A.2 Literature Review on Aircraft Turbines and Gas Turbines

Aircraft engine manufacturers have made considerable improvements in the efficiency of aircraft engines, resulting in low levels of CO and Hydrocarbon (HC) emissions. Because the increase in efficiency is a direct result of higher combustion temperatures, newer aircrafts emit higher levels of NO_x. For example, during a two-day campaign at London Heathrow Airport, Popp et al. (1999) made 122 valid measurements from 90 different aircrafts. They realized that 69 of the idling aircraft had emission indices less than 5 grams per kilogram (g/kg) of NO, and the other 35 on the runway in position-high power had emission indices between 5 and 15 g/kg of NO (Popp et al. 1999). In another study, Mazaheri et al. (2009) showed that NO_x emissions was the highest for takeoff and landing (~0.4 ppm) and the lowest during idling (~0.05 ppm), during which the temperature is lowest. The PM mass and number concentrations also had the same behavior.

Studies conducted by Spicer et al. (1992, 1994) provided additional information on the detailed organic composition of turbine engine emissions. During engine idle they found products from fuel cracking, unburned fuel, and products of incomplete combustion, with ethene, propene,

acetylene, and formaldehyde, comprising 30 to 40 percent of the total HC emissions. Furthermore, Slemr et al. (2001) noted that the emission indices (EIs) for these engines are highly power dependent and dominated by alkenes and alkynes related to fuel cracking and aromatic compounds arising from unburned fuel. Emission indices of non-methane hydrocarbons (NMHCs) were measured by Fast Fourier Transform Infrared Spectrometer (FTIR) and continuous fast measurement of carbon monoxide (CO) and carbon dioxide (CO_2) Slemr et al. (2001). The turbines studied were modern commercial high by-pass turbofan (CFM56-2C1) with an older technology engine (Rolls Royce M45H Mk501).

A similar observation can be seen in findings of Anderson et al. (2006). Anderson et al. observed that NMHC emissions are a strong function of engine power, with idle values being drastically higher. At idle up to 70 percent of the NMHC belonged to alkenes; whereas, 61 percent of max rated thrust resulted for over 50 percent of NMHC. They reported negative methane (CH_4) and dimethyl sulfides (DMS) emission, suggesting that they were actually burned out of background air as it passed through the engine. To understand the role of volatile organic carbons (VOCs), Kinghton et al. (2007) deployed a proton mass spectrometer (PTR-MS) and measured concentration of select volatile organic compounds. They found out that the emission characteristic and emission indices are highly variable, upward to a factor of 10 for the same nominal engine power.

Agrawal et al. (2008) in an in-flight on-wing experiment investigated the effect of aircraft engine load on turbine exhaust emissions, including particulate matter, elemental and organic carbon, carbonyls, polycyclic aromatic hydrocarbons (PAHs), alkanes, dioxins, and others. Their study also showed the dependency of emissions on power. Hydrocarbon emissions were most significant at idling conditions; whereas, PM emissions are significant at higher power levels associated with takeoff and landing. Particulate matter emission indices were found to increase from 1.1×10^{-2} to 2.05×10^{-1} g/kg fuel with increase in power from idle to 85 percent. The carbonyl emissions were dominated by formaldehyde.

Petzold et al. (2011) conducted a study to evaluate methods for measuring particle properties in the exhaust of aircraft engines. They applied both filter-based offline methods (gravimetric/chemical speciation of elemental carbon and organic carbon (EC/OC), and online methods (size distribution/particle count/optical measurements). They reported up to 70 percent of PM mass was made of carbonaceous matter while the remaining 30 percent were attributed to hydrated sulfate. Elemental and black carbon were correlated with 5 percent deviation with respect to mass for low-medium load. Their particles showed bimodal size distributions peaking at 10–30 nm and 70–130 nm depending on the organic content and number of particles. In another study, Petzold et al. (1999) measured black carbon (BC) during ground and in-flight tests. The total BC concentration was 2.9×10^{7} cubic centimeters (cm^3) and size distribution was primary BC mode at 45 nm. The emission indices of BC come to 0.11 to 0.15 g BC (kg fuel)$^{-1}$ (Petzold et al. 1999). The data contains various engine thrust settings.

A.3 Emissions from Stationary Gas Turbines and EPA AP-42 Values

The U.S. EPA lists six criteria air pollutants for which ambient air limits have been set. These air pollutants are nitrogen dioxide (NO_2), CO, sulfur dioxide (SO_2), lead (Pb), ozone (O_3),and

particulate matter (PM). The most important characteristic of simple cycle gas turbine combustor is the amount of nitrogen oxide emitted in the exhaust gas. Pollutants such as sulfur oxides (SO_x) and PM are primarily dependent on the fuel used. For example, the sulfur content of the fuel determines emissions of sulfur compounds, primarily SO_2. However, pollutants such as CO, total hydrocarbons (THC), soot, NO_x, and SO_2 are formed during combustion process as result of various combustion reactions.

A.3.1 Nitrogen Oxide (NOx) Formation in Gas Turbines

Nitrogen oxide (NO_x) emissions are the primary pollutant generated by gas turbines (Sloss et al. 1992; Hung and Campbell 1998; Mee 1999). NO_x is a mixture of mostly nitric oxide (NO) and NO_2 in variable compositions (Mee 1999). While gas turbines are described as NO_x emitters, most of the NO_x is emitted in form of NO (Romaine 2001), which subsequently oxidizes in the atmosphere to produce NO_2. Nitric oxide is a toxic gas that makes up about 90 to 95 percent of the NO emissions from fossil-fuel combustion. The average lifetime of NO in the atmosphere is short. Within minutes, or even seconds, it is rapidly oxidized to form NO_2 (Mee 1999). Nitrogen dioxide significantly affects human well-being. Moreover, in a complex chemical reaction with other pollutants and sunlight, NO_x contributes to the formation of ground level ozone that causes smog and respiratory problems. According to Mee (1999), three mechanisms produce NO_x during the combustion of fossil fuels: thermal NO_x, prompt NO_x, and fuel-bound NO_x.

Thermal NO_x is the predominant NO_x formation mechanism associated with gas turbines. Nitrogen oxide is formed from thermal dissociation and subsequent oxidation of atmospheric nitrogen, which occurs at high combustion temperatures. The rate of thermal NO_x formation increases rapidly with flame temperature. The formation of thermal NOx is highly dependent on the flame temperature, the air-to-fuel ratio, and the residence time at the flame temperature. These factors are affected by the combustor design and percentage load. The higher the load, the higher the temperature will be. The maximum NO_x production occurs when excess oxygen is present within the hot flame zone, which occurs at slightly lean fuel mixture ratios. The rate of NO_x production is exponentially related to the combustion temperature (Zachary 2001; Ely 2003). Thermal NO_x production starts at temperatures above about 2370°F (1300°C) and increases markedly with rising temperature (Figure A.1) (Mee 1999).

Prompt NO_x forms within flame and is usually negligible when compared to the amount of thermal NO_x formed. It is only significant in very fuel-rich flames and is produced by high-speed reactions at the flame front. It is formed from early reactions of nitrogen molecules in combustion air and hydrogen radicals from the fuel. Since natural gas and distillate oil have no chemically bound nitrogen, prompt NO_x formation is not a significant source of gas turbine emissions (Mee 1999).

Fuel-bound NO_x forms when the fuel contains nitrogen as part of the hydrocarbon structure. It is caused by the evolution and reaction of fuel-bound nitrogen compounds with oxygen in the combustion air. Since natural gas and distillate oils have negligible chemically bound fuel nitrogen, fuel-bound NO is an insignificant source of gas turbine NO_x emissions (Mee 1999). Table A-2 and A-4 show NO_x emission factors from different type of turbines (see EPA AP-42).

A.3.2 Carbon Monoxide (CO) Formation in Gas Turbines

Carbon monoxide emitted from gas turbines is formed because of incomplete combustion of carbon-based fuel. Carbon monoxide is poisonous gas and a criterion pollutant. Its emissions are dependent on residence time in the chamber and loading of the gas turbine. The shorter the residence time, the more the CO emissions are produced. A gas turbine working under a light to medium load will experience reduced fuel efficiencies (incomplete combustion), which will increase CO formation (Romaine 2001). The following figure shows the range of temperatures over which both low NOx and low CO can be achieved, ranging from 1700 K to a little over 1900 K (Figure A-1). Table A-2 contains emission factors from different type of fuels, extracted from the U.S. EPA's AP-42.

Figure A-1. NOx and CO vs. combustion temperature (K)

Source: Rokke et al. (2003)

A.3.3 Sulfur Dioxide (SO_2) Formation in Gas Turbines

Sulfur dioxide is formed from burning sulfur compounds contained in fuel. Emissions of these pollutants depend on fuel type, and are generally considered negligible for natural gas. Emissions are greater when oil is fired, due to the higher ash and sulfur content of oil, but they are relatively lower with distillate oil. In general, PM and SO_2 emissions are dependent on the selection of fuel. Sulfur oxide control is thus a fuel-purchasing issue rather than a gas turbine technology issue (Romaine 2001). Tables A-2 and A-4 include emission factors regarding different type of turbines running on landfill and digester gas extracted from the U.S. EPA's AP-42.

A.3.4 Greenhouse Gas Formation in Gas Turbines

Greenhouse gases include CO_2, CH_4, and nitrous oxide (N_2O). Carbon dioxide emissions are produced during natural gas and distillate oil combustion in gas turbines. Nearly all the fuel carbon is converted to CO_2 during the combustion process. This conversion is relatively independent of firing configuration. Emissions of CO_2 are of concern due to its contribution to global warming. Methane (CH_4) is also present in the exhaust gas and is the unburned fuel (in the case of natural gas) or a product of combustion (in the case of distillate fuel oil). Another oxide of nitrogen (N_2O), which is also formed during the combustion, has become important in recent

years, due to its role in the stratosphere as a greenhouse gas. The formation mechanism of N_2O is not very temperature sensitive (Rokke et al. 2003). (See Table A-3 for greenhouse gases from EPA AP-42). The U.S. EPA has also published a list of criteria pollutants and hazardous pollutants for natural gas-fired stationary turbines. These components are all listed in Tables A-3 and A-5 respectively, and come from the U.S. EPA's AP-42.

A.3.5 Ambient Conditions

Ambient conditions affect the air charge entering the gas turbine. As the ambient temperature decreases or the relative humidity increases, the peak combustion temperature decreases, and thus NO_x emissions decrease. Holden and Huntley (1998) summarized the effect of humidity on emissions, as shown in Table A-1. They attributed the effect of humidity to two main mechanisms: First, increased humidity levels result in higher air total heat capacity and lower chamber temperature. Second, a richening of the air-fuel ratio occurs as water vapor displaces oxygen in the air stream.

Table A-1. Effect of humidity on emissions

Combustion characteristic	*General effect of increased humidity*	*Variability of characteristic based on humidity levels (%)*
Fuel consumption	Increases	1.5–1.9
NO, (g/BHP-hr)	Decreases	18–25
THC (g/BHP-hr)	Increases	0–12
CO (g/BHP-hr)	Falls then rises	6–14
CH_2O (g/BHP-hr)	Increases	11–18

Source: Holden and Huntley (1998)

Table A-2. Emission factors for nitrogen oxides (NOx) and carbon monoxide (CO) from stationary gas turbines - AP-42

Emission Factors[a]				
Turbine Type	Nitrogen Oxides		Carbon Monoxide	
Natural Gas-Fired Turbines[b]	(lb/MMBtu)[c] (Fuel Input)	Emission Factor Rating	(lb/MMBtu)[c] (Fuel Input)	Emission Factor Rating
Uncontrolled	3.2 E-01	A	8.2 E-02[d]	A
Water-Steam Injection	1.3 E-01	A	3.0 E-02	A
Lean-Premix	9.9 E-02	D	1.5 E-02	D
Distillate Oil-Fired Turbines[e]	(lb/MMBtu)[f] (Fuel Input)	Emission Factor Rating	(lb/MMBtu)[f] (Fuel Input)	Emission Factor Rating
Uncontrolled	8.8 E-01	C	3.3 E-03	C
Water-Steam Injection	2.4 E-01	B	7.6 E-02	C
Landfill Gas-Fired Turbines[g]	(lb/MMBtu)[h] (Fuel Input)	Emission Factor Rating	(lb/MMBtu)[h] (Fuel Input)	Emission Factor Rating
Uncontrolled	1.4 E-01	A	4.4 E-01	A
Digester Gas-Fired Turbines[j]	(lb/MMBtu)[k] (Fuel Input)	Emission Factor Rating	(lb/MMBtu)[k] (Fuel Input)	Emission Factor Rating
Uncontrolled	1.6 E-01	D	1.7 E-02	D

Source: AP-42, Vol. 1, Ch. 3.1.

[a] Factors are derived from units operating at high loads (80 percent load) only. For information on units operating at other loads, consult the background report for this chapter (Popp et al. 1999), available at www.epa.gov/ttn/chief.

[b] Source Classification Codes (SCCs) for natural gas-fired turbines include 2-01-002-01, 2-02-002-01, 2-02-002-03, 2-03-002-02, and 2-03-002-03. The emission factors in this table may be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value.

[c] Emission factors based on an average natural gas heating value (HHV) of 1,020 Btu/scf at 60°F (16°C). To convert from lb/MMBtu to lb/10^6 scf, multiply by 1,020.

[d] It is recognized that the uncontrolled emission factor for CO is higher than the water-steam injection and lean-premix emission factors, which is contrary to expectation. The U.S. EPA could not identify the reason for this behavior, except that the data sets used for developing these factors are different.

[e] SCCs for distillate oil-fired turbines include 2-01-001-01, 2-02-001-01, 2-02-001-03, and 2-03-001-02.

[f] Emission factors based on an average distillate oil heating value of 139 MMBtu/10^3 gallons. To convert from lb/MMBtu to lb/10^3 gallons, multiply by 139.

[g] SCC for landfill gas-fired turbines is 2-03-008-01.

[h] Emission factors based on an average landfill gas heating value of 400 Btu/scf at 60°F (16°C). To convert from lb/MMBtu, to lb/10^6 scf, multiply by 400.

[j] SCC for digester gas-fired turbine is 2-03-007-01.

[k] Emission factors based on an average digester gas heating value of 600 Btu/scf at 60°F (16°C). To convert from lb/MMBtu to lb/10^6 scf, multiply by 600.

Table A-3. Emission factors for criteria pollutants and greenhouse gases from stationary gas turbines - AP-42

Emission Factors[a] - Uncontrolled				
Pollutant	Natural Gas-Fired Turbines[b]		Distillate Oil-Fired Turbines[d]	
	(lb/MMBtu)[c] (Fuel Input)	Emission Factor Rating	(lb/MMBtu)[e] (Fuel Input)	Emission Factor Rating
CO_2[f]	110	A	157	A
N_2O	0.003[g]	E	ND	NA
Lead	ND	NA	1.4 E-05	C
SO_2	0.94S[h]	B	1.01S[h]	B
Methane	8.6 E-03	C	ND	NA
VOC	2.1 E-03	D	4.1 E-04[j]	E
TOC[k]	1.1 E-02	B	4.0 E-03[l]	C
PM (condensible)	4.7 E-03[l]	C	7.2 E-03[l]	C
PM (filterable)	1.9 E-03[l]	C	4.3 E-03[l]	C
PM (total)	6.6 E-03[l]	C	1.2 E-02[l]	C

Source: AP-42, Vol. 1, Ch. 3.1.

[a] Factors are derived from units operating at high loads (80 percent load) only. For information on units operating at other loads, consult the background report for this chapter (Popp et al. 1999), available at www.epa.gov/ttn/chief. ND = No Data, NA = Not Applicable.

[b] SCCs for natural gas-fired turbines include 2-01-002-01, 2-02-002-01 & 03, and 2-03-002-02 & 03.

[c] Emission factors based on an average natural gas heating value (HHV) of 1,020 Btu/scf at 60°F (16°C). To convert from lb/MMBtu to lb/10^6 scf, multiply by 1,020. Similarly, these emission factors can be converted to other natural gas heating values.

[d] SCCs for distillate oil-fired turbines are 2-01-001-01, 2-02-001-01, 2-02-001-03, and 2-03-001-02.

[e] Emission factors based on an average distillate oil heating value of 139 MMBtu/10^3 gallons. To convert from lb/MMBtu to lb/10^3 gallons, multiply by 139.

[f] Based on 99.5 percent conversion of fuel carbon to CO_2 for natural gas and 99 percent conversion of fuel carbon to CO_2 for distillate oil. CO_2 (Natural Gas) [lb/MMBtu] = (0.0036 scf/Btu)(%CON)(C)(D), where %CON = weight percent conversion of fuel carbon to CO_2, C = carbon content of fuel by weight, and D = density of fuel. For natural gas, C is assumed at 75 percent, and D is assumed at 4.1 E+04 lb/10^6scf. For distillate oil, CO_2 (Distillate Oil) [lb/MMBtu] = (26.4 gal/MMBtu) (%CON)(C)(D), where C is assumed at 87 percent, and the D is assumed at 6.9 lb/gallon.

[g] Emission factor is carried over from the previous revision to AP-42 (Supplement B, October 1996) and is based on limited source tests on a single turbine with water-steam injection (Mee 1999).

[h] All sulfur in the fuel is assumed to be converted to SO_2. S = percent sulfur in fuel. Example, if sulfur content in the fuel is 3.4 percent, then S = 3.4. If S is not available, use 3.4 E-03 lb/MMBtu for natural gas turbines, and 3.3 E-02 lb/MMBtu for distillate oil turbines (the equations are more accurate).

[j] VOC emissions are assumed equal to the sum of organic emissions.

[k] Pollutant referenced as THC in the gathered emission tests. It is assumed as TOC, because it is based on EPA Test Method 25A.

[l] Emission factors are based on combustion turbines using water-steam injection.

Table A-4. Emission factors for criteria pollutants and greenhouse gases from stationary turbines - AP-42

Emission Factors[a] - Uncontrolled				
Pollutants	Landfill Gas-Fired Turbines[b]		Digester Gas-Fired Turbines[d]	
	(lb/MMBtu)[c]	Emission Factor Rating	(lb/MMBtu)[e]	Emission Factor Rating
CO_2[f]	50	D	27	C
Lead	ND	NA	< 3.4 E-06[g]	D
PM-10	2.3 E-02	B	1.2 E-02	C
SO_2	4.5 E-02	C	6.5 E-03	D
VOC[h]	1.3 E-02	B	5.8 E-03	D

Source: AP-42, Vol. 1, Ch. 3.1.

[a] Factors are derived from units operating at high loads (80 percent load) only. For information on units operating at other loads, consult the background report for this chapter (Popp et al. 1999), available at www.epa.gov/ttn/chief. ND = No Data, NA = Not Applicable.

[b] SCC for landfill gas-fired turbines is 2-03-008-01.

[c] Emission factors based on an average landfill gas heating value (HHV) of 400 Btu/scf at 60°F (16°C). To convert from lb/MMBtu to lb/10^6 scf, multiply by 400.

[d] SCC for digester gas-fired turbine include 2-03-007-01.

[e] Emission factors based on an average digester gas heating value of 600 Btu/scf at 60°F (16°C). To convert from lb/MMBtu to lb/10^6 scf, multiply by 600.

[f] For landfill gas and digester gas, CO_2 is presented in test data as volume percent of the exhaust stream (4.0 percent to 4.5 percent).

[g] Compound was not detected. The presented emission value is based on one-half of the detection limit.

[h] Based on adding the formaldehyde emissions to the NMHC.

Table A-5. Emission factors for hazardous air pollutants from natural gas-fired stationary gas turbines - AP-42[a]

Emission Factors[b] - Uncontrolled		
Pollutant	Emission Factor (lb/MMBtu)[c]	Emission Factor Rating
1,3-Butadiene[d]	< 4.3 E-07	D
Acetaldehyde	4.0 E-05	C
Acrolein	6.4 E-06	C
Benzene[e]	1.2 E-05	A
Ethylbenzene	3.2 E-05	C
Formaldehyde[f]	7.1 E-04	A
Naphthalene	1.3 E-06	C
PAH	2.2 E-06	C
Propylene Oxide[d]	< 2.9 E-05	D
Toluene	1.3 E-04	C
Xylenes	6.4 E-05	C

Source: AP-42, Vol. 1, Ch. 3.1.

[a] SCC for natural gas-fired turbines include 2-01-002-01, 2-02-002-01, 2-02-002-03, 2-03-002-02, and 2-03-002-03. Hazardous Air Pollutants as defined in Section 112 (b) of the *Clean Air Act*.

[b] Factors are derived from units operating at high loads (80 percent load) only. For information on units operating at other loads, consult the background report for this chapter (Popp et al. 1999), available at www.epa.gov/ttn/chief.

[c] Emission factors based on an average natural gas heating value (HHV) of 1020 Btu/scf at 60°F (16°C). To convert from lb/MMBtu to lb/10^6 scf, multiply by 1,020. These emission factors can be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this heating value.

[d] Compound was not detected. The presented emission value is based on one-half of the detection limit.

[e] Benzene with SCONOX catalyst is 9.1 E-07, rating of D.

[f] Formaldehyde with SCONOX catalyst is 2.0 E-05, rating of D.

Table A-6. Emission factors for hazardous air pollutants from distillate oil-fired stationary gas turbine AP-42[a]

Emission Factors[b] - Uncontrolled		
Pollutant	Emission Factor (lb/MMBtu)[c]	Emission Factor Rating
1,3-Butadiene[d]	< 1.6 E-05	D
Benzene	5.5 E-05	C
Formaldehyde	2.8 E-04	B
Naphthalene	3.5 E-05	C
PAH	4.0 E-05	C

Source: AP-42, Vol. 1, Ch. 3.1.

[a] SCCs for distillate oil-fired turbines include 2-01-001-01, 2-02-001-01, 2-02-001-03, and 2-03-001-02. Hazardous Air Pollutants as defined in Section 112 (b) of the *Clean Air Act*.

[b] Factors are derived from units operating at high loads (80 percent load) only. For information on units operating at other loads, consult the background report for this chapter (Popp et al. 1999), available at www.epa.gov/ttn/chief.

[c] Emission factors based on an average distillate oil heating value (HHV) of 139 MMBtu/10^3 gallons. To convert from lb/MMBtu to lb/10^3 gallons, multiply by 139.

[d] Compound was not detected. The presented emission value is based on one-half of the detection limit.

Table A-7. Emission factors for hazardous air pollutants from landfill gas-fired stationary gas turbines - AP-42[a]

Emission Factors[b] - Uncontrolled		
Pollutant	Emission Factor (lb/MMBtu)[c]	Emission Factor Rating
Acetonitrile[d]	< 1.2E-05	D
Benzene	2.1E-05	B
Benzyl Chloride[d]	< 1.2 E-05	D
Carbon Tetrachloride[d]	< 1.8 E-06	D
Chlorobenzene[d]	< 2.9 E-06	D
Chloroform[d]	< 1.4 E-06	D
Methylene Chloride	2.3 E-06	D
Tetrachloroethylene[d]	< 2.5 E-06	D
Toluene	1.1 E-04	B
Trichloroethylene[d]	< 1.9 E-06	D
Vinyl Chloride[d]	< 1.6 E-06	D
Xylenes	3.1 E-05	B

Source: AP-42, Vol. 1, Ch. 3.1.

[a] SCC for landfill gas-fired turbines is 2-03-008-01. Hazardous Air Pollutants as defined in Section 112 (b) of the *Clean Air Act*.

[b] Factors are derived from units operating at high loads (80 percent load) only. For information on units operating at other loads, consult the background report for this chapter (Popp et al. 1999), available at www.epa.gov/ttn/chief.

[c] Emission factors based on an average landfill gas heating value (HHV) of 400 Btu/scf at 60°F (16°C). To convert from lb/MMBtu to lb/10^6 scf, multiply by 400.

[d] Compound was not detected. The presented emission value is based on one-half of the detection limit.

Table A-8. Emission factors for hazardous air pollutants from digester gas-fired stationary gas turbines - AP-42[a]

Emission Factors[b] - Uncontrolled		
Pollutant	Emission Factor (lb/MMBtu)[c]	Emission Factor Ratings
1,3-Butadiene[d]	< 9.8 E-06	D
1,4-Dichlorobenzene[d]	< 2.0 E-05	D
Acetaldehyde	5.3 E-05	D
Carbon Tetrachloride[d]	< 2.0 E-05	D
Chlorobenzene[d]	< 1.6 E-05	D
Chloroform[d]	< 1.7 E-05	D
Ethylene Dichloride[d]	< 1.5 E-05	D
Formaldehyde	1.9 E-04	D
Methylene Chloride[d]	< 1.3 E-05	D
Tetrachloroethylene[d]	< 2.1 E-05	D
Trichloroethylene[d]	< 1.8 E-05	D
Vinyl Chloride[d]	< 3.6 E-05	D
Vinylidene Chloride[d]	< 1.5 E-05	D

Source: AP-42, Vol. 1, Ch. 3.1.

[a] SCC for digester gas-fired turbines is 2-03-007-01. Hazardous Air Pollutants as defined in Section 112 (b) of the *Clean Air Act*.

[b] Factors are derived from units operating at high loads (80 percent load) only. For information on units operating at other loads, consult the background report for this chapter (Popp et al. 1999), available at www.epa.gov/ttn/chief.

[c] Emission factors based on an average digester gas heating value (HHV) of 600 Btu/scf at 60°F (16°C). To convert from (lb/MMBtu) to (lb/10^6 scf), multiply by 600.

[d] Compound was not detected. The presented emission value is based on one-half of the detection limit.

A.4 British ISO 11042 Standards for Aircraft Emissions

In addition to reviewing the U.S. EPA's AP-42 tables of emission factors for turbines, we reviewed the standard protocols for measuring emissions from turbines. As the new SAE protocol for turbines is being revised, information was extracted from British ISO 11042- Measuring emissions. This part of ISO 11042 establishes the monitoring program and the requirements for the selection and operation of hardware to be used for continuous measurement over an extended, not limited, time. The concentration and absolute magnitude of specified emissions in the exhaust gas are monitored, as well as related gaseous components from gas turbines, together with essential operating conditions. Appropriate terms and symbols in addition to those defined in ISO 11042-1 are used. It presents requirements for the monitoring environment, the instrumentation and recording as well as for quality assessment and correction of data. As stated by ISO 11042, this standard is applicable for all gas turbines producing mechanical shaft power and/or which are used as drivers for electrical generation. Also this standard is applicable for gas turbines that use the open cycle process, semi-closed cycle, and for gas turbines equipped with free piston compressors or with special heat sources.

A.4.1 Emissions

Measurable emissions using British ISO11042 standard comprises the following:

Nitrogen oxides NO_x; sum of NO and NO_2, expressed as NO_2

Nitrogen dioxide NO_2 **Carbon monoxide** CO **Carbon dioxide** CO_2

Sulfur oxides SO_x; sum of SO_2 and

SO_3, expressed as SO_2

Unburned or partially burned hydrocarbon products UHCs; sum of all individual products, expressed as CH_4

Volatile organic compounds

VOCs; UHCs excluding CH_4 and C_2H_6 but expressed as CH_4

Ammonia NH_3

Solid particles all solid particles produced by the combustion process

A.5 Conditions

A5.1 Gas Turbine and Fuel

In connection with gas turbine emissions, the following shall be indicated for the respective measurement conditions:

Manufacturer of the gas turbine

Type of gas turbine

Power output and exhaust gas mass flow and/or fuel flow at the conditions at which the emission measurements are taken

Ambient conditions, i.e., pressure, temperature and humidity of the surrounding air

Fuel details

Equipment in operation that affects the emissions and which is part of the complete system (e.g., catalytic converters, water or steam injection, evaporative coolers, condensers). Relevant details of all flow rates shall be noted.

A.5.2 Measured Values

The following values shall be measured:

Volumetric concentration of gaseous constituents related to wet exhaust gas (wet) or to dry exhaust gas (dry)

Exhaust gas emission value for smoke—Bacharach number (ES) (smoke number according to ISO 5063)

Gravimetric concentration of solid particles within the wet exhaust gas (EP), if specifically agreed upon

A.5.3 Standard Conditions

Standard conditions shall be:

Pressure: 101,3 kilopascals (kPa)

Temperature: 15°C (59°F)

Relative humidity: 60 percent

A.6 Guidelines for the Arrangement of the Measurement System

A.6.1 General

Three parts shall be considered:

Sampling probe

Transfer and conditioning system

Analytical instruments and the data acquisition system

The measurements shall be performed by continuous flow sampling and be representative of the gas flow. In the case of a gas turbine installation, the sampling point shall be determined beforehand, in one of three ways:

By modeling, i.e., simulation of the gas veins (dependent on the obstacles and on the gas flow rate - turbulent laminar flow)

By determination of the mean velocity within the sleeve which becomes the point representative of the gas sample

By mutual agreement based on an existing standard or on experience

In cases where the gas turbine plant is not provided with any system other than a silencer, a ducting system, and a chimney between the engine exhaust and discharge to atmosphere, the sampling site should be selected as close as practical to engine exhaust. In cases where any of the following systems are provided, such as a heat recovery system, subsequent firing systems, dilution systems, de-NO_x systems, etc., the sampling site shall be determined by mutual agreement between the parties involved.

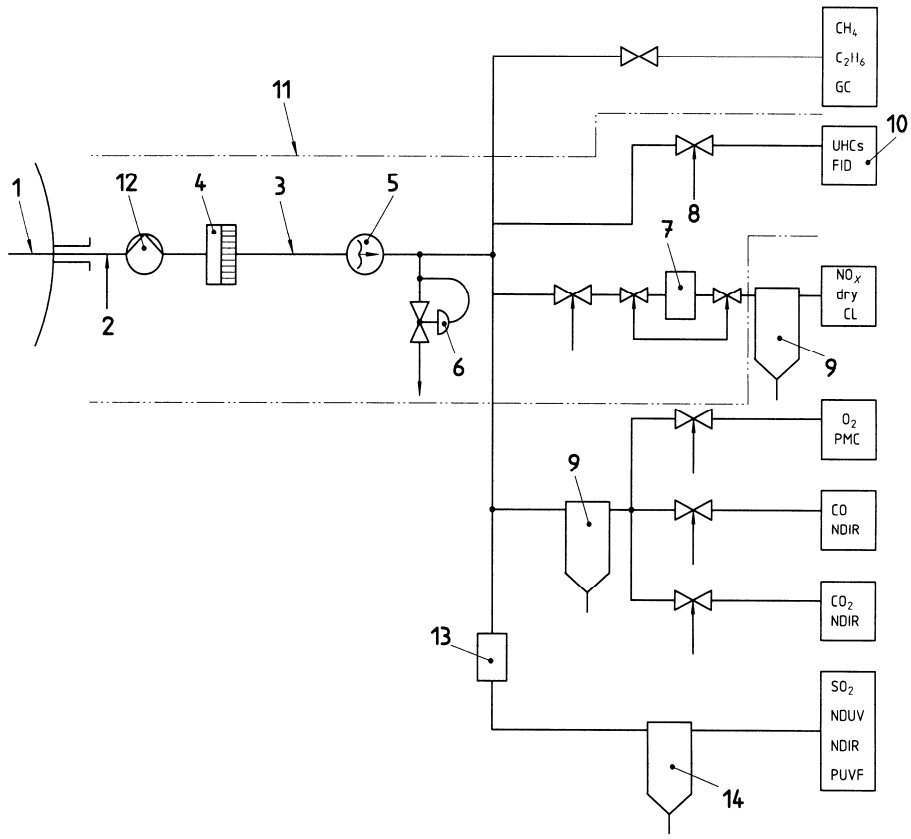
A.6.2 Sampling Probe

The sampling probe should provide a representative sample of the exhaust gas. The use of a multi-hole averaging probe with holes covering equal areas of the cross section of the exhaust duct is recommended for obtaining such a representative sample. A demonstration should be made to ensure that the probe actually measures a sample representative of the main gas flow. This should be done regardless of the type of sampling probe used. The sampling probe and vacuum pump to be used for the test shall be capable of continuously supplying a sufficient volume of sample gas to the analyzers. If traverse measurements are required to demonstrate representativeness, then the probe shall be adequate to allow full assessment of the exhaust channel. The probe shall be long enough to allow full traverse of the exhaust channel. Procedures to establish probe positions shall be agreed upon between parties involved.

A.6.3 Transfer and Conditioning System

The sample transfer lines for samples for measurement of smoke, solid particles, and gaseous constituents shall be separate. A principal system containing the important components is shown in Figure A-2. When special analytical equipment is used, this arrangement may need modification.

Figure A-2. Measurement System Design for Gaseous Constituents



Key

1 Probe
2 Gas inlet for system check
3 Sample line
4 Filter
5 Sample pump
6 Back-pressure regulator
7 $NO_2 \rightarrow NO$ converter
8 Gas inlet for instrument calibration
9 Chiller/separator (operating at ≤ 3 °C)
10 Analyser
11 Heated section
12 Dump pump to vent (if required)
13 $SO_x \rightarrow SO_2$ converter
14 Water trap or permeation tube dryer

Depending on the operating principle of the analyzer, the sample shall be conditioned accordingly. To avoid condensation of the sample constituents, the entire sample line shall be heated up to temperatures at least 10 K above the condensation temperature of the exhaust gas. When the sample is processed through a water separator, the sample line shall be heated to at least as far as this device. For natural gas or light hydrocarbon fuels with a sulfur content of less than 1 percent mass per total mass, a minimum temperature of 150°C (423 K) shall be applied. For this reason, it is recommended that all the equipment, including the pump(s), be heated. The temperature level shall always be kept constant within ± 5 K. For all items in the sampling line, the following points apply:

All material in contact with the sample shall be made of non-reactive material (stainless steel or equivalent).

It is recommended as being consistent with good practice to purge PTFE (polytetrafluoroethylene) by means of a continuous flow of pure nitrogen, to remove residual solvents from the manufacturing process. During this procedure, the line shall be heated to the temperature specified for the analysis of the particular component.

All connections and items shall be free of leaks.

All components shall be designed to operate up to required temperatures.

Where long lines are unavoidable, it is recommended to insert a second dump pump, which provides sample gas in larger quantities. The sample transfer time between probe and instruments should be as short as possible, preferably less than 30seconds.

A.6.4 Analytical Instruments

The instruments used shall be complete with all necessary control components of flow rate, such as regulators, valves, flow meters, etc. Material in contact with the sample shall be corrosion resistant, i.e., stainless steel or carbon-loaded PTFE. The overall temperature of the sample shall be maintained at a value consistent with local pressures and which avoids condensation of water and hydrocarbons.

A.7 Performing the Test, Test Report, and Evaluation

The test shall be performed after the gas turbine has reached steady operating conditions, as specified in ISO 2314. Variation of ambient humidity expressed as water mass content in dry air should not exceed ± 0.5 g/kg during testing. If ambient conditions vary and exceed the above limitations, corrections may be applied if agreed upon between the parties involved.

The analyzers shall be calibrated before and after the test. The whole system shall be checked before testing and at regular intervals. Special checks on the tightness of the assembly shall be performed. All the equipment to be used shall have had the necessary performance checks carried out within the time specified in the manufacturer's specified measurement test procedures. Multiple measurements (a minimum of three) shall be taken only when the analytical equipment is providing stable readings, and at the same time the readings of gas turbine performance shall be taken. Instruments subject to calibration drift problems due to temperature variations shall be housed in a stable thermal environment.

The arithmetic average value of measurements of three individual test runs constitutes a complete test. The minimum sampling time for each measurement shall be at least one minute plus the average system response time.

A.8 Location of Sampling Probe and Arrangement of Sampling System

The solid particle sample train shall be installed separate from the sample train for the gaseous constituents. The sample train is built with the main separator inside (Figure A-3) or outside (Figure A-4) the gas/air duct. As stainless steel may not be suitable under certain conditions, the

following parts of the sample train shall be made of corrosion- and temperature-resistant material such as glass: the sampling probe, the bend, the transport tube, and the separator casing. The main separator consists of a filter. A pre-separator, e.g., a cyclone, is required only with very high particle loads that would otherwise overload the filter in less than the sampling time. The filter medium shall withstand the sample temperature under consideration, shall be chemically stable, and shall be fine enough for "total" filtration.

In addition, the sampling stations shall be located at least 8 × Dh (Dh = hydraulic diameter) downstream and 2 × Dh upstream of any type of consecutive flow disturbance (bend, expansion, contraction, etc.). If these conditions cannot be achieved in practice, then the distances shall be 2 × Dh and 1 × Dh, respectively. In this case, the number of sampling stations shall be increased.

The bend and the transport tube shall be designed and operated in such a way as to minimize transport losses due to Brownian diffusion, gravitational settling, inertial deposition, electrostatic collection, and/or thermophoretic effects. It is consistent with good practice to make the tubes as short as possible, to arrange them vertically (and if possible, without bends), to use grounded metallic tubes, and to avoid temperature gradients. The tube diameter shall not be smaller than 5 mm. An example of an appropriate arrangement of probe, bend, tube and separator for the main-separator-inside-duct technique is given in Figure A-5.

A.9 Methods for Calibration

Instrument calibration shall be carried out by comparison with a calibration gas. The calibration gas shall have a certificate of mixture preparation according to ISO 6141. It is consistent with good practice to provide calibration gas mixtures with the relevant constituent in nitrogen at concentration levels of approximately 60 percent and 90 percent of the full scale of the metering ranges of the analyzer. The manufacturer of the calibration gases has to make sure that these gases are provided with the accuracies listed in Table A-9. Carbon monoxide and CO_2 calibration gases may be blended singly or used as dual-component mixtures. Three-component mixtures of CO, CO_2, and propane in zero air may be used, provided the stability of the mixture is assured. Zero gas, as specified for the HC analyzer, shall be zero air, which includes "artificial" air with 20 to 22 percent O_2 blended with N_2. For the remainder of the analyzers, pure nitrogen shall be used as the zero gas. Impurities in both kinds of zero gas shall be restricted to be less than the following concentrations:

C 1 ppm

CO 1 ppm

CO_2 100 ppm

NO_x 1 ppm

SO_2 1 ppm

A.10 Conversion between Wet and Dry Exhaust Gas

The measurements are considered "dry" when the water content of the gas sample has been condensed out; otherwise, they are considered "wet." The water content is the difference between the "wet" and the "dry," and is obtained by calculation or measurement to be agreed upon by the interested parties. Humidity of the air in the compressor inlet, water content in the fuel, water formed by combustion of the fuel, as well as water or steam injection shall be considered. The conversion is carried out by using the following equation:

$$\varphi_{i,\mathrm{dry}} = \varphi_{i,\mathrm{wet}} \cdot \frac{1}{1-\varphi_{H_2O}}$$

A.11 Conversion to the Particular Exhaust Gas Oxygen Level

To relate measurements to a standardized exhaust gas, the following correction can be applied to give reference to a particular exhaust gas oxygen level. The emission value as the volumetric concentration of the component related to oxygen volumetric concentration of e.g., 15 percent in dry exhaust gas is given by:

$$EV_{i,15,\mathrm{dry}} = \frac{20{,}95-15}{20{,}95-\varphi_{O_2,\mathrm{dry}}} \cdot \varphi_{i,\mathrm{dry}}$$

whereby the oxygen content of the dry ambient air is in accordance with ISO 2533. Theoretically, this correction can be applied to other oxygen levels and for "wet" and "dry" gases.

A.12 Conversion to the Constituent Mass Flow Related to the Dry Exhaust Gas Volume Flow at Normal Conditions and to a Specific Oxygen Content

The emission value of exhaust gas a constituent concentration related to the dry exhaust gas at normal condition and with oxygen content of, for example, 15 percent, is given by:

$$EM_{i,15,\mathrm{dry}} = EV_{i,15,\mathrm{dry}} \cdot \frac{M_i}{V_{\mathrm{mn}}} = EV_{i,15,\mathrm{dry}} \cdot \rho_{\mathrm{n}}$$

The above emission values have the unit mg/m^3, if the molar mass is in kg/kmol and the concentration in cubic centimeters per cubic meter (cm^3/m^3). In the case of NO_x, the unit is mg NO_2/m^3; in the case of SO_x, the unit is mg SO_2/m^3, and in the case of unburned hydrocarbon (UHC), the unit is mg CH^4/m^3.

A.13 Conversion to Power Output-Related Values

The power output related emission values are defined by the following equation:

$$EM_{i,P} = \frac{q_i}{\ }$$

The emissions can be calculated by this equation:

$$\frac{q_{m_i}}{P} = \varphi_{i,\mathrm{wet}} \cdot \frac{M_i}{M_{\mathrm{tot}}} \cdot \frac{q_{m_{gf}}}{P}$$

This yields the power output-related values in grams per kilowatt-hour.

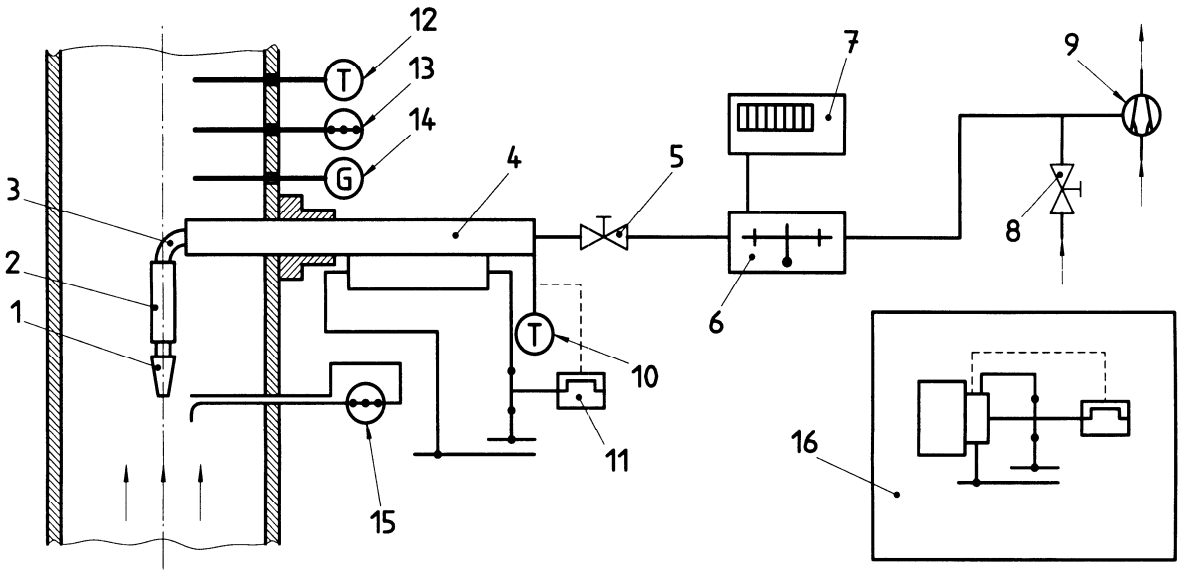
Table A-9. Concentration accuracies for calibration gases

Analyser	Gas	Accuracy[a]
HC	Propane in (10 ± 1) % O_2; balance, N_2	± 2% or ± 0,05 ppm[b]
HC	Propane in (20,95 ± 1) % O_2; balance, N_2	± 2% or ± 0,05 ppm[b]
HC	Propylene in zero air	± 2% or ± 0,05 ppm[b]
HC	Toluene in zero air	± 2% or ± 0,05 ppm[b]
HC	*n*-hexane in zero air	± 2% or ± 0,05 ppm[b]
CO	CO in N_2	± 2% or ± 2 ppm[b]
CO_2	CO_2 in N_2	± 1% or ± 100 ppm[b]
NO_x	NO in N_2	± 1% or ± 1 ppm[b]
O_2	O_2 in N_2	± 0.2% or ± 100 ppm[b]
SO_2	SO_2 in N_2	± 1% or ± 1 ppm[b]

[a] Taken over the 95% confidence interval.

[b] Whichever is greater.

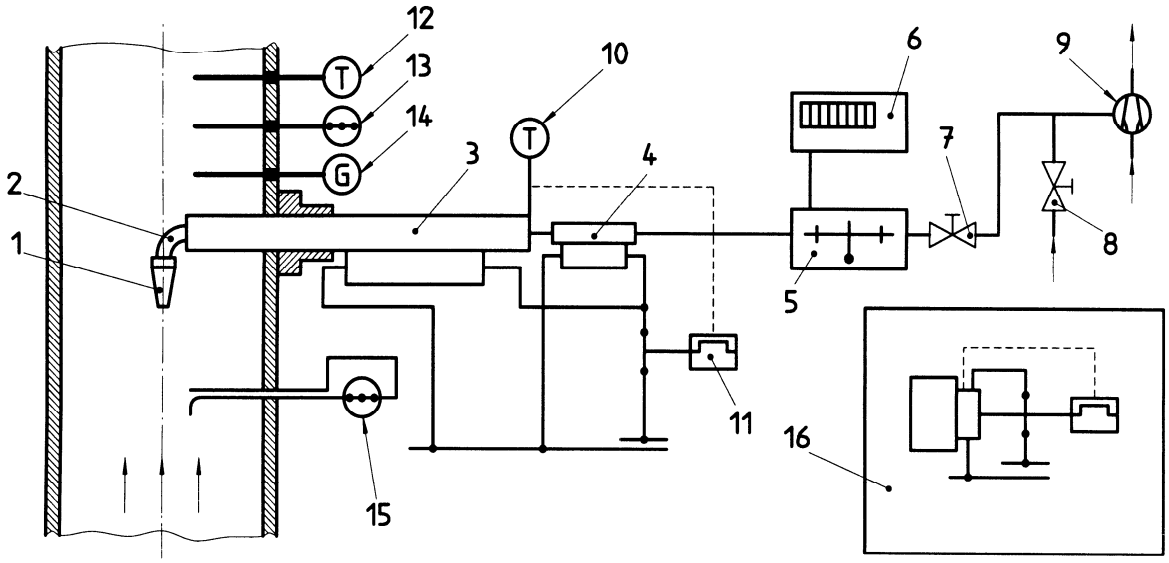
Figure A-3. Sample train for measurement of solid particle concentration by weight



Key

1 Sampling probe
2 Separator
3 Bend
4 Temperature-controlled transport tube
5 Start/stop valve
6 Throttling device } flow meter
7 Transmitter/indicator } flow meter
8 Suction control
9 Ejector, blower
10 Sample temperature measurement
11 Temperature control device
12 Temperature probe
13 Pressure probe
14 Sample train for gaseous constituents
15 Velocity measurement (near sampling probe)
16 Separator preheating device

Figure A-4. Sample train for measurement of solid particle concentration by weight



Key

1 Sampling probe
2 Bend
3 Temperature-controlled transport tube
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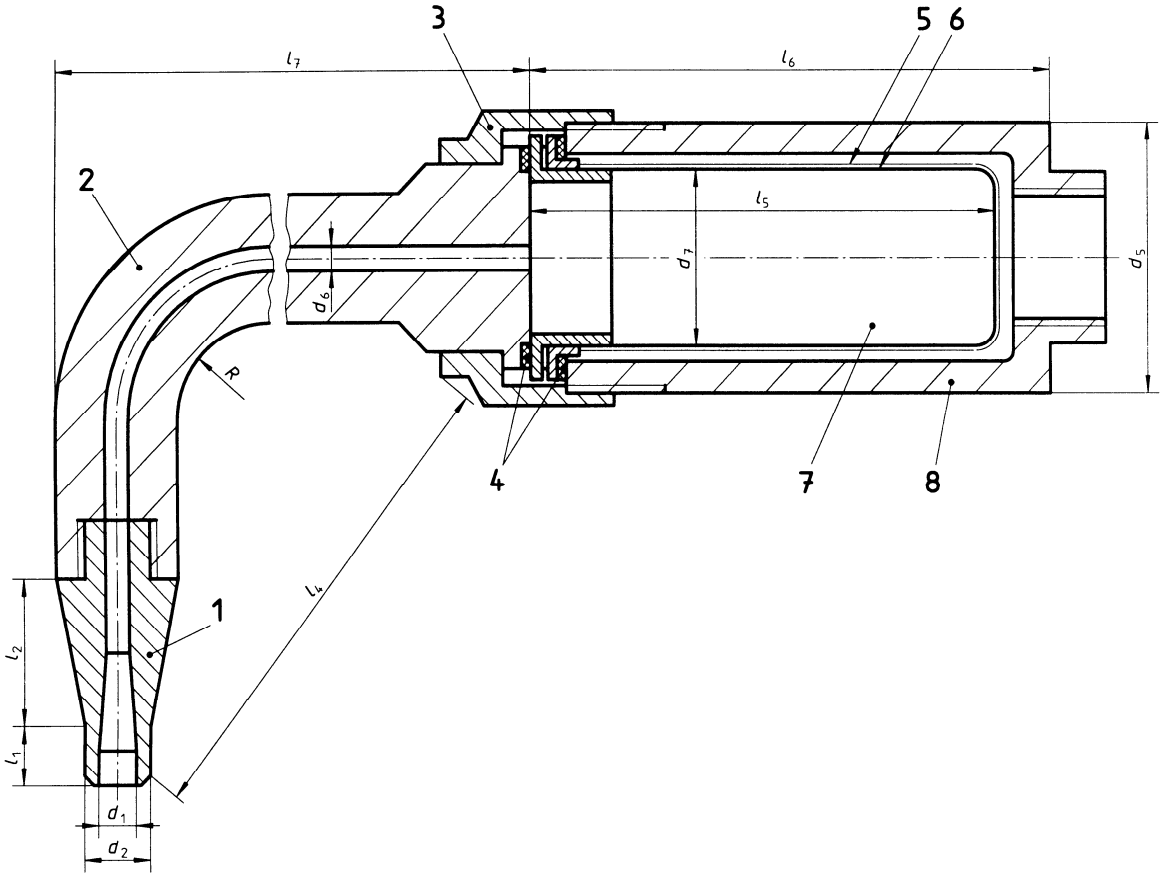
5 Throttling device } flow meter
6 Transmitter/indicator } flow meter
7 Start/stop valve
8 Suction control
9 Ejector, blower
10 Sample temperature measurement
11 Temperature control device
12 Temperature probe
13 Pressure probe
14 Sample train for gaseous constituents
15 Velocity measurement (near sampling probe)
16 Separator preheating device

Figure A-5. Example of probe, bend, tube, and separator assembly



Key

1	Probe	$d_5 < 50$ mm
2	Bend	$d_6 > 5$ mm
3	Joint	$d_7 = 30$ mm; diameter of the cartridge
4	Sealing	$l_4 > 2d_R$
5	Support cage	$l_5 = 70$ mm; length of the cartridge
6	Glass fibre cartridge	$l_6 \approx 80$ mm
7	Quartz fibres (packed)	$l_7 \geqslant l_6$
8	Separator casing	

NOTE The probe may be connected to the separator by a straight tube, and the bend arranged downstream of the separator.
NOTE The length l_1 of the cylindrical part at the probe tip shall be l_1 W $d_{eff}/2$.