HOPPING BOYD GREEN & SAMS

ATTORNEYS AND COUNSELORS

123 SOUTH CALHOUN STREET

POST OFFICE BOX 6526

TALLAHASSEE, FLORIDA 32314

(904) 222-7500

FAX (904) 224-8551

FAX (904) 425-3415

MEMORANDUM

TO: Bruce Mitchell

FROM: Doug Roberts DR

RE: FPL Martin Project; Paper on Relation of VOCs to UHCs

DATE: September 12, 1994

To follow up our call last Friday, I have attached a GE paper on the relation of VOCs to UHCs in GE combustion turbines. This is related to our scheduled conference call this afternoon at 2PM.

I trust this is useful to you.

Unburned Hydrocarbon, Volatile Organic Compound, and Aldehyde Emissions from General Electric Heavy-Duty Gas Turbines

ROOINTON E. PAVRI, Senior Engineer
RICHARD A. SYMONDS, Senior Engineer
General Electric Company
Schenectady, New York

ABSTRACT

Field data clearly show that the emissions of UHC, VOC, (sometimes also called Reactive Organic Gases), and Aldehydes from GE heavy-duty gas turbines are very low. At loads exceeding 75% of base, these emissions are less than 2 ppm. In fact, stack emissions are often less than background concentration. Proper methods of measurement and quality assurance are necessary to detect and measure such low values. Allowance for background hydrocarbons should be made when guaranteeing UHC/VOC.

INTRODUCTION

It has been suspected for years that VOC's (Volatile Organic Compounds) are a precursor to smog/ozone formation which is detrimental to human health at ground level. As such, the VOC's (which are a fraction of the UHC's - Unburned HydroCarbons) are one of the "criteria pollutants" (others are NOx, SOx, CO, particulates and lead) for which National Ambient Air Quality Standards (NAAQS) have been established.

Since the 1970's, many groups perceived a need to go beyond the criteria pollutants in NAAQS and also control the emissions of toxic or hazardous substances. A toxic or hazardous substance is any substance which may cause or contribute to increased mortality or illness, or which may pose a hazard to human health on either a short or long term basis. Formaldehyde, the simplest aldehyde molecule (HCHO), has been defined as a potential carcinogen; its emission and allowable maximum concentration are being increasingly monitored. For example, one state's requirement is that the formaldehyde emissions may not result in an additional cancer risk of one per million. All aldehydes are of interest due to their health risks.

VOC's and aldehydes are products of partial oxidation of fuel molecules or fragments in any combustion process; thus, all gas turbines are a potential source of these emissions. For more than a decade now, GE has collected extensive field data to show that total UHC emissions from the heavy duty gas turbines, at high loads, are quite low. In the last two years, testing methods and programs have been established to measure the VOC fraction of the UHC and aldehydes. Even though the program is continuing to measure these emissions at all operating conditions of load, NOx levels, fuels and water/steam injection, the data to date clearly show that these emissions are almost negligible at high loads. (Hydrocarbon concentrations in this report are expressed as equivalent methane.)

UNBURNED HYDROCARBONS AND VOLATILE ORGANIC COMPOUNDS

Definitions

UHC's. The total unburned hydrocarbons in the gas turbine exhaust. VOC's are a part of UHC's. Normally, aldehydes are not included in UHC's because the usual method of UHC detection and measurement does not detect aldehydes, especially formaldehyde.

VOC's - EPA. Any organic compound that participates in atmospheric photochemical reactions

VOC's - TYPICAL STATE. Any chemical compound of carbon with a true vapor pressure greater than .002 PSIA at standard conditions excluding CO, CO2, carbonic acid, metallic carbonates, metallic carbides, ammonium carbonates, CH4, ethane, benzene, methylene chloride, methyl chloroform and freon 113.

*Presented at the Gas Turbine and Aeroengine Congress and Exposition—June 11-14, 1990—Brussels, Belgium

VOC's - G.E. All non-methane organic compounds in the exhaust. Note that this definition is most conservative.

MEASUREMENT METHODS

Measurement methods of UHC/VOC are well defined and established by the EPA and given in detail in the Code of Federal Regulations, Vol. 40, Part 60 (40CFR60), Appendix A, Methods 18, 25, and 25A, and 40CFR87, Subpart G for aircraft engine exhaust gas sampling. A brief description of the methods is given below.

Method 25

This is the method of measuring non-methane hydrocarbons in gases where their concentration is relatively high. Figures 1 and 2 show the schematics of sampling and analysis techniques. As shown later, this method is not recommended for measuring gas turbine exhaust VOC's.

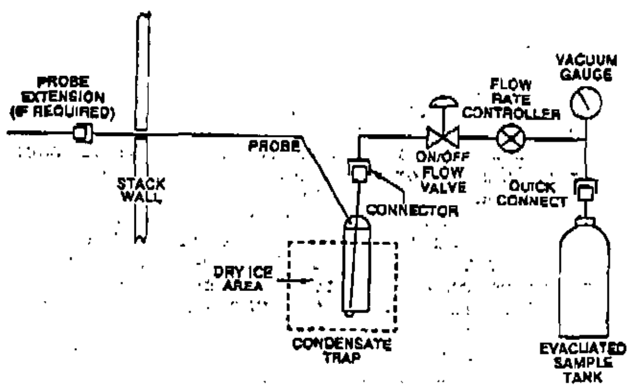


FIGURE 1: EPA METHOD 25 SAMPLING APPARATUS

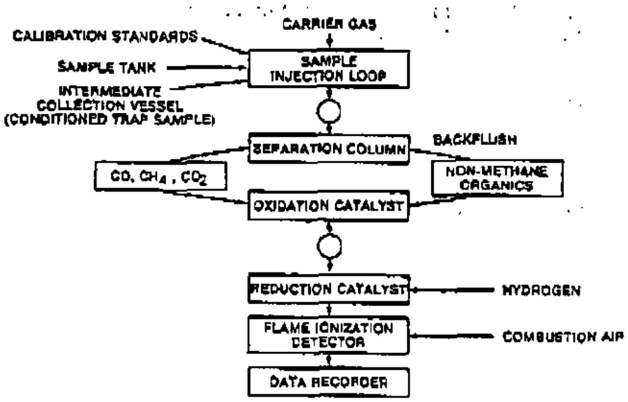


FIGURE 2: EPA METHOD 25
SIMPLIFIED SCHEMATIC OF NON-METHANE ORGANIC (NMO) ANALYZER

Method 25A

This is an accurate method to measure UHC's in gas turbine exhaust. It does not separate the hydrocarbons into its constituents and hence is unsuitable to measure VOC's. After the gases are properly treated, they are analyzed using an on-line flame ionization detector (FID). See Figure 3.

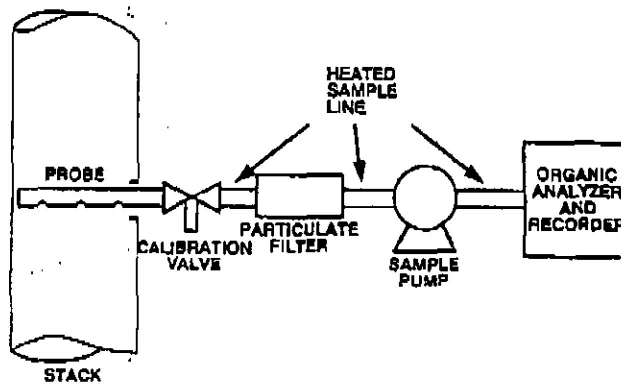


FIGURE 3: EPA METHOD 25A: ON-LINE FID
ORGANIC CONCENTRATION MEASUREMENT SYSTEM

Method 18

This method is for measurement of UHC's and VOC's.

Method 18.7.1

This is an integrated bag sampling method where the gases are collected in a grab bag and analyzed with off-line gas chromatograph (GC). A schematic of this method is shown in Figure 4.

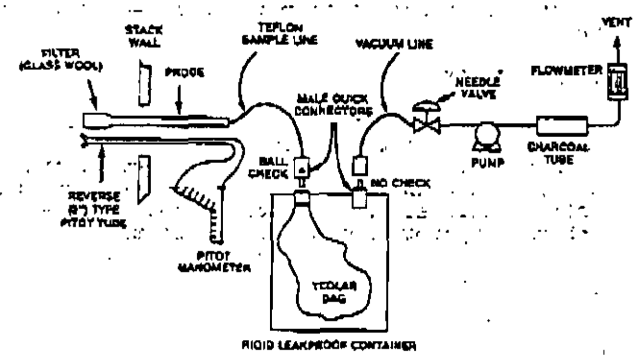


FIGURE 4: EPA METHOD 18: GRAB BAG WITH OFF-LINE GC

Method 18.7.2

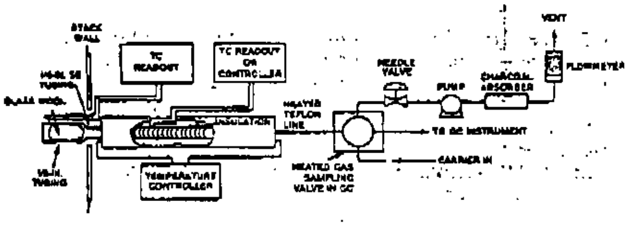
As shown in Figure 5, this is the direct interface sampling system for measuring the UHC/VOC's. It requires an on-line gas chromatograph in the field to measure the total UHC as well as separate them into VOC components. This is the most accurate method and is recommended for VOC measurement in gas turbine exhaust.

TABLE I
MEASUREMENT METHODS

METHODS	FOR	VOC	ACCURACY (PPM)	PRINCIPLE	REMARKS
EPA-25	TOTAL GASEOUS NON-METHANE	YES	± 20(1)	WET CHEMISTRY, & FID	PRONE TO CONTAMINATION ORIGINALLY DESIGNED FOR VARNISH PLANTS. NOT RECOMMENDED FOR GT EXHAUST
EPA-25A	TOTAL GASEOUS ORGANIC	NO	± .1	ON-LINE FID	ACCURATE METHOD FOR UHC
EPA-18	TOTAL GASEOUS ORGANIC	YES	± 5(2) ± 20(3)	GRAB BAG & GC (18.7.1)	UNRELIABLE METHOD. NEEDS EXTREME CARE TO PRODUCE REPEATABLE RESULTS
			±.1 to .2	ON-LINE GC (18.7.2)	BEST METHOD FOR GT EXHAUST. MODIFIED VERSION OF THIS USED AT UE AND GILROY. (GE RECOMMENDED METHOD WITH MODIFICATIONS AS SPECIFIED)
40CFR87 SUBPART G	AIRCRAFT ENGINE EXHAUST GAS INCLUDING TOTAL GASEOUS ORGANICS	NO	± .1	FID	ACCURATE METHOD FOR UHC

(1) TRUESDAIL LAB'S ESTIMATE
GE's ESTIMATE IS ± 50 PPM
(2) TEDLAR BAGS
(3) ALUMINIZED MYLAR BAGS

ON-LINE GC IS THE ONLY RELIABLE METHOD TO ACCURATELY MEASURE VOC's IN GAS TURBINE EXHAUSTS



DIRECT INTERFACE SAMPLING SYSTEM

FIGURE 1: EPA METHOD 18.7.2 ON-LINE GC

Method of 40CFR87, Subpart G

This is an on-line FID technique similar to Method 25A.

Table I summarizes these methods including their expected accuracy and measurement principle. The accuracy for Method 25 and Method 18.7.1 could be very poor. The conclusion from this table is that the on-line FID and on-line GC are the only reliable methods to accurately measure UHC's and VOC's, respectively , in gas turbine exhaust.

FIELD AND FACTORY DATA

Table II summarizes field data on twelve GE heavy-duty gas turbines. The data include operation on MS7C/7E/7EA and 6B, on oil, natural gas, propane and butane with NOx levels varying from NSPS to 25 PPM with water and/or steam injection. The effect of the VOC/UHC measurement method is clearly discernible. Where EPA Method 25 was used, the measured values are extremely high and the variation in data is very wide. Both these are non-representative of a gas turbine. The grab bag plus GC method also shows wide variations from <1 PPM UHC to as high as 14 PPM UHC, and the VOC variation is also large, from <1 to 8 PPM. This points out the unreliability of this method. Using the most reliable method of on-line FID and on-line GC, the data show that the total UHC emissions from GE heavy-duty gas turbines at base load are less than 2 PPM on oil or natural gas.

TABLE II
GE HEAVY DUTY GAS TURBINE UHC/VOC EMISSIONS
FIELD DATA (BASE LOAD, METHOD)

DATE	MACHINE	FUEL	NOx LEVEL	DILUENT	UHC/VOC(PPM)	METHOD (VENDOR)
MAY, 78	7001C	OIL	USEPA	WATER	1.2/ND	FID (GE, BECKMAN) ON LINE GC (ACCUREX)
SEPT, 84	7001E	COAL GAS	20 PPM	STEAM OR MOISTURIZATION	ND/ND	ON LINE GC (RADIAN CORP.)
JUNE, 85	7001E(4)	NAT. GAS	42 PPM	WATER	0-3/ND	GRAB BAG + GC (EPA-18)
		OIL	42 PPM	WATER	0-3/0-2.3 (0-97% WT)	GC BY ZAL CO + CHEMACOLOGY
DEC, 85	6001B	NAT. GAS	42 PPM	WATER	10-48(TNM) GASEOUS 8-10 CONDENSIBLE 2-38	EPA-25 (TRUESDAIL)
		OIL	65 PPM	WATER	41-50 (TNM) GASEOUS 7-10 CONDENSIBLE 43-31	" "
JULY, 87	6001B	NAT. GAS	42 PPM	WATER	1.2-1.6/ND-0.2 (0-20% WT)	ON LINE GC (GE, CUBIX)
NOV, 87	7001EA	NAT. GAS	25 PPM	STEAM	1-1.6/ND	ON LINE GC (GE, CUBIX)
MAY, 88	6001B	NAT. GAS	42 PPM	STEAM	4/3	GRAB BAG + GC
		PROPANE	65 PPM	"	11/8	(EPA - 18.7.1)
		BUTANE	65 PPM	"	7/4	(ENGRG. SCIENCE INC.)
MAY, 88	7001EA	NAT. GAS	42 PPM	STEAM	1-14/<1-2.1	GRAB BAG + GC
		BUTANE	65 PPM	STEAM		(ENGRG. SCIENCE INC.)
MAR, 89	7001E	NAT. GAS	25 PPM	WATER	<1.0/<1.0	ON LINE GC
		OIL	42 PPM	WATER	<1.0/<1.0	(ENGRG. SCIENCE INC.)

NOTES:
FID = FLAME IONIZATION DETECTION
ND = NONE DETECTED
GC = GAS CHROMATOGRAPH
TNM = TOTAL NON-METHANE

FIELD TEST ON MS6001B

A detailed test was run on a MS6001B machine in July 1987. The fuel was natural gas. Test purposes were to:

- Measure total UHC using on-line GC
- Measure VOC and separate the compounds into C1, C2, C3, and C4
- Compare the grab bag plus GC method vs. on-line GC method
- Evaluate the effect of background hydrocarbons

Figure 6 shows the measuring equipment train set-up using on-line GC. Cubix Corporation was hired as an independent contractor to measure the emissions. Results of the test are summarized in Tables III and IV. Table III shows that the only UHC compounds detected were CH_4 and C_2H_6 (last two columns on right). Also, the highest amount of C_2H_6 detected was about 20% of the total UHC (C1 + C2). For natural gas burning, then, VOC's are C2 only, and are about 20% of the total UHC measurement, which at base load was never more than 3ppm. (Details of the sampling location are shown in Figure 7. Calibration gases were:

A. 10 ppm CH_4, air balance
B. 15% O_2, 3% CO_2, N_2 balance
C. 10 ppm C1-C4
D. 100 ppm C1-C6

Gas chromatographs were:

1. Varian C5+
2. Shimadzu C1-C4
3. AID THC Analyzer)

Of particular interest are the background hydrocarbon levels at the site of 2-3 PPM, while the average UHC level integrated over the stack area was about 1.2 PPM. The machine is incinerating some of the background hydrocarbons.

Table IV shows the analysis of exhaust gas samples using grab bags. Two types of bags were used, Tedlar(R) and Aluminized Mylar(R). Of the two, the Tedlar bags gave better results although not as accurate as on-line GC. Note that bag #6, a certified zero calibration gas sample, showed a reading of 2.0 PPM of non-methane hydrocarbons. Aluminized Mylar bags are totally unacceptable. Bag 15, a certified zero gas sample, read 23.0 PPM non-methane hydrocarbons.

FACTORY TEST ON MS7001F

Table V summarizes the UHC/VOC emissions from the MS7001F on oil in the factory prototype test. The test was run over the load range at various NOx levels. Again, the UHC/VOC emissions are almost negligible. The VOC fraction on oil on 7001F varied from none detected (<0.2 PPM) to about 0.35 PPM. The

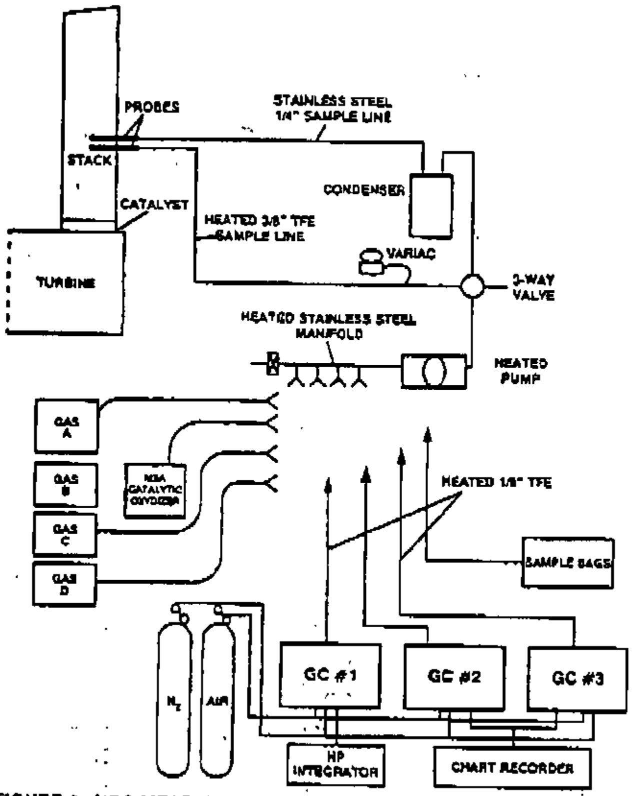


FIGURE 6: VOC MEASUREMENT USING ON-LINE GAS CHROMATOGRAPH USED BY CUBIX CORP. AT UNIVERSITY ENERGY

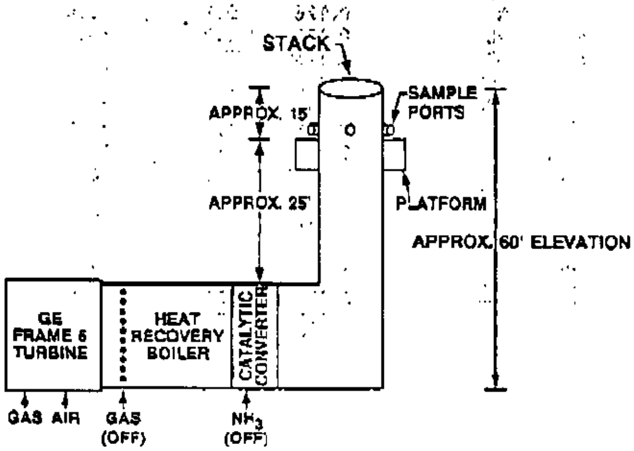


FIGURE 7. SAMPLING LOCATIONS, MS6001B

highest VOC fraction was 47% of the UHC. The only VOC species detected was butane. For distillate burning, then, the VOC's are C4, and are less than 50% of the total UHC measured which was less than 2 ppm.

EFFECT OF BACKGROUND HYDROCARBONS

Anywhere in the USA, for that matter, anywhere in the world, there is a background level of hydrocarbons present in the ambient air. The level of these hydrocarbons varies widely depending on the location (e.g., oil fields, process plants, marshes, etc.) as well as with time. These hydrocarbons are sucked into the gas turbine. A fraction of these will be burned as they pass through the high temperature section of the combustor and the rest then go up the stack. It is important to realize that the stack hydrocarbons do not all arise in the gas turbine. A substantial portion could be coming from the ambient air itself.

The test on the MS6001B, described earlier, proved this. Another test was run on a MS7001EA in west Texas. The background hydrocarbon levels varied from 10 PPM to 100 PPM. In all cases, the stack hydrocarbons were 50% of the ambient levels. A test on a MS6001B in New Jersey also showed similar results. The background values varied from 10 to 30 PPM while the stack concentration was about half that.

Since the gas turbine is not the source of these hydrocarbons, this fact becomes very significant when obtaining the environmental permit for the turbine. An allowance for background hydrocarbons needs to be made.

ALDEHYDES

As mentioned previously, aldehydes are products of incomplete combustion. They are collected in an integrated sample, analyzed and reported as the simplest aldehyde, namely formaldehyde.

ALDEHYDE MEASUREMENT METHODS

Aldehyde measurement methods are well established. They usually involve a wet chemistry method with the gas sample bubbled through impingers where aldehydes are captured. The sample is then analyzed by titration, spectrometer or liquid chromatography. The titration method is usually good for detection to 0.5 PPM while the liquid chromatography can detect 0.02 PPM formaldehyde.

FIELD TESTS

Within the last year, several field tests have been run to measure formaldehyde emissions from GE heavy-duty gas turbines. These are listed in Table VI. As can be seen, the values are very low, especially at high loads. Also, the repeatability of the results is very good. At base load (100%) the formaldehyde emissions on gas fuel (natural gas, propane and butane) are less than 1.0 PPM. On oil, the value is less than 1.5 PPM.

CONCLUSIONS

1. UHC/VOC emissions from GE heavy-duty gas turbines are very low at high loads.

2. Correct measurement and proper quality control are crucial to obtaining representative results.

TABLE III

SUMMARY OF C1 THROUGH C4 ANALYSES

G.E. Turbine Test - MS6001B
15 July 87

Shimadzu Mini-2 Data

Injection No.	Time	Description	Sample Line	Peak Height (in mm) C1	C2	C3	i-C4	n-C4	C1 Calibration Factor	ppmv as methane C1	C2
1	0911	C1-C4 calibration gas	TFE	70	109	150	149	133	0.125	8.8	13.6
2	0914	C1-C4 calibration gas	direct	75	122	163	164	149	0.117	8.8	14.3
3	0918	C1-C4 calibration gas	direct	75	122	164	164	150	0.117	8.8	14.3
4	0921	10ppm methane	direct	89	ND	ND	ND	ND	0.112	10.0	<0.2
5	0924	10ppm methane	direct	89	ND	ND	ND	ND	0.112	10.0	<0.2
6	0928	ambient air @ stack	TFE	27	ND	ND	ND	ND	0.112	3.0	<0.2
7	0956	ambient air @ stack	TFE	24	ND	ND	ND	ND	0.112	2.7	<0.2
8	0957	sample point C-1	TFE	10	2	ND	ND	ND	0.112	1.1	0.2
9	0959	sample point C-1	TFE	5	1	ND	ND	ND	0.112	0.6	<0.2
10	1000	sample point C-2	TFE	2	2	ND	ND	ND	0.112	0.6	<0.2
11	1001	sample point C-3	TFE	8	1	ND	ND	ND	0.112	0.9	<0.2
12	1003	sample point C-4	TFE	7	0.5	ND	ND	ND	0.112	0.8	<0.2
13	1006	sample point D-1	TFE	25	0.5	ND	ND	ND	0.112	2.8	<0.2
14	1007	sample point D-1	TFE	19	0.5	ND	ND	ND	0.112	2.1	<0.2
15	1008	sample point D-2	TFE	18	0.5	ND	ND	ND	0.112	2.0	<0.2
16	1010	sample point D-3	TFE	20	2	ND	ND	ND	0.112	2.2	0.2
17	1012	sample point D-4	TFE	7	2	ND	ND	ND	0.112	0.8	0.2
18	1014	sample point D-4	TFE	6	2	ND	ND	ND	0.112	0.7	0.2
19	1016	10ppm methane	direct	80	ND	ND	ND	ND	0.125	10.0	<0.2
20	1020	10ppm methane	direct	79	ND	ND	ND	ND	0.127	10.0	<0.2
21	1021	sample point A-1	TFE	9	ND	ND	ND	ND	0.126	1.1	<0.2
22	1023	sample point A-1	TFE	10	0.5	ND	ND	ND	0.126	1.3	<0.2
23	1025	sample point A-2	TFE	11	3	ND	ND	ND	0.126	1.4	0.4
24	1027	sample point A-3	TFE	7	2	ND	ND	ND	0.126	0.9	0.3
25	1029	sample point A-4	TFE	7	3	ND	ND	ND	0.126	0.9	0.4
26	1031	sample point B-1	TFE	10	ND	ND	ND	ND	0.126	1.3	<0.2
27	1044	10ppm methane	direct	70	ND	ND	ND	ND	0.143	10.0	<0.2
28	1128	10ppm methane	direct	70	ND	ND	ND	ND	0.143	10.0	<0.2
29	1207	10ppm methane	direct	84	ND	ND	ND	ND	0.119	10.0	<0.2
30	1212	10ppm methane	direct	85	ND	ND	ND	ND	0.118	10.0	<0.2
31	1215	C1-C4 calibration gas	direct	68	120	164	168	155	0.129	8.8	15.5
32	1225	sample @ stack center	TFE	6	2	ND	ND	ND	0.119	0.7	0.2
33	1230	sample @ stack center	TFE	6	.2	ND	ND	ND	0.119	0.7	0.2
34	1238	sample @ stack center	TFE	6	1	ND	ND	ND	0.119	0.7	<0.2
35	1245	sample @ stack center	TFE	6	1	ND	ND	ND	0.119	0.7	<0.2
36	1253	sample @ stack center	TFE	5	.2	ND	ND	ND	0.119	0.6	0.2
37	1306	10ppm methane	direct	79	ND	ND	ND	ND	0.127	10.0	<0.2
39	1332	10ppm methane	direct	78	ND	ND	ND	ND	0.128	10.0	<0.2
40	1335	sample @ stack center	SS	6	ND	ND	ND	ND	0.128	0.8	<0.2
41	1338	sample @ stack center	SS	5	ND	ND	ND	ND	0.128	0.6	<0.2
42	1540	10ppm methane	direct	88	ND	ND	ND	ND	0.114	10.0	<0.2
43	1541	ambient air @ intake	TFE	18	ND	ND	ND	ND	0.114	2.1	<0.2
44	154	ambient air @ intake	TFE	18	ND	ND	ND	ND	0.114	2.1	<0.2
45	1545	ambient air	TFE	18	ND	ND	ND	ND	0.114	2.1	<0.2
46	1546	10ppm methane	TFE	90	ND	ND	ND	ND	0.111	10.0	<0.2

THC via Shimadzu Mini-2

Run	Conc. (ppm) in methane equivalents
1	1.6
2	1.2
Average	1.4

ND = Not Detected, TFE = Heat Traced Teflon Sample Line,
SS = Stainless Steel Sample Line

TABLE IV
SUMMARY OF BAG SAMPLE ANALYSES

General Electric/MS6001B
Gas Turbine/Generator

Bag samples from a General Electric Gas Turbine

Tedlar (R) sample bags

Bag	1	2	3	4	5	6	7
Time	0937	1312	1325	1359	1416	1435	1538
Source	ambient	stack	stack	stack	stack	zero	stack
Temp (°F)	90	96	98	99	103	82	98
Atm. Press.(in. Hg)	28.56	28.55	28.55	28.50	28.50	28.50	28.50
Sample Line	TFE	TFE	SS	SS	TFE	TFE	TFE
methane (ppm)	2.9	<0.5	0.8	0.8	<0.5	<0.5	2.0
non-methane THC	2.4	1.9	2.0	2.0	3.5	2.0	2.2

Aluminized Mylar (R) sample bags

Bag	11	12	13	14	15
Time	0937	1312	1325	1435	1538
Source	ambient	stack	stack	stack	zero
Temp (°F)	90	96	98	98	82
Atm. Press.(in. Hg)	28.56	28.55	28.55	28.50	28.50
Sample Line	TFE	TFE	SS	TFE	TFE
methane(ppm)	3.2	<0.5	1.0	2.0	<0.5
non-methane THC	23.6	37.5	29.8	21.4	23.0

* SS = stainless steel, TFE = heat raced Teflon sample line

TABLE V

MS7001F PROTOTYPE FACTORY TEST
UNBURNED HYDROCARBON EMISSIONS

T_f (°F)	MW	FUEL	IGV	UHC(1) (PPM)	%VOC(2)	NOx(3) (PPM)	DILUENT
2023	65	0.1	53	.57	47	188	--(DRY)
1984	66	"	53	.32	ND(4)	79	WATER
1940	65	"	53	.11	"	39	"
1909	65	"	53	.26	"	27	"
1876	65	"	"	.96	35	21	"
1656	35	"	"	.39	ND	160	--(DRY)
1631	35	"	"	.4	40	71	WATER
1607	35	"	"	2.0	ND	37	"
1386	15	"	"	.76	ND	129	"
2289	78	"	80	.43	ND	247	--(DRY)
2100	78	"	80	.04	ND	22	WATER

NOTES

(1) UHC measured by GE using on-line FID

(2) VOC measured by Cubix using on-line GC

(3) NOx @ 15% O_2 and ISO humidity

(4) ND = None Detected (< 0.2 PPM)

(5) T_f = Firing Temperature

3. Allowance for background hydrocarbons should be made when guaranteeing UHC/VOC.

4. On natural gas, VOC's are 20% of UHC and the principal constituent is ethane. On distillate oil, VOC's are 50% of UHC and the principal constituent is butane.

5. Formaldehyde emissions from GE heavy-duty gas turbines are also very low. At base load, these emissions are less than 1.0 - 1.5 PPM on all fuels.

REFERENCES

1. Code of Federal Regulations, Title 40 - Protection of Environment, Parts 53 to 80, Office of the Federal Register, Washington, 1984.