



CONTRACT NO. A132-104
FINAL REPORT
JANUARY 1995

NO_x and VOC Species Profiles for Gas Fired Stationary Combustion Sources

*Volume 1:
Final Report*

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY



AIR RESOURCES BOARD
Research Division

NOx and VOC Species Profiles for Gas Fired Stationary
Combustion Sources

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Contract No. A132-104

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January 1995

ABSTRACT

The California Air Resources Board is developing strategies for reducing ambient ozone concentrations in many parts of the State. These strategies include modeling efforts which require a reliable and comprehensive database of volatile organic compound (VOC) and nitrogen oxide (NO_x) species profiles for a variety of source types. This project focused on developing these profiles for gas fired stationary combustion sources, a key source category in California. Selected air toxic emissions also were quantified.

Eight gas fired sources were tested including three reciprocating internal combustion engines, a gas turbine, two refinery process heaters, a steam generator, and a utility boiler. Various fuel types were used including natural gas, refinery gas, landfill gas, and field gas. NO_x control devices included selective catalytic reduction, low NO_x burners, and exhaust gas recirculation. Over 100 substances were included on the target analyte list for each source including paraffins, olefins, acetylenes, naphthenes, aromatics, 1,3-Butadiene, aldehydes, ketones, NO, and NO_x.

Of the 100 plus substances on the target analyte list, 21 were detected. Methane was the most prevalent VOC in the exhaust gases from each source. The reciprocating IC engines had the highest levels of total VOC emissions and the most detections. 1,3-Butadiene was detected at low levels at the landfill and field gas IC engines. Aromatics including benzene and toluene were detected at each of the sources except one of the refinery gas process heater and the utility boiler. Formaldehyde, acetaldehyde, and acetone were detected at each of the sources.

The IC engines had the highest NO_x concentrations. In general, sources with NO_x control devices had lower NO_x emission concentrations. These sources also had the lowest ratio of NO to NO_x. NO_x emissions from sources without NO_x control were almost entirely composed of NO.

ACKNOWLEDGEMENTS

Results from this program are provided in Volume 1 and the field sampling and laboratory data are contained in Volume 2. Dr. Robert Grant was the CARB program manager, and Mr. David Hansell and Mr. Glenn England were the principal investigator and program manager, respectively, for Energy and Environmental Research (EER). The program managers and principal investigator would like to acknowledge the contributions of the participating facilities who provided their time and resources. The project also benefitted greatly from the efforts of Kevin Mongar (responsible for 1,3-Butadiene sampling and analysis) and Bob Okamoto (assisted in preparation and performance of tedlar bag stability test) of the CARB. In addition, the efforts of Jon Kawaguchi and Rob Campbell of EER were greatly appreciated.

This report was submitted in fulfillment of A132-104 "Development of NO_x and VOC Species Profiles for Gas Fired Stationary Combustion Sources" by EER under the sponsorship of the CARB.

DISCLAIMER

The statements and conclusions in this report are those of the contractors and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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E.0 EXECUTIVE SUMMARY

The California Air Resources Board (ARB) is developing strategies for reducing ambient ozone concentrations in many parts of the State. The basis for these strategies will be computational modeling of atmospheric transport and chemistry processes for ozone formation. This modeling effort requires a reliable and comprehensive database of source emissions data to ensure the modeling results will be valid. While a volatile organic species profile database currently exists for approximately 270 source categories, there are still a number of natural gas and refinery gas fired source types prevalent in California for which species profiles are unreliable or do not exist. In addition, speciation of oxides of nitrogen (NO_x) has not been well established. Therefore, a need exists for additional data to characterize volatile organic and NO_x species for these sources. In response to this need, the objectives of this program included:

- Providing accurate and complete speciation profiles for volatile organic compounds (VOC);
- Quantifying selected toxic air contaminants from the California Air Toxics "Hot Spots" Information and Assessment Act of 1987 (AB2588);
- Providing the ARB with high quality data which is fully defensible and meets Quality Assurance goals commensurate with use in development of ozone reduction strategies; and
- Providing the first comprehensive evaluation of nitrogen oxides speciation (NO and NO₂) from gas fired combustion sources.

The following sections summarize the substances quantified, sources tested, and results from the VOC and NO_x sampling programs.

E.1 Target Analytes and Sampling

To accurately model ozone formation resulting from combustion sources requires detailed VOC and NO_x speciation profiles for a variety of source types. VOCs which can participate in ozone formation reactions include:

TABLE E-1. EMISSIONS AND FUEL ANALYSES (2).

Paraffins	Olefins	Acetylenes
Methane*		
Ethane*	Ethylene*	Ethyne*
Propane*	Propylene*	Propyne**
Butanes*	Butenes*	Butynes**
Pentanes*	Pentenes**	Pentyne**
Hexanes**		
Other C6*	Naphthenes	Aromatics**
C7 Plus*	Cyclopropane**	Benzene
	Cyclobutane**	Toluene
	Cyclopentane*	Ethylbenzene
	Cyclohexane**	Xylenes (m,p,o)
		Styrene
		Phenol
		1,3,5-Trimethylbenzene
		1,2,4-Trimethylbenzene
		Naphthalene
Oxygenates**	Chlorinated Hydrocarbons (1)**	Carbon Disulfide**
Aldehydes (C1-C4)		
Ketones (C3-C4)		
Ethers		
NOx **	Diolefins**	
NO	1,3-Butadiene	
NO2	Propadiene	

(1) 29 halogenated organics including ethylene dibromide and ethylene dichloride.

(2) Detailed fuel and emission target substances given in Tables 4-2 and 4-3.

* Fuel and emission analysis.

** Emission analysis only.

- Paraffins (Alkanes)
- Olefins (Alkenes)
- Diolefins
- Acetylenes (Alkynes)
- Naphthenes (Cycloparaffins or Cyclanes)
- Aromatics
- Oxygenates (Alcohols, Aldehydes, Ketones, Ethers)
- Chlorinated hydrocarbons

Extensive resources would be required to quantify substances in each of the major VOC categories. For most systems it is not necessary to quantify all of the VOCs listed above and substances should be eliminated based on:

- (1) Negligible photochemical reactivity;
- (2) Low potential for emission; and
- (3) Sampling and analytical limitations.

Considering items 1 to 3, the list of VOC and NO_x species shown in Table E-1 was developed. All of these compounds were included on the exhaust target analyte list. Selected species were quantified in the fuel. Paraffins, olefins, acetylenes, naphthenes and aromatics were quantified using either GC/FID no cryogenic trap or GC/MS with cryogenic trap. Cryogenic trapping concentrates target analytes thus reducing the analytical detection limit. Hydrocarbons with three carbon atoms or less could not be concentrated due to their low boiling points. The samples were collected using tedlar bags which contained stack gases and varying amounts of dilution nitrogen. 1,3-Butadiene was quantified using an on-site GC/PID system supplied and operated by the CARB. The aldehydes and ketones were determined with CARB method 430. NO_x species were determined using a continuous emission monitoring system which included a NO_x converter.

E.2 Sources Tested

One of the key objectives of this project was to select sources which are representative of the population of devices present in California. The Southern California Air Basin (SCAB) was selected as the primary target for testing due to its severe pollution problems. The 1989 criteria pollutant inventory was consulted to determine significant gas fired combustion sources in the SCAB based on total organic gas emissions (TOG). The internal and external combustion sources

TABLE E-2a. INTERNAL COMBUSTION ENGINE DESIGN AND OPERATION SUMMARY.

SOURCE TYPE	RECIPROCATING IC ENGINE			GAS TURBINE
	A	D	E	
SOURCE ID	10/11/93	10/22/93	10/26,27/93	F
TEST DATE				11/2/93
DESIGN				
Manufacturer	Cooper	Waukesha	Waukesha	General Electric
Model	16 SGTA	F1197	5108	na
Power	2650 bhp	162 bhp	548 bhp	85 MWe
Number of Strokes per Cycle	4	4	4	-
Duct Burners	-	-	-	Yes
Turbo Charging	Yes	No	No	-
Post Combustion Controls	No	No	SCR	SCR, CO Catalyst
OPERATION				
Stack Parameters				
Flow (dscfm)	5941	270	667	564000
Moisture (%)	12	16	19	11
Temperature (F)	876	582	973	339
Oxygen (% dry)	8.3	2.5	0	14
Carbon Dioxide (% dry)	10.7	8.9	11.9	4
Heat Input (MMBtu/hr)	42	1.6	4.7	1337

TABLE E-2b. EXTERNAL COMBUSTION DESIGN AND OPERATION SUMMARY.

SOURCE TYPE	EXTERNAL COMBUSTION			UTILITY BOILER
	PROCESS HEATER	STEAM GENERATOR	PROCESS HEATER	
SOURCE ID	B	C	G	H
TEST DATE	10/13,14/93	10/20/93	11/3,4/93	11/16/93
DESIGN				
Manufacturer	na	Struthers	Foster Wheeler	Riley Stoker
Air Preheater	na	No	No	Yes
Low NOx Burners	Yes	Yes	No	No
Exhaust Gas Recirculation	No	Yes	No	No
Heat Input	5X99	62.5	215	510
Post Combustion Controls	No	No	SCR	No
OPERATION				
Stack Parameters				
Flow (dscfm)	32789	9396	34200	32167
Moisture (%)	12	17	16	13
Temperature (F)	468	342	334	223
Oxygen (% dry)	9.9	2.5	1.6	5
Carbon Dioxide (% dry)	6.9	12.9	12.2	9.2
Heat Input (MMBtu/hr)	233	51	585	114

selected for testing are listed in Table E-2a and b, respectively.

Each reciprocating IC engine is fired on a different type of fuel. These fuels are representative of those burned in the SCAB. The natural gas fired engines are manufactured by Waukesha and the landfill gas engine is manufactured by Cooper. The engines range in size from small (162 Bhp) to large (2650 Bhp) and only one of the engines has a post-combustion control device. The turbine is manufactured by General Electric and has duct burners, CO catalyst, and SCR. The gas turbine is fired on natural gas, while the duct burners are fired on refinery gas. Refinery gas is only a small fraction of the fuel burned.

The external sources include a utility boiler, two process heaters, and a steam generator. To control NO_x, three of the sources have low-NO_x burners, flue gas recirculation, and/or selective catalytic reduction. The utility boiler does not have NO_x controls. The furnaces range in size from small (62.5 MMBtu/hr) to large (510 MMBtu/hr). Source B includes 5 process heaters each with a heat input of 99 MMBtu/hr.

Table E-3 lists fuel VOC profiles for each source tested. These profiles are expressed as the weight fraction of total organic gases in the fuel. Most of the natural gases burned had similar profiles. The natural gas burned at the steam generator did have a lower methane concentration and a higher C₆ plus concentration. The landfill gas had a comparable profile to the natural gas source profiles. The field gas and refinery gases had higher concentrations of C₂ through C₄ hydrocarbons than the other fuels.

E.3 Emission VOC Speciation Results

Table E-4 lists emission VOC profiles for the IC Engine sources. Profiles were not generated for the other sources because the sensitivity of the analysis procedures was not sufficient. Additional discussion of the accuracy of the profiles is provided later in this section. The IC engine profiles were developed by averaging the run specific weight fractions for each VOC target analyte at each source. As specified in AB2588 (see Air Toxics "Hot Spots" Information and Assessment Act of 1987 as adopted on June 10, 1993), 1/2 the detection limit was used when averaging detected and nondetected weight fractions. These averages are noted as 98. If a target substance was not detected in any of the runs, no value was calculated as specified in AB2588. Instead the average was given as ND and noted as 99. Detection limits are provided in Table 5-5. Next the total weight fraction of detected VOCs in the stack gas at each source was calculated by summing the average VOC weight fractions for each detected target analyte. The average VOC weight fractions

TABLE E-4. EMISSION VOC PROFILES
 (Only substances detected at one or more sources listed. See Table 5-5 for complete listing of over 100 target substances and detection limits).

SUBSTANCE	PROFILE (Weight Fraction of Total Organic Gas)			
	Landfill Gas	Field Gas	Natural Gas	SCR
	No Control	No Control	No Control	SCR
Methane (a)	0.9468	0.4564	0.8592	
Ethane (a)	0.0205	0.1218	0.0581	
Propane (a)	0.0041	0.1237	0.0125	
Ethene (a)	0.0202	0.1132	0.0357	
Propene (a)	0.0042	0.0354	0.0040	
Ethyne (a)	ND	0.1348	0.0118	
1,3-Butadiene (b)	0.0002	0.0017	ND	
Benzene (a)	0.0003	0.0017	0.0003	
Toluene (a)	0.0006	{0.0010}	0.0008	
m,p-Xylenes (a)	99	0.0004	99	
Formaldehyde	b (0.0020)	b (0.0078)	b (0.0168)	
Acetaldehyde	b (0.0005)	b (0.0015)	b (0.0005)	
Acrolein	0.0002	0.0003	0.0002	
Propanal (a)	0.0000	0.0001	0.0001	
Acetone (a)	b (0.0001)	b (0.0001)	b (0.0002)	
Crotonaldehyde (a)	0.0000	ND	0.0001	
Isobutyraldehyde (a)	0.0000	ND	0.0001	
Methyl Ethyl Ketone (a)	0.0001	0.0001	0.0001	
Total Weight Fraction	1.0000	1.0000	1.0000	
Detection Limit Ratio (c)	0.0079	0.0096	0.0099	

SCR - Selective Catalytic Reduction

(a) - Full ARB QA/QC standards were not applied to these results.

(b) - Matrix spike recovery less than 70% (See Table 6-4 and 6-6 for listing of recoveries).

(c) - Ratio of the sum of detection limits in ppbw,dry for nondetected substances to the sum of detections in ppbw,dry for detected substances.

98 - Average of detected and nondetected runs. 1/2 detection limit used for nondetected runs as specified in AB2588.

99 - All runs below the detection limit. No value reported as specified in AB2588.

() - Field blank corrected.

{ } - Field blank > 20% of sample value.

TABLE E-3. FUEL VOC PROFILES.

SUBSTANCE	PROFILE (Weight Fraction of Total Organic Gas)									
	Natural Gas		Field Gas			Refinery Gas		Process Gas		Landfill Gas
	Internal Combustion Engine (SCR)	Gas Turbine (SCR/CO Catalyst)	Steam Generator (LNB, EGR)	Utility Boiler (Uncontrolled)	Internal Combustion Engine (Uncontrolled)	Process Heater (LNB)	Process Heater (SCR)	Internal Combustion Engine (Uncontrolled)	Steam Generator (LNB, EGR)	
Methane	0.9439	0.8064	0.7346	0.9004	0.5079	0.1873	0.2337	0.9134	0.8059	
Ethane	0.0373	0.0595	0.0830	0.0713	0.1518	0.1756	0.1774	0.0510	0.0181	
Propane	0.0098	0.0473	0.0443	0.0179	0.2227	0.3484	0.2908	0.0203	0.0102	
Isobutane	0.0015	0.0089	0.0161	0.0023	0.0347	0.1158	0.0484	0.0034	0.0023	
Butane	0.0024	0.0526	0.0274	0.0027	0.0640	0.0679	0.1029	0.0049	0.0409	
Neopentane	0.0000	0.0001	0.0002	ND	0.0001	0.0001	0.0001	ND	0.0018	
Isopentane	0.0009	0.0045	0.0140	0.0010	0.0103	0.0174	0.0250	0.0019	0.0015	
n-Pentane	0.0008	0.0039	0.0131	0.0008	0.0060	0.0104	0.0233	0.0015	0.0015	
Ethylene	ND	0.0090	ND	ND	ND	0.0636	0.0604	ND	ND	
cis-2-Butene	ND	0.0012	ND	ND	ND	ND	0.0069	ND	ND	
Cyclopentane	ND	ND	0.0038	ND	0.0005	ND	ND	ND	ND	
Ethyne	ND	ND	ND	ND	ND	0.0002	ND	ND	ND	
C6+	0.0031	0.0057	0.0634	0.0033	0.0019	0.0119	0.0215	0.0033	0.0001	
Unknown C4										0.1161
Unknown C5		0.0008				0.0014	0.0094			

ND - Not Detected
 SCR - Selective Catalytic Reduction
 LNB - Low NOx Burner
 EGR - Exhaust Gas Recirculation

also had the highest percentage of C2 and C3 hydrocarbons in the fuel. The fuel and emissions profiles for the landfill gas and natural gas IC engine also are similar. This indicates that the VOC profile changes little as a result of the combustion process at least for IC Engines. This is expected since IC Engines have short residence times and it is expected that some fuel will escape the engine without being exposed to combustion conditions.

1,3-Butadiene was detected at the landfill and field gas IC engines. In both cases, the overall contribution to the profile was small. It should be noted that the hold time for the natural gas IC engine exceeded two hours. Over this time period, significant decay in 1,3-Butadiene levels may have occurred resulting in the nondetection.

E.4 NO_x Speciation

Another key objective of the program was to speciate NO_x emissions from each source. Species that were measured include NO and NO_x. NO₂ was determined by difference of the NO_x and NO measurements. Table E-5 summarizes the NO_x speciation results for each source. The type of NO_x control device at each source, 7% O₂ corrected NO, NO₂ and NO_x concentrations, and NO to NO_x ratio are also provided in Table E-5. Most of the sources except the natural gas IC engine operated fuel lean as indicated by the stack oxygen levels. The natural gas IC engine, however, was operated fuel rich. Overall, the IC engines had the highest NO_x concentrations. The natural gas utility boiler also had a high NO_x concentration. Sources with NO_x control devices had lower NO_x emission concentrations. These sources also had the lowest ratio of NO to NO_x. NO_x emissions from sources without NO_x control were almost entirely composed of NO.

for each detected target analyte were then divided by the total weight fraction of detected VOCs in the stack gas to generate the profiles in Table E-4. The values are provided to four digits as specified in the ARB Speciation Manual dated July, 1989. Only those VOC target analytes detected at one or more of the sources tested are shown. A complete list of target analytes and detection limits is provided in Table 5-5.

It is important to note the method of generating the profiles assumes that VOCs which were not detected in any of the runs do not contribute to the profile. This assumption can generate significant error if the sum of detection limits for nondetected substances is on the same order of magnitude as the sum of detections. The detection limit ratios, defined as the ratio of the sum of detection limits in parts per billion weight dry (ppbw,dry) for nondetected substances to the sum of detections in ppbw,dry for detected substances, were 0.0079, 0.0096, and 0.0099 for the landfill, field, and natural gas IC engines, respectively. These detection limit ratios are low indicating the detection limit treatment procedures have little influence on the IC Engine profiles. For the other sources, the detection limit ratios were 0.86 (utility boiler), 0.96 (process heater with LNB), 1.1 (gas turbine), 1.8 (steam generator), and 2.5 (process heater with SCR). For these sources, the assumptions described above may result in significant error. The detection limits had a significant impact on the uncertainty as indicated by the detection limit ratio of the external combustion sources and gas turbine VOC emissions profiles because:

- 1.) these devices have low total organic emissions, from 1 to 10 ppmv. Low total organic emission levels require very sensitive analysis techniques especially for C1 through C3 hydrocarbons. These techniques were beyond the scope of the program; and
- 2.) the extensive list of target analytes, over 100, yielded a large number of nondetected substances. One of the goals of the program was to quantify all VOCs in the emissions. Because of this goal, many substances were included on the target list even though there was a low probability of their presence in the emissions.

Because of the high uncertainty of the profiles for the external combustion sources and the gas turbine, no profiles were presented for these sources.

The IC engine profiles in Table E-4 indicate that methane was the most prevalent VOC in the exhaust gases from each source. The field gas IC engine had the lowest percentage of methane and the highest percentage of C2 and C3 hydrocarbons. This is not surprising since this source

1.0 PROJECT DESCRIPTION

The California Air Resources Board (ARB) is developing strategies for reducing ambient ozone concentrations in many parts of the State. The basis for these strategies will be computational modeling of atmospheric transport and chemistry processes for ozone formation. A key assumption in such modeling efforts is the amount of each species involved in the transport and chemistry of ozone formation which is released into the atmosphere by specific sources. While a considerable database exists for emissions of ozone precursors from stationary sources, there are significant gaps in the database for gaseous fuel fired sources in California. These sources account for nearly all of the fossil fuels burned in a wide variety of stationary emissions sources in California.

1.1 Background

It is well established that oxides of nitrogen (NO_x) and volatile organic compounds (VOC) are precursors to ozone formation in the atmosphere. Ozone is an irritant in the lower atmosphere but is an essential component of the upper atmosphere as it reflects harmful ultraviolet radiation. The 1990 Clean Air Act Amendments have established stringent requirements for areas which do not meet National Ambient Air Quality Standards for ozone. California has several ozone non-attainment areas including Los Angeles which is widely recognized as the worst in the country. Sources in ozone non-attainment areas will need to install Reasonably Available Control Technology (RACT) to control NO_x and VOC emissions from combustion sources emitting as little as 10 tons per year to achieve an overall emissions reduction of 15% per year for the next six years.

To ensure that available resources are applied in the most cost-effective manner, the California Air Resources Board (ARB) is evaluating ozone control strategies based on computational modeling of atmospheric transport and chemistry. This modelling effort requires a reliable and comprehensive database of source emissions data to ensure the modeling results will be valid. While a volatile organic species profile database currently exists for approximately 270 source categories, there are still a number of natural gas and refinery gas fired source types prevalent in California for which species profiles are unreliable or do not exist. In addition, speciation of oxides of nitrogen has not been well established. Therefore, the need exists for new data to characterize volatile organic and NO_x species profiles for these sources.

TABLE E-5. CONTINUOUS EMISSION MONITORING NO AND NO_x RESULTS.

DEVICE	Air Pollution Control Device	NO ppmv, Dry 7%O ₂	NO _x ppmv, Dry 7%O ₂	NO ₂ (1) ppmv, Dry 7%O ₂	NO/NO _x Ratio (%)
RICE					
Landfill Gas	None	102.7	102.5	-0.2	100
Field Gas	None	375.5	377.0	1.5	100
Natural Gas	SCR	77.6	91.6	14.0	85
Gas Turbine					
Natural Gas	SCR/CO Catalyst	15.1	17.5	2.4	86
Process Heater					
Refinery Gas	LNB	29.2	29.8	0.7	98
Refinery Gas	SCR	8.4	8.9	0.6	94
Steam Generator					
Natural Gas	LNB,EGR	17.5	17.6	0.1	99
Utility Boiler					
Natural Gas	None	90.3	90.2	-0.1	100

(1) Difference between NO_x and NO measurements.

RICE - Reciprocating Internal Combustion Engine.

EGR - Exhaust Gas Recirculation

LNB - Low NO_x Burner

SCR - Selective Catalytic Reduction

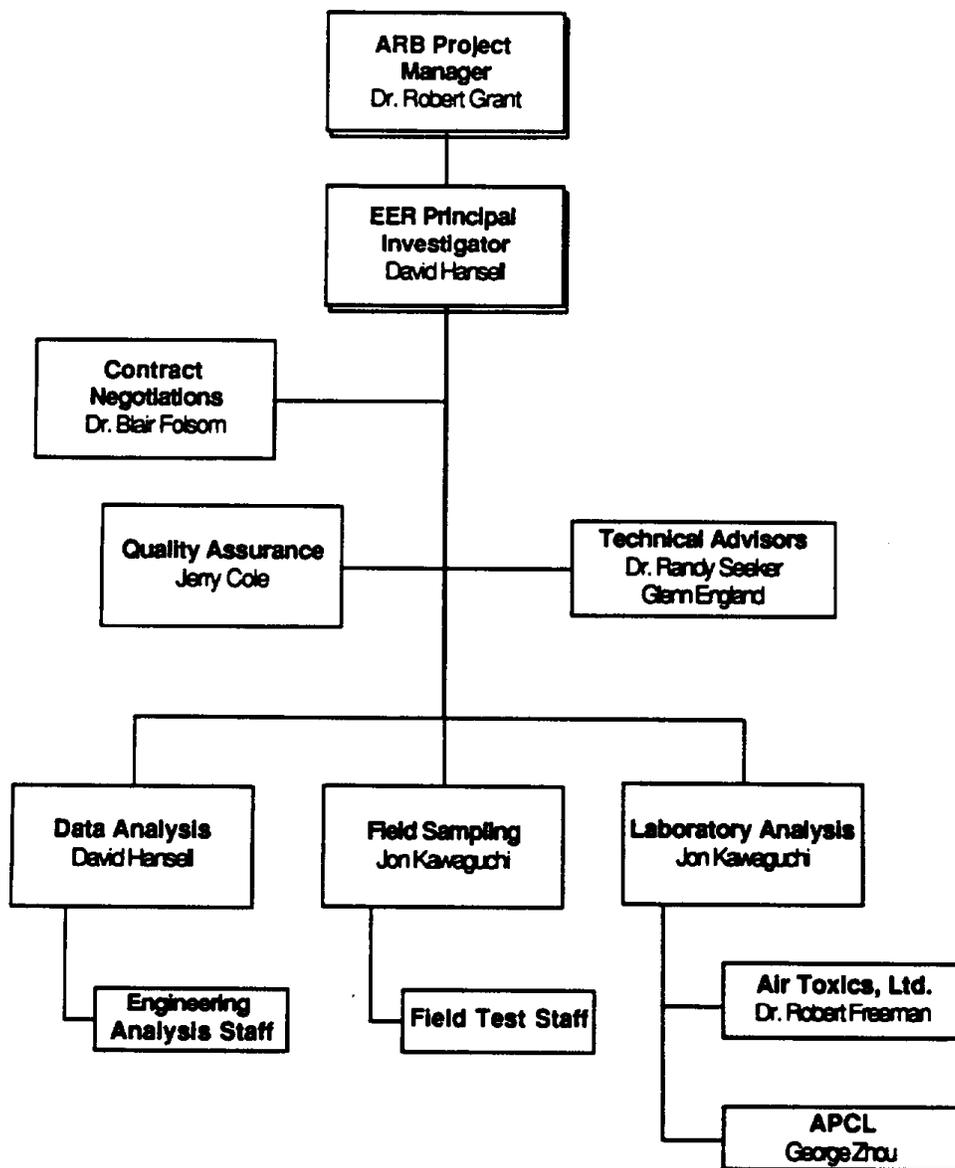


Figure 1-1. Project Team

1.2 Objectives

The objectives of this program included:

- Providing accurate and complete speciation profiles for volatile organic compounds (VOC);
- Quantifying selected toxic air contaminants from the California Air Toxics “Hot Spots” Information and Assessment Act of 1987 (AB2588);
- Providing the ARB with high quality data which is fully defensible and meets Quality Assurance goals commensurate with use in development of ozone reduction strategies; and
- Providing the first comprehensive evaluation of nitrogen oxides speciation (NO and NO₂) from gas fired combustion sources.

1.3 Project Team

This section describes EER’s project team for the program. The project structure is illustrated in Figure 1-1. The project team included:

- Energy and Environmental Research Corporation — was responsible for source selection, emissions measurements, and engineering analysis;
- Air Toxics Ltd. — was responsible for the aldehyde, ketone, and fuel analyses.
- Applied P & Ch Laboratory, Inc. — was responsible for the remainder of the volatile organic analysis.

The organization in Figure 1-1 establishes clearly defined areas of responsibility and lines of communication for the project team members. The EER Principal Investigator, Mr. David Hansell, was responsible for the schedule and cost performance on the program and reported to the ARB Program Manager, Mr. Robert Grant. Mr. Hansell also was responsible for coordinating all sites to be tested in the program and the data reduction. Mr. Jon Kawaguchi was responsible for carrying out all field sampling activities, including equipment calibration and preparation,

2.0 SOURCE AND SUBSTANCE SELECTION

To develop a representative database of VOC and NO_x species profiles requires detailed planning and an accurate and complete emissions characterization. Key steps in the planning phase of the program included the selection of substances and sources for testing. The following sections describe the rationale for selecting the sources and substances included in this program.

2.1 Substance Selection

To accurately model ozone formation resulting from combustion sources requires detailed VOC and NO_x speciation profiles for a variety of source types. VOCs which can participate in ozone formation reactions include¹:

- Paraffins (Alkanes)
- Olefins (Alkenes)
- Diolefins
- Acetylenes (Alkynes)
- Naphthenes (Cycloparaffins or Cyclohexanes)
- Aromatics
- Oxygenates (Alcohols, Aldehydes, Ketones, Ethers)
- Chlorinated hydrocarbons

Extensive resources would be required to quantify substances in each of the major VOC categories. For most systems it is not necessary to quantify all of the VOCs listed above and substances should be eliminated based on:

- (1) Negligible photochemical reactivity;
- (2) Low potential for emission; and
- (3) Sampling and analytical limitations.

Considering items 1 to 3, the list of VOC and NO_x species shown in Table 2-1 was developed. All of these compounds were included on the exhaust target analyte list. Selected species were quantified in the fuel. The rationale for the selection of the VOCs and Air Toxics listed in Table 2-1 is provided in the following sections.

mobilization, procurement of reagents, sampling and recovery of field samples, and all other activities in the field. Mr Kawaguchi was assisted by Mr. Rob Campbell.

The CARB also provided equipment and resources to conduct initial method validation tests and sample and analyze 1,3-Butadiene onsite. Bob Okamoto of the CARB assisted in planning the stability tests and he analyzed the tedlar bag sample prepared for the stability test. Kevin Mongar also of the CARB operated the onsite GC for 1,3-Butadiene and prepared the report given in Attachment 1.

1.4 Guide to Test Report

This test report contains the following information:

Executive Summary

Section 1 - Project Description

Section 2 - Source and Substance Selection

Section 3 - Source Process and Equipment Description

Section 4 - Test Program

Section 5 - Test Results

Section 6 - Quality Assurance

Appendices

Section 2 summarizes the procedures used to select sources and substances for the testing program. Detailed descriptions of the equipment presented in Section 2.0 are provided in Section 3.0. Process schematics also are given in Section 3.0. The process and emissions sampling matrix, source testing methods and analytical procedures are described in Section 4.0. Section 5.0 describes the results from the testing program including the testing schedule, process operation, and NOx and VOC results. Key QA/QC results also are presented in Section 5.0 so the reader can assess the quality of the results. The complete QA/QC program which was implemented is described in Section 6.0. Raw sampling and analytical results for each source are provided in Appendices A through H.

2.1.1 VOC Selection

There are several basic VOC emission mechanisms for combustion sources. Key mechanisms for gas fired units include:

- (1) Emissions resulting from incomplete destruction of organics in the fuel; and
- (2) Emissions resulting from reactions between precursors.

The first mechanism indicates that organics in the fuel also will be present in the exhaust. Table 2-2 illustrates the composition of gaseous fuels used in combustion units in California². This table shows that lighter hydrocarbons (C3 or less) dominate the profiles. Refinery gas has the greatest concentration of higher molecular weight substances. This is expected since refinery gases are generally off-gases from distillation towers where crude oils are heated. To represent a wide range of fuel compositions, lighter paraffin, olefin, diolefin, acetylene, naphthene, and aromatic substances were selected for quantification as shown in Table 2-1. To ensure that complete profiles were developed, other C6 and C7 plus hydrocarbons also were included on the target analyte list.

The second mechanism contributing to organic emissions from combustion devices involves reactions between precursors. This mechanism may result in the formation of organics which are not present in the fuel. Table 2-3 compares fuel and exhaust organic profiles for IC Engines fired on pipeline and field natural gas². Differences in the composition of the fuel and exhaust shown may result from the destruction and/or formation of organic substances. Table 2-3 indicates that there is a shift from methane in the fuel to heavier hydrocarbons (C2-6) in the exhaust. This shift probably results from the fast rate of combustion of methane in the fuel as opposed to the generation of heavy hydrocarbons.

Additional analysis of the assumptions discussed above will be included in the results section.

2.1.2 Air Toxics

Another goal of the program was to quantify AB2588 substances which may be present in the exhaust. To this end, AB2588 was reviewed and a list of potential air toxics was compiled. This list is shown in Table 2-4. AB2588 requires that formaldehyde stack testing be conducted for natural gas fired utility boilers (see AB2588 appendix D). Formaldehyde, acetaldehyde, and acrolein were included on the target list for each source as shown in Table 2-1.

TABLE 2-1. EMISSIONS AND FUEL ANALYSES (2).

Paraffins	Olefins	Acetylenes
Methane*		Ethyne*
Ethane*	Ethylene*	Propyne**
Propane*	Propylene*	Butynes**
Butanes*	Butenes*	Pentyne**
Pentanes*	Pentenes**	
Hexanes**		
Other C6*	Naphthenes	Aromatics**
C7 Plus*	Cyclopropane**	Benzene
	Cyclobutane**	Toluene
	Cyclopentane*	Ethylbenzene
	Cyclohexane**	Xylenes (m,p,o)
		Styrene
		Phenol
		1,3,5-Trimethylbenzene
		1,2,4-Trimethylbenzene
		Naphthalene
Oxygenates**	Chlorinated Hydrocarbons (1)**	Carbon Disulfide**
Aldehydes (C1-C4)		
Ketones (C3-C4)		
Ethers		
NOx **	Diolefins**	
NO	1,3-Butadiene	
NO2	Propadiene	

(1) 29 halogenated organics including ethylene dibromide and ethylene dichloride.

(2) Detailed fuel and emission target substances given in Tables 4-2 and 4-3.

* Fuel and emission analysis.

** Emission analysis only.

TABLE 2-3. COMPARISON OF EMISSIONS AND FUEL ORGANIC COMPOSITION FOR GAS FIRED IC ENGINES (Data from previous testing).²

SUBSTANCE	PROFILES (% of Total Hydrocarbons)		PROFILE RATIO (1)
	Fuel	Exhaust	
<i>Field Natural Gas</i>			
C1	86.12	61	0.71
C2	3.49	6.5	1.86
C3	3.71	8.6	2.32
C4	3.38	8.6	2.54
C5	3.27	11.6	3.55
Acetaldehyde	na	0.38	na
Formaldehyde	na	2	na
Acrolein	na	0.1	na
PAH	na	0.01	na
Benzene	0.017	0.28	16.05
Toluene	0.013	0.09	6.88
xylenes	0.004	0.03	8.09
propylene	0.006	0.83	149.30
<i>Pipeline Natural Gas</i>			
C1	89.50	70	0.78
C2	8.10	13.67	1.69
C3	3.30	12.01	3.64
C4	0.53	1.91	3.60
C5	0.06	0.34	5.67
Acetaldehyde	na	0.12	na
Formaldehyde	na	0.91	na
Acrolein	na	0.03	na
PAH	na	0.01	na
Benzene	0.00020	0.08	400.00
Toluene	0.00008	0.02	250.00
xylenes	0.00006	0.007	116.67
propylene	0.016	0.74	46.25

(1) Ratio of exhaust to fuel hydrocarbon profile.

TABLE 2-2. FUEL ANALSES FROM OTHER TESTING PROGRAMS.²

Substance	Concentration (Volume %)			
	Field NG	Pipeline NG	Refinery Gas	TEOR Gas
C1	86.1	89.5	36	4.2
C2	3.5	8.1	17	0.32
C3	3.7	3.3	16	0.19
C4	3.4	0.53	4	0.09
C5	3.3	0.06	1	0.14
C6	na	na	0.77	2.3
xylene	0.0034	0.00006	na	0.032
naphthalene	nd	nd	na	na
propylene	0.005	0.016	na	0.013
toluene	0.012	0.00008	na	0.0068
benzene	0.016	0.0002	na	0.0039
ethyl benzene	na	na	na	0.012
carbon dioxide	na	na	0.22	91.28
carbon monoxide	na	na	0.61	na
hydrogen	na	na	22	na
nitrogen	na	na	3.2	1.27
oxygen	na	na	1.8	0.24
hydrogen sulfide	na	na	na	0.098

NG - Natural Gas

Several air toxics also must be quantified by source test or engineering analysis as shown in Table 2-4 and described in AB2588 appendices C-I and -II. The exhaust from each source was analyzed for EDB, EDC, benzene, toluene, xylenes, propylene, carbon disulfide, and phenol as shown in Table 2-1. To determine if PAH testing was warranted, EER's AB2588 Western States Petroleum Association (WSPA) database was surveyed to determine the levels of PAH quantified in previous testing programs. The WSPA database contains over 1000 data points for gas fired combustion devices. From the database it was found that, in general, congener specific PAH emissions are less than 2 ppb. For IC Engines, the maximum emission concentration was 41 ppb for naphthalene. This is approximately 0.0027 percent of the hydrocarbon profile. For boilers and process heaters, the maximum emission concentration was 9 ppb for anthracene. This is approximately 0.2 percent of the hydrocarbon profile. In most cases, the PAH contribution to the hydrocarbon profile is less than 0.05% for boilers and process heaters. Because PAH compounds do not contribute significantly to the overall VOC distribution, these compounds were not included on the target analyte list.

2.2 Source Selection

One key objectives of this project was to select sources which are representative of the population of devices present in California. The Southern California Air Basin (SCAB) was selected as the primary target for testing due to its severe pollution problems. To select sources for testing in the SCAB, EER used the following procedure:

(1) Source Classes of Interest

For this project, the ARB identified the following source classes for testing:

Natural Gas Fired

- Utility Boilers & Heaters
- Oil and Gas Extraction Boilers & Heaters
- Refuse Systems
- Internal Combustion Engines

Process Gas Fired

- Refinery Boilers & Heaters

TABLE 2-4. AB2588 AIR TOXICS OF INTEREST

Substance	AB2588 Appendices		
	C-I	C-II	D
Acetaldehyde	ng	p	
Acrolein	ng		
Benzene	ng,pg	p	
Carbon Disulfide		p	
Cresol		p	
Dimethyl Sulfate		p	
EDB		p	
EDC		p	
Formaldehyde	ng,pg	p	ng (1)
PAH	ng	p	
Phenol	pg	p	
POM	ng	p	
Propylene	ng		
Toluene	ng	p	
Xylenes	ng	p	

(1) Utility boilers only.

ng: Natural Gas

pg: Process Gas

p: Petroleum Combustion

C-I: Device/process listing, quantified by engineering analysis or source test.

C-II: Industry/emitting process listing, quantified by engineering analysis or source test.

D: Listing of required source tests.

TABLE 2.5. SUMMARY OF BASELINE EMISSIONS FOR THE SOUTH COAST AIR BASIN (1989 INVENTORY)

SCC	INDUSTRY TYPE	DEVICE CLASS	DEVICE TYPE	NUMBER OF SOURCES	TOG EMISSIONS (TONS/YR)			TOG PROFILE (%)
					MAX	MIN	AVE	
10100702	ELECTRIC GENERATION	BOILERS	<100 MMBTU/HR	2	0.1	0.1	0.0	0.00
20100702	ELECTRIC GENERATION	IC ENGINE	RECIPROCATING	1	2	2	0.0	0.03
10200603	INDUSTRIAL	BOILERS	<10 MMBTU/HR	5	1.9	0.7	105.3	0.06
10300603	COMMERCIAL	BOILERS	<10 MMBTU/HR	9	1	0.5	66.4	0.07
31000414	OIL AND GAS PRODUCTION	STEAM GENERATOR	NATURAL GAS	2	3	3	0.0	0.02
10300601	COMMERCIAL	BOILERS	>100 MMBTU/HR	5	2	1.4	42.1	0.10
10200604	INDUSTRIAL	BOILERS	COGENERATION	1	8.7	8.7	0.0	0.13
10201402	INDUSTRIAL	BOILERS	CO BOILER	4	6	3.2	65.2	0.19
20300203	COMMERCIAL	IC ENGINE	TURBINE: COGEN	2	12	6.5	119.7	0.12
10201401	INDUSTRIAL	BOILERS	CO BOILER	3	11.3	4.5	132.3	0.20
10900602	COMMERCIAL	BOILERS	10-100 MMBTU/HR	23	1	0.8	32.0	0.27
10200601	INDUSTRIAL	BOILERS	>100 MMBTU/HR	26	2.2	0.1	55.0	0.34
30600105	PETROLEUM INDUSTRY	PROCESS HEATER	NATURAL GAS	51	5.3	0.6	146.7	0.45
10200602	INDUSTRIAL	BOILERS	10-100 MMBTU/HR	59	2	0.1	55.2	0.59
10100602	ELECTRIC GENERATION	BOILERS	<100 MMBTU/HR	5	27.5	10	128.5	0.75
20200204	INDUSTRIAL	IC ENGINE	RECIPROCATING: COGEN	9	35.9	7.5	163.7	1.01
20300204	COMMERCIAL	IC ENGINE	RECIPROCATING: COGEN	4	25	8.6	40.2	1.07
20300202	COMMERCIAL	IC ENGINE	RECIPROCATING	2	72.6	6	119.8	1.18
10200701	INDUSTRIAL	BOILERS	REFINERY	48	10.4	2	102.8	1.43
20200201	INDUSTRIAL	IC ENGINE	TURBINE	10	74	14	161.1	2.09
20100202	ELECTRIC GENERATION	IC ENGINE	RECIPROCATING	10	57	17	72.1	2.55
20200203	INDUSTRIAL	IC ENGINE	TURBINE: COGEN	12	126	18.1	194.7	3.25
30600106	PETROLEUM INDUSTRY	PROCESS HEATER	PROCESS GAS	158	5.7	0.3	85.1	3.34
20300201	COMMERCIAL	IC ENGINE	TURBINE	13	78	25.7	90.0	5.01
20100201	ELECTRIC GENERATION	IC ENGINE	TURBINE	27	93	17.6	123.6	7.11
10100601	ELECTRIC GENERATION	BOILERS	>100 MMBTU/HR	35	60.1	0.6	120.1	7.67
20200202	INDUSTRIAL	IC ENGINE	RECIPROCATING	72	296	51.4	106.5	60.82

UNDERLINE - DEVICES SPECIFIED IN THE RFT

RSD - Relative standard deviation

(2) Number of Devices to Test in Each Source Class

The number of sources tested in a class of devices depended on the contribution of that class to emissions in the SCAB and the variability of the design practices used. As the contribution of the source class to overall emissions increased and/or the number of different designs increased; more devices needed to be tested to represent emissions from the class.

(3) Specific Devices to Test in a Source Class

If there was extensive information available about the design and operating parameters influencing emissions within a source class, sources were selected based on their design and operation.

OR

If insufficient information was available about the range of designs used in a source class, the specific device tested depended on its emissions level relative to the other sources.

To determine the significant emitters in the SCAB (Step 2), EER contacted the California Air Resources Board to obtain a listing of the 1989 criteria pollutant inventory. The 1991 inventory was not requested because it was not complete. The 1989 inventory lists total organic gas emissions (TOG), reactive organic gas emissions (ROG), and NO_x emissions for each stationary combustion source in the State. Table 2-5 lists statistics for the source classes identified by the CARB in the RFP and other similar source classes. Only sources in the SCAB are listed. Table 2-5 shows that Industrial Reciprocating IC Engines emit the largest quantity of TOG at 4057 tons/yr. This is over 60% of the TOG emissions for the source classes listed in Table 2-5. Industrial Reciprocating IC Engines also have the highest average per source TOG emissions at 51.4 tons/yr. The classes identified by the CARB for this study account for approximately 97% of the TOG emissions in the SCAB.

Table 2-6 summarizes the sources which were selected for testing. The sources were selected using one of the criteria specified in Step 3 described above. The following sections describe the sources in each class.

2.2.1 Utility Boiler

Utility boilers contributed to over 7% of the TOG emissions in the SCAB in 1989 (see Table 2-5). This percentage ranks utility boilers as the second most important TOG source category. Even though utility boilers had a significant contribution to overall TOG emissions, only one source was tested. Additional utility boilers were not tested because of the uniform composition of the fuels burned, pipeline natural gas, and the need to test additional reciprocating IC engines. As discussed in Section 2.1.1, one of the primary factors influencing emissions is the fuel composition. Generally, the pipeline natural gas which utility boilers burn has a relatively uniform composition.

Since little utility boiler design information was available, a utility boiler with average emissions was selected for testing. This unit is representative of the average operating schedule and combustor size within the SCAB.

2.2.2 Gas Turbine

Overall gas turbines contributed to over 17% of the TOG emissions in the SCAB in 1989 (see Table 2-5). Even though gas turbines had a significant contribution to overall TOG emissions, only one source was tested. Additional gas turbines were not tested because of the uniform composition of the fuels burned, pipeline natural gas, and the need to test additional reciprocating IC engines. As discussed in Section 2.1.1, one of the primary factors influencing emissions is the fuel composition. Generally, the pipeline natural gas which gas turbines burn has a relatively uniform composition.

2.2.3 Reciprocating IC Engines

Due to the significant TOG contribution (over 60%) of reciprocating IC engines in the SCAB, three IC engines, two industrial and one utility, were tested. To determine the specific engine types to be tested, results from an extensive series of tests conducted on IC Engines for WSPA in the Santa Barbara area were analyzed. During this program, it was found that the type of natural gas burned, field or pipeline natural gas, had a major impact on TOG emissions and the VOC profile⁴. Table 2-3, presented in Section 2.1.1, shows that field natural gas fired engines have a larger percentage of C4 through C5 hydrocarbons, and BTX. This is a direct result of the fuel composition. Field natural gas is taken directly from crude oil production streams at the well and has no further processing. As a result, field natural gas generally has more C4 and C5

TABLE 2-6. SOURCES TESTED.

SOURCE CLASSIFICATION CODE	SOURCE TYPE	FUEL TYPE	UNIT ID	CAPACITY	APC DEVICE	REASON SELECTED
10100601	Utility Boiler	Pipeline NG	H	510 MMBtu/hr	None	Average Emissions
20100201	Gas Turbine: Cogen	Pipeline NG	F	85 MWe	SCR/CO Cal/ Duct Burners	Sophisticated Control System
20100202	Refuse System IC Engine	Landfill Gas	A	2650 Hp	None	Landfill Gas
20200202	Industrial Reciprocating IC Engine	Field NG	D	162 Hp	None	Field Gas
20200202	Industrial Reciprocating IC Engine	Pipeline NG	E	500 Hp	SCR	Pipeline Gas
31000414	Steam Generator	Natural/TEOR Gas	C	62.5 MMBtu/hr	LNB,EGR	Average Emissions
30600106	Petroleum Refinery Process Heater	Refinery Gas	G	215 MMBtu/hr	SCR	Low Molecular Wt.
30600106	Petroleum Refinery Process Heater	Refinery Gas	B	5X99.4 MMBtu/hr	LNB	High Molecular Wt.

NG - Natural Gas

LNB - Low NOx Burners

SCR - Selective Catalytic Reduction

EGR - Exhaust Gas Recirculation

Section 2 References

- (1) RG Derwent and AM Hough, Atmospheric Ozone Research and its Policy Implications, Elsevier Science Publishers B.V., Amsterdam, (1989), pp. 589-603.
- (2) Petroleum Industry Combustion Device Emission Factor Database, prepared for the Western States Petroleum Association by Energy and Environmental Research.
- (3) JH Gary and GE Handwerk, Petroleum Refining, Marcel Dekker, New York, (1975), Vol. 5, p. 21.
- (4) R. Stockdale, M. Lev-On, N. Meeks, CH Reheis, Western States Petroleum Association Pooled Source Test Program: Industry Specific Emissions Factors, Presented at the SARA III Title Conference, New Orleans, March 1991.

hydrocarbons than pipeline natural gas (see Table 2-3). To represent emissions in California, an IC engine operating on field natural gas as well as one firing pipeline natural gas was tested. In addition to these fuels, an IC engine fired on landfill gas also was tested.

2.2.4 Industrial Process Heaters

Two refinery process heaters were tested. Process heaters do not have a large contribution to TOG emissions in the SCAB at 3.34%, however, the composition of refinery gas can vary substantially from facility to facility. Fuel composition has a significant impact on the emissions profile. Thus, it was critical that devices with different process gas compositions be tested. Process heaters from facilities with high and low molecular weight fuels were tested. The high molecular weight fuels have larger C2 - C6 percentages which may result in larger C2 - C6 percentages in the exhaust.

2.2.5 Steam Generators

Since there were only 2 steam generators in the SCAB, a unit was selected from Kern county. Kern has a large population of steam generators. 62% (449 out of 720) of the combustion units in Kern county are natural gas fired steam generators. However, TOG emissions from steam generators only account for 2% of the total TOG emissions. Industrial reciprocating IC engines have the largest contribution to TOG emissions in Kern county at 85% of the total. To represent steam generators in Kern county, a unit with average emissions and a typical configuration was chosen.

2.2.6 Control Equipment

To select representative control equipment, the SCAB NOx and TOG emission inventory as discussed previously was used. From this inventory it was found that most gas fired combustion equipment do not have controls in place. Those devices which do have NOx controls, mainly refinery sources, use ammonia injection, burner modification, and/or catalytic reduction. To represent these technologies, refinery process heaters with and without selective catalytic reduction (SCR) and low NOx burners were tested. In addition, a gas turbine with a state of the art control system including a SCR, CO catalyst, and duct burners was tested. Since most non-refinery sources are not currently using post combustion control equipment, uncontrolled sources were a primary focus of the project. However, one industrial IC Engine with an SCR was tested.

3.0 SOURCE DESCRIPTION

Process design and operation were documented as part of the source test program. Process design and operation documentation is especially important for describing the device in sufficient detail to determine the applicability of its emissions to other similar devices. Design parameters also aid in the interpretation of the emissions results.

3.1 Design Parameters

Through site visits and conversations with facility staff, a listing of design parameters for each device tested was compiled. Design parameters for reciprocating and axial internal combustion engines are listed in Tables 3-1a. Each reciprocating IC engine is fired on a different type of fuel. These fuels are representative of those burned in the Southern California Air Basin. The natural gas fired engines are manufactured by Waukesha and the landfill gas engine is manufactured by Cooper. The engines range in size from small (162 Bhp) to large (2650 Bhp) and only one of the engines has a post-combustion control device. The turbine is manufactured by General Electric and has duct burners, CO catalyst, and SCR. The gas turbine is fired on natural gas, while the duct burners are fired on refinery gas. Refinery gas is only a small fraction of the fuel burned.

Table 3-1b lists design parameters for the external combustion sources tested. These sources include a utility boiler, two process heaters, and a steam generator. To control NO_x, three of the sources have low-NO_x burners, flue gas recirculation, and/or selective catalytic reduction. The utility boiler does not have NO_x controls. The furnaces range in size from small (62.5 MMBtu/hr) to large (510 MMBtu/hr). Source B includes 5 process heaters each with a heat input rate of 99 MMBtu/hr.

3.2 Sample Locations

Schematics for each device tested are included in figures 3-1a through h. The sources are listed in the order that they were tested. Stack diameters, number of sample points, and upstream and downstream disturbance distances are summarized in Table 6-2. All of the samples were collected at the stack except at the natural gas IC engine, Source E. At this source, the VOC samples were collected before the SCR and the NO_x CEM was located after the SCR. As shown in Figure 3-1b, Source B has five process heater whose emissions are vented to a single duct which has two stacks. As discussed in Section 4, only a single stack was sampled and total emission

TABLE 3-1a. INTERNAL COMBUSTION ENGINE DESIGN AND OPERATION SUMMARY.

SOURCE TYPE	RECIPROCATING IC ENGINE			GAS TURBINE
SOURCE ID	A	D	E	F
DESIGN				
Manufacturer	Cooper	Waukesha	Waukesha	General Electric
Model	16 SGTA	F1197	5108	na
Power	2650 bhp	162 bhp	548 bhp	85 MWe
Number of Strokes per Cycle	4	4	4	-
Duct Burners	-	-	-	Yes
Turbo Charging	Yes	No	No	-
Post Combustion Controls	No	No	SCR	SCR, CO Catalyst

TABLE 3-1b. EXTERNAL COMBUSTION DESIGN AND OPERATION SUMMARY.

SOURCE TYPE	PROCESS HEATER	STEAM GENERATOR	PROCESS HEATER	UTILITY BOILER
SOURCE ID	B	C	G	H
DESIGN				
Manufacturer	na	Struthers	Foster Wheeler	Riley Stoker
Air Preheater	na	No	No	Yes
Low NOx Burners	Yes	Yes	No	No
Exhaust Gas Recirculation	No	Yes	No	No
Heat Input	5X99	62.5	215	510
Post Combustion Controls	No	No	SCR	No

were determined by multiplying the single stack emission rate by two. The process heater at Source G has three stacks as shown in Figure 3-1g. Only a single stack was sampled and total emissions were determined by multiplying the single stack emission by three.

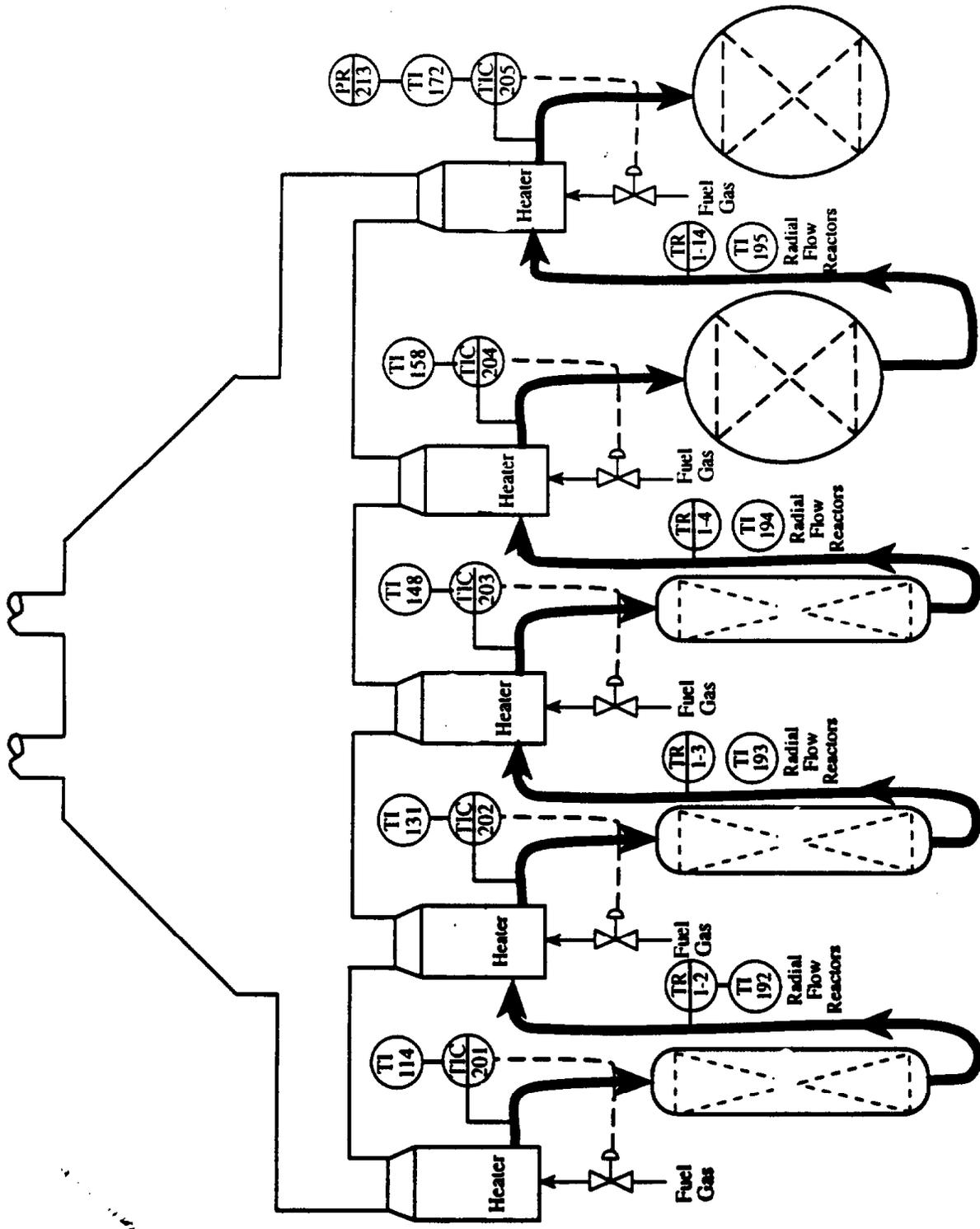


Figure 3-1b. Refinery process heater (source B)

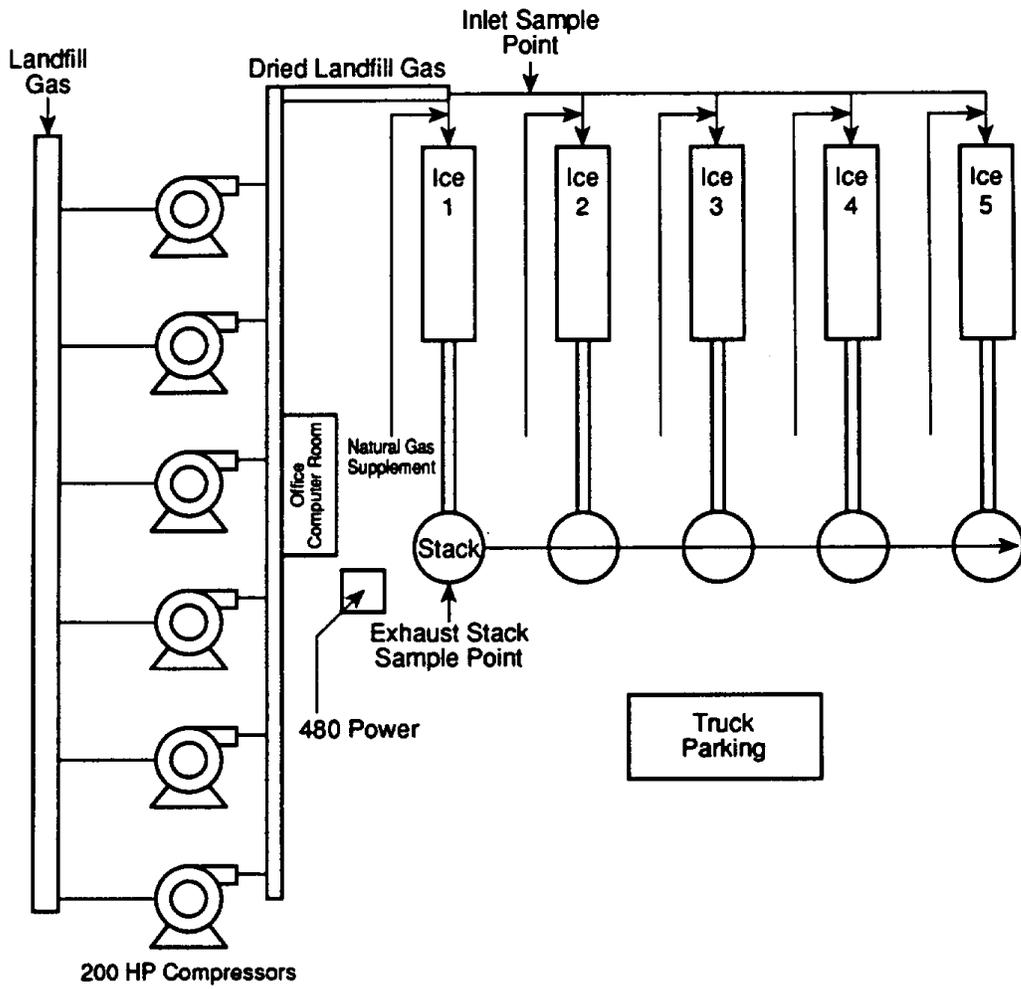


Figure 3-1a. Landfill gas fired IC engine plot plan (source A).

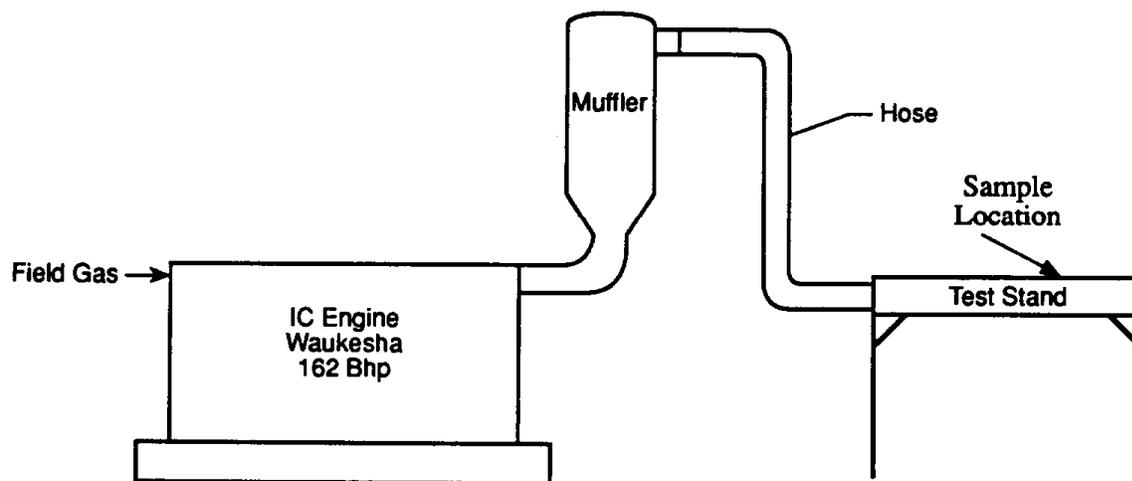


Figure 3-1d. Field gas fired IC engine (source D).

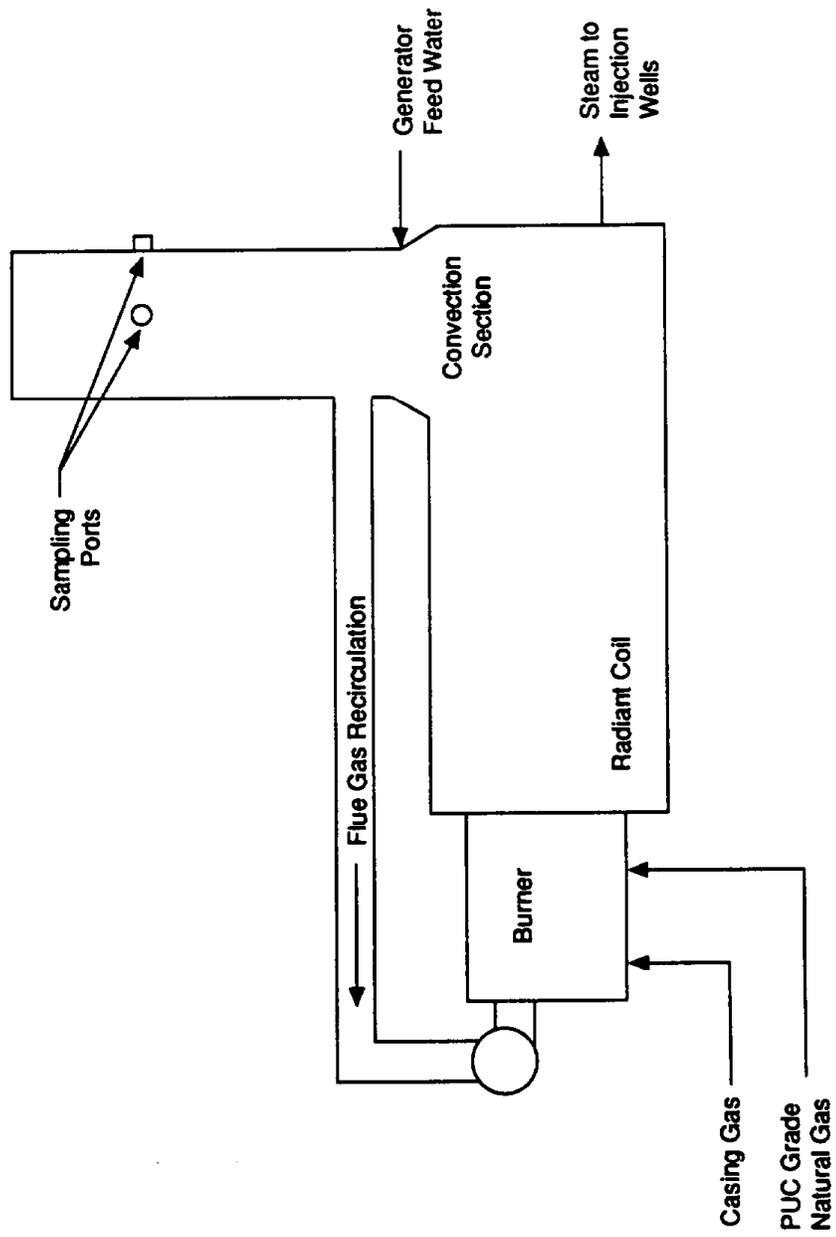


Figure 3-1c. Steam generator (Source C).

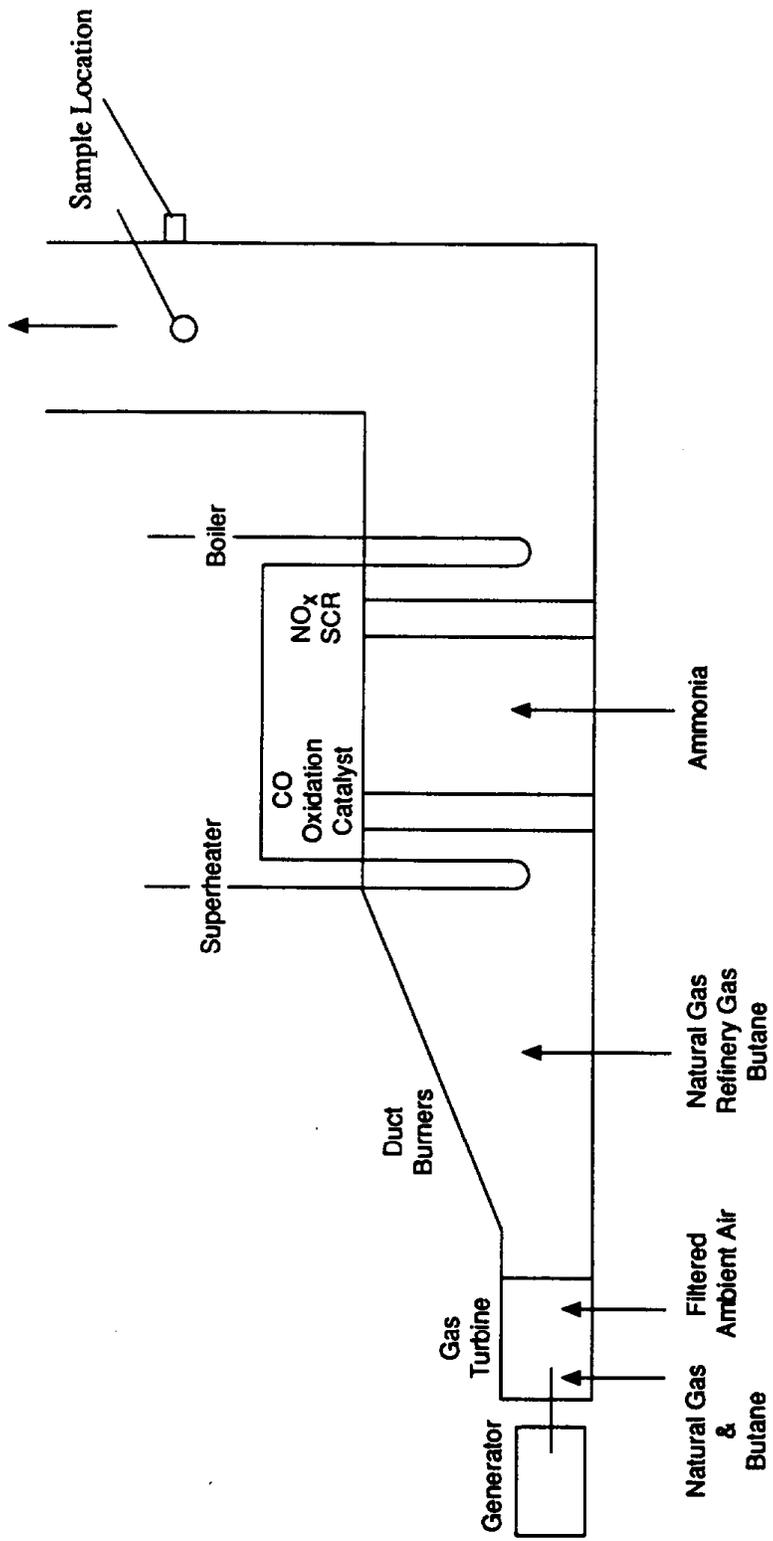


Figure 3-1f. Gas turbine (Source F).

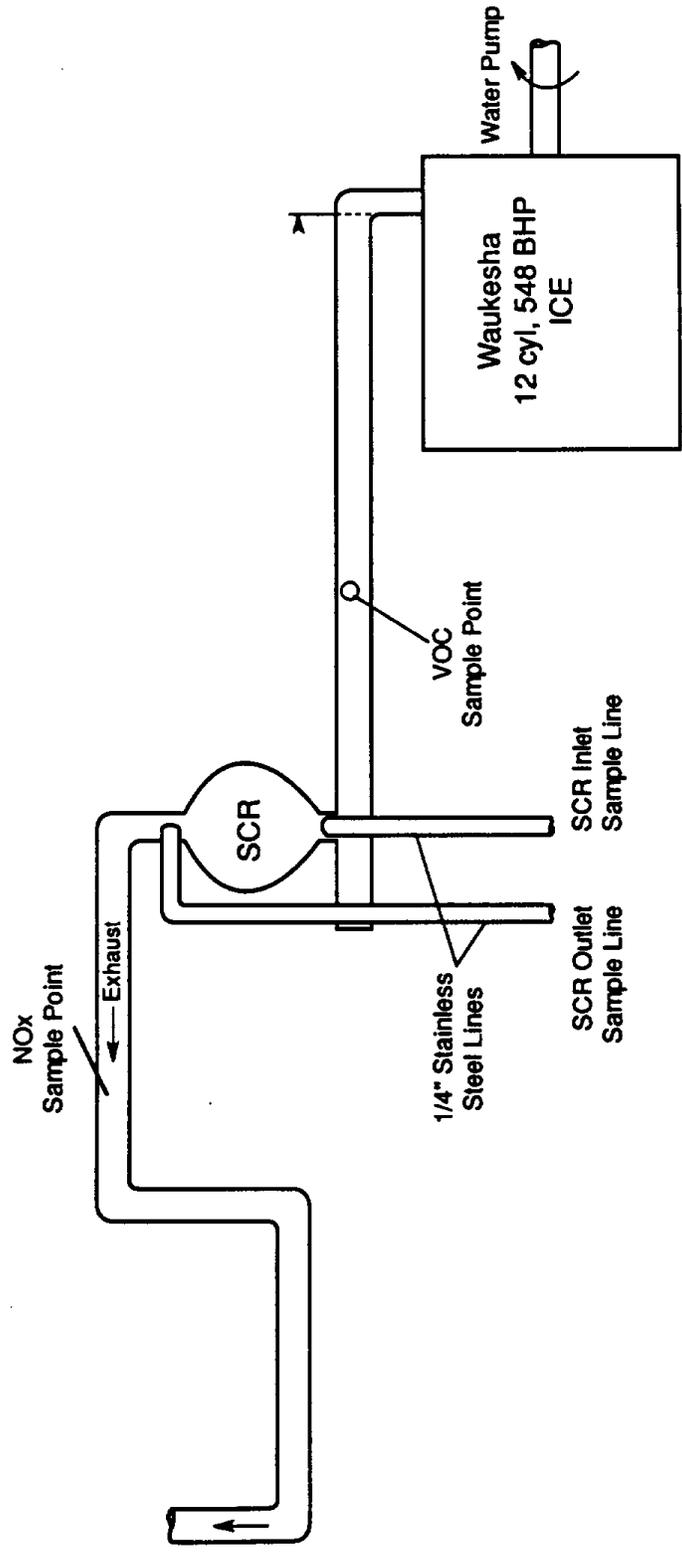


Figure 3-1e. Pipeline natural gas fired IC engine (Source E).

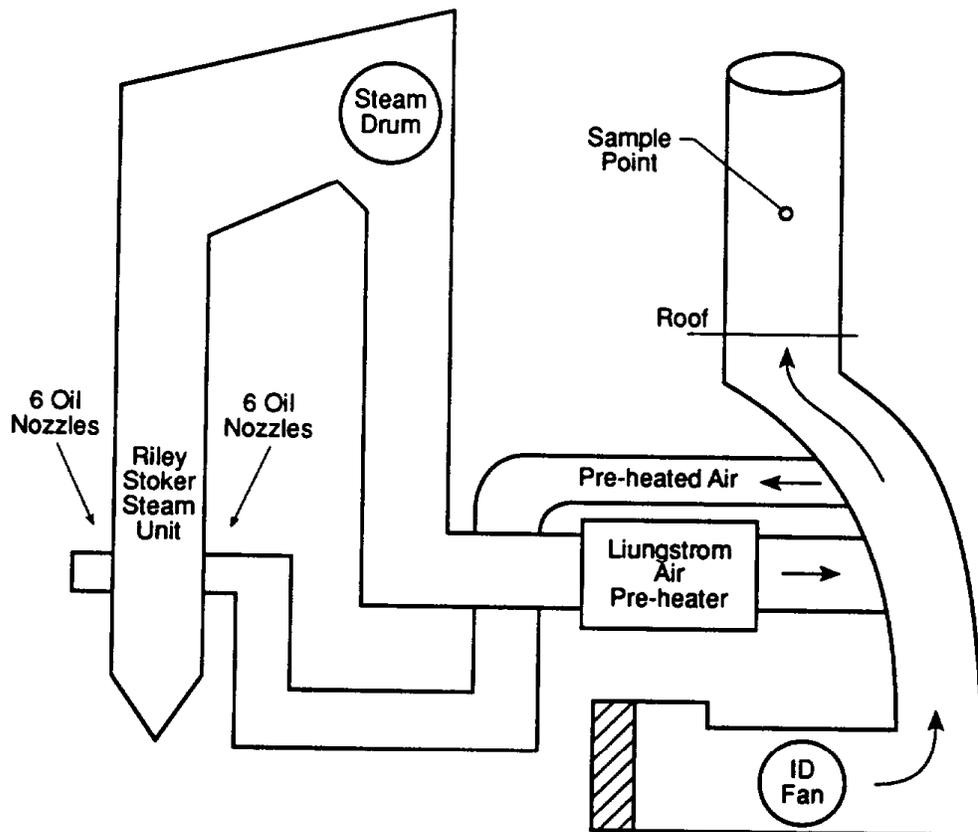


Figure 3-1h. Utility boiler (source H).

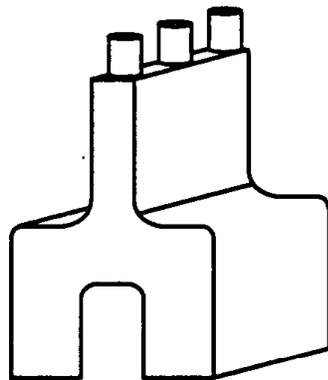
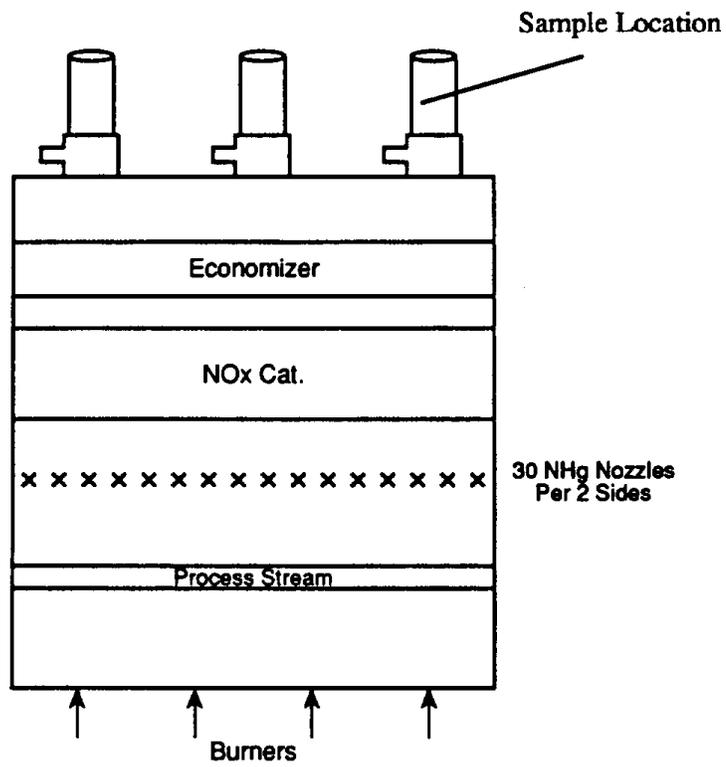


Figure 3-1g. Refinery process heater process drawing (source G).

4.0 TEST PROGRAM

This section describes the on-site test program, sample collection, and sample analysis. The scope of the program is well defined in this section to aid the reader in evaluating the results presented in Section 5.0. Each on-site test program included these activities:

- Process sample collection and analysis
- Process operating and design data collection
- The emission measurements for selected air toxics, volatile organic compounds (VOCs), and oxides of nitrogen (NO_x).

4.1 Test Matrix

The process and emissions sampling matrix for the field testing program is given in Table 4-1. The exhaust was sampled using:

- CARB method 1, 2, and 4;
- Continuous Emission Monitoring for O₂, CO₂, NO and NO_x;
- Modified CARB method 422; and
- CARB method 430.

Highlights from the emissions and fuel sample test matrix and QA/QC procedures are briefly described below. Detailed sampling and analytical descriptions are provided in section 4.2. The QA/QC program is described in section 6.0.

4.1.1 Emissions Test Matrix

CARB method 422 was modified significantly to include an extended target analyte list and modified dilution sampling procedures. CARB method 422 is valid for VOCs except those which are (1) polymeric (high molecular weight), (2) can polymerize before analysis or (3) have very low vapor pressures at stack or instrument conditions. While CARB method 422 has general applicability to VOCs, it has only been validated for selected halogenated VOCs and 1,3-Butadiene. To develop complete VOC profiles, the target analyte list had to be extended beyond halogenated VOCs and 1,3-Butadiene to include those substances listed in Table 4-2. To quantify these compounds, the electron capture detector (ECD) specified in the method was replaced with either a mass spectrometry (MS) detector or flame ionization detector (FID). All of the compounds listed

TABLE 4-2. TEDLAR BAG EXHAUST ANALYSES.

DILUTED SAMPLE (3)	Paraffins (C4-C6)	Ketones (C3-C4)	UNDILUTED SAMPLE (4)
Chlorinated Hydrocarbons			Paraffins (C1-C3)
Chloromethane	n-Butane	Acetone	Methane
Bromomethane	Isobutane [2-methylpropane]	Butanone	Ethane
Chloroethane	n-Pentane	1,3 - Butadiene (2)	Propane
1,1-Dichloroethane	Isopentane [2-methylbutane] (1)	Propadiene	Olefins (C2-C3)
Methylene Chloride	Neopentane [2,2-dimethylpropane] (1)	Olefins (C4-C5)	Ethene
1,1-Dichloroethane	n-Hexane	1-Butene	Propene
cis-1,2-Dichloroethane	2-methylpentane	cis-2-Butene	Acetylenes (C2-C3)
Chloroform	3-methylpentane	trans-2-Butene	Ethyne
1,1,1-Trichloroethane	2,2-dimethylbutane	2-methylpropene	Propyne (1)
Carbon Tetrachloride	2,3-dimethylbutane	1-Pentene	
1,2-Dichloroethane	Aromatics	cis-2-Pentene	
Trichloroethane	Benzene	trans-2-Pentene	
1,2-Dichloropropane	Toluene	2-methyl-2-Butene	
cis-1,3-Dichloropropene	Ethyl Benzene	2-methyl-1-Butene	
trans-1,3-Dichloropropene	m-Xylene	3-methyl-1-Butene	
1,1,2-Trichloroethane	p-Xylene	Acetylenes (C4-C5)	
Tetrachloroethane	o-Xylene	1-Butyne (1)	
Ethylene Dibromide	Styrene	2-Butyne	
Ethylene Dichloride	1,3,5-Trimethylbenzene	1-Pentyne	
Chlorobenzene	1,2,4-Trimethylbenzene	2-Pentyne	
1,1,2,2-Tetrachloroethane	Phenol	Ethers	
1,3-Dichlorobenzene	Naphthalene	MTBE	
1,4-Dichlorobenzene	Naphthenes	Dimethyl Ether	
Chlorotoluene	Cyclopropane	Ethyl Methyl Ether (1)	
1,2-Dichlorobenzene	Cyclobutane (1)	Diethyl Ether	
1,2,4-Trichlorobenzene	Cyclopentane	Ethyl Propyl Ether (1)	
Hexachlorobutadiene	Cyclohexane	Dipropyl Ether	
trans-1,2-Dichloroethane	Other Hydrocarbons		
1,1,1,2-Tetrachloroethane	Other C6		
Carbon Disulfide	C7 Plus		

MTBE - Methyl Tertiary Butyl Ether

(1) No calibration standard available.

(2) 1,3-Butadiene will be analyzed by GC/PID onsite.

(3) Analysis GC/MS. Detection limit 27 to 61 ppbv, dry (depends on dilution).

(4) Analysis GC/FID. Detection limit 550 to 600 ppbv, dry.

TABLE 4-1. SAMPLING MARTIX.

SAMPLE MATRIX SUBSTANCES	EXHAUST				FUEL
	• Paraffins (C1-C6) • Olefins (C2-C5) • Acetylenes (C2-C5) • Other C6 Hydrocarbons • C7 Hydrocarbons • Naphthenes • Aromatics (C3-C4) • Ethers • 1,3-Butadiene (4) • Chlorinated Hydrocarbons	• Aldehydes Formaldehyde Acetaldehyde Acrolein Propenal Butanal • Ketones (C3-C4)	• Oxides of Nitrogen NO NO2 • Carbon Dioxide • Oxygen	• Moisture • Stack Velocity	
METHODS	Modified CARB 422	CARB 430	CEM	CARB 1-4	BAG SAMPLE
SAMPLING METHOD	GC/MS w/ cryogenically-cooled trap or GC/FID no trap	CARB 430	NO detected by Chemiluminescent	CARB 1-4	ASTM D1945
ANALYTICAL METHOD	Applied P & Ch Laboratory	Air Toxics	EER	EER	Air Toxics
LABORATORY	Tedlar bag with continuous nitrogen dilution analyzed by GC/MS and GC/FID (4)	Impingers w/DNPH analyzed by HPLC	Continuous Monitoring	Standard Procedure	Bag sample analyzed by GC/TCD/FID
METHOD HIGHLIGHTS	Additional Analyses, Modified Sampling (1)	Additional Analyses, Field Extraction	Catalyst before chiller (NOx), Heated sample line	None	Additional Analyses
MODIFICATIONS					
SAMPLE PARAMETERS					
DETECTION LIMIT	27 to 800 ppbv, dry (5)	0.5 ug/sample	1 ppmv	-	10 to 100 ppmv
SAMPLE DURATION (MIN)	30	60	90	-	Grab sample
SAMPLE VOLUME	Undiluted: 10 L (Bags 1/2 Full) Diluted: 12 L (Bags 2/3 Full)	30 L	-	-	5 L
SAMPLES	48 (8 per source)	24 (3 per source)	8 (1 per source)	24 (3 per source)	12 (1 per source)
FIELD SAMPLES					
FIELD BLANKS	8 (1 per source) (2)	24 (3 per source)	-	-	-
MATRIX SPIKES	2 (Before, Middle)	8 (1 per source)	-	-	-
FIELD DUPLICATES	3 (1st source test)	-	-	-	-
LABORATORY GC SAMPLES (2)					
LABORATORY BLANK	-	8 (1 per source)	-	-	8 (1 per source)
LABORATORY REPLICATES	-	8 (1 per source)	-	-	1 (1 for program)
LABORATORY SPIKE	-	8 (1 per source)	-	-	1 (1 for program)
CEM GC SAMPLES (3)					
NOx CONVERTER CHECK	-	-	2 (Before/After Program)	-	-
ZERO CHECK	-	-	16 (2 per source)	-	-
NO-SPAN CHECK	-	-	16 (2 per source)	-	-
SPAN CHECK	-	-	16 (2 per source)	-	-
ZERO BIAS	-	-	16 (2 per source)	-	-
NO BIAS	-	-	16 (2 per source)	-	-

(1) Two samples were collected per modified CARB 422 run.
Diluted Sample - This sample had a heated sample line (250 F) and was diluted with nitrogen. Analysis - GC/MS.
Undiluted Sample - This sample had a heated sample line (250 F), water knockout, and was not diluted. Analysis - GC/FID.
(2) Field blanks were collected at each site by pulling nitrogen through the sample system.
(3) Complete QA/QC discussion is provided in Section 6.0.
(4) On-site GC/PID was used for 1,3-Butadiene (see Attachment 1 for methods).
(5) Detection limits ranged from 27 to 81 ppbv, dry for GC/MS analysis of diluted bags and 550 to 600 ppbv, dry for GC/FID analysis of undiluted bags.

TABLE 4-3. DETAILED EXHAUST ANALYSES AND MODIFICATIONS.

<p>ASTM D1945</p> <p><i>Paraffins (C1-C6)</i></p> <p>Methane</p> <p>Ethane</p> <p>Propane</p> <p>n-Butane</p> <p>Isobutane</p> <p>n-Pentane</p> <p>Isopentane</p> <p>Neopentane</p> <p>Other</p> <p>≥ C6 Hydrocarbons</p> <p>Oxygen</p> <p>Nitrogen</p> <p>Carbon Monoxide</p> <p>Carbon Dioxide</p>	<p>MODIFIED ASTM D1945</p> <p><i>Olefins (C2-C4)</i></p> <p>Ethylene</p> <p>Propene</p> <p>1-Butene</p> <p>cis-2-Butene</p> <p>trans-2-Butene</p> <p><i>Acetylenes (C2)</i></p> <p>Ethyne</p> <p><i>Naphthenes</i></p> <p>Cyclopentane</p>
<p>ASTM D3588</p> <p><i>Heating Value</i></p> <p><i>Specific Gravity</i></p>	

in Table 4-2 were quantified by GC/MS except paraffins, olefins and acetylenes with three carbon atoms or less. These substances are difficult to quantify using a MS detector so a FID detector was utilized. Standards were used to calibrate the instruments for all compounds except those denoted with a "1". As specified in the method, 1,3-Butadiene was sampled and analyzed at the source using a photo ionization detector. The CARB provided both the equipment and personnel to quantify 1,3-Butadiene. A complete description of the 1,3-Butadiene method is provided in Attachment 1.

Another modification to the CARB 422 sampling procedures was the collection of diluted and undiluted samples. The diluted samples were collected to reduce losses of polar VOCs and reactions of branched olefins and acetylenes, and diolefins with NO₂. Dilution ratios for each source are given in Section 5.0. Dilution of the samples resulted in an increase in the analytical detection limit and sampling complexity. To maintain reasonable detection limits for the non-polar and non-reactive VOCs (C1 to C3 paraffins, olefins, and acetylenes), a separate undiluted CARB 422 sample was collected. The undiluted sample was analyzed by GC/FID and the diluted was analyzed by GC/MS. The target analytes for the diluted and undiluted bags are provided in Table 4-2.

To determine the effectiveness of the proposed tedlar bag sampling procedures at reducing NO₂ reactions, a stability test was conducted. The stability tested included spiking 1-Butene, 2-Methylpropene, 2-Methyl-1-Butene, and 1,3-Butadiene into bags containing exhaust gases with NO_x levels of 5, 50, 140, and 1400 ppmv. The samples were analyzed at 2, 8, 24, 48, and 72 hours. Only 1,3-Butadiene decayed in the samples. In the high NO_x level bags, the decay rate was quick, < 2 hrs. In the low level NO_x bags, the decay was less. These results indicate that to obtain accurate emissions levels for 1,3-Butadiene, an on-site GC was necessary. However, the tedlar bag sampling procedures were sufficient for the other compounds at least for the matrix and time period examined.

4.1.2 Fuel Test Matrix

The fuel was sampled and analyzed for volatile organic compounds at each source. A single grab sample of the fuel was collected and analyzed for the substances listed in Table 4-3. The fuel flow rate and heating value also were determined so that emissions factors could be computed.

coefficient assigned to it.

- Manometer - An incline manometer with a range of 0-0.25 or 0-10 inches of water was used to measure flow rates.
- Temperature - A type K thermocouple was attached to the pitot to determine gas temperature at each traverse point.
- Barometer - A barometric reading from a nearby weather station was used and corrected for elevation between the station and the sampling point.
- Gas Density - Dry gas molecular weight was determined by CARB Method 100 and moisture was determined by CARB Method 4.

4.2.2 CARB Method 3 & 4 Dry Molecular Weight & Moisture Content

CARB Method 100 was used to determine the CO₂ and O₂ content of the stack gas for the determination of the dry molecular weight. CARB Method 4 was utilized for the determination of moisture content of the stack gas. A schematic diagram of the moisture sampling system is located in Figure 4-1. The apparatus necessary for this method include:

- Probe - Stainless steel heated probe with a glass wool plug at the upstream end of the probe to remove particulate matter.
- Condenser - The condenser consisted of four impingers connected in series. The second, third and fourth impingers were of the Greensburg-Smith design modified by replacing the tip with a 1/2 inch tube. The first impinger was of the standard Greensburg-Smith design. The first two impingers contained approximately 100 ml of DI water, the third was empty and the fourth contained about 300 grams of indicating silica gel. This impinger system was placed in a water bath during the test and maintained to keep the exhaust temperature of the last impinger at or below 68 °F.

The four impingers were weighed to determine their weight before sampling. The impinger system was connected to the heated probe and placed in a ice bath. The probe was then placed in

4.1.3 QA/QC

To determine the quality of the sampling and analysis procedures, several field and laboratory QC samples were collected and analyzed as shown in Table 4-1. One CARB 422 and three CARB 430 field blanks were collected at each source as required. These blanks indicate interference in the sample preparation, sampling, recovery, transport, and analytical procedures. The CARB 422 field blank was prepared by pulling nitrogen through the complete sampling system. One CARB 430 matrix spike was prepared and analyzed per site. Normally one CARB 422 field spike is required per source, however due to the detailed validation work conducted before the program, only a single matrix spike was collected during the program. Three field duplicates also were collected at the first source for CARB 422. No field duplicates were collected for CARB 430 but a duplicate laboratory analysis was conducted for each source.

Zero, mid-span and high-span analyzer checks, and zero and mid-span system checks were conducted before and after each test. The analyzer checks are used to determine the error of the analyzer and if the drift was acceptable over the test. The system checks are used to determine the error of the complete system (analyzer and sample lines) and if the drift for the complete system was acceptable over the test. NO_x converter tests were conducted before and after the program to determine the effectiveness of the catalyst at converting NO₂ to NO.

4.2 Emissions Sampling and Analytical Procedures

The emissions sampling procedures listed in Table 4-1 are described in the following sections. Separate sections for the diluted and undiluted modified CARB 422 sample procedures are provided. Deviations from these methods are provided in Section 4.2.7. 1,3-Butadiene sampling was conducted by the CARB. A detailed description of their procedures is provided in Attachment 1.

4.2.1 CARB Method 1 & 2 Sample Point Determination & Stack Gas Velocity

CARB Method 1 was utilized to determine the sample points. Section 6.2 summarizes the stack diameter, number of ports and sample points, and the upstream and downstream disturbance distances for each source. CARB Method 2 was used to determine the stack gas velocity and volumetric flow rate. The key apparatus used include:

Pitot Tube - The pitot tube was of the S-Type. It was calibrated and the proper

the gas stream and the stack gas was collected for approximately 30 minutes at a rate of 0.75 scfm. At the end of the test the impingers were reweighed and the amount of moisture was calculated.

4.2.3 Modified CARB Method 422 (Diluted Sample)

As discussed in section 4.1, CARB method 422 was modified to include an extended target analyte list and continuous dilution. The complete list of diluted sample target substances is shown in Table 4-2. Dilution of the sample was necessary to ensure the stability of the reactive and polar hydrocarbons. The diluted sampling and analysis procedures are described in detail in the following sections.

Sampling

A schematic diagram of the dilution sampling system for VOC species is provided in Figure 4-2. All samples except the aldehydes were collected using this equipment. The key apparatus of the sampling system included:

- Sample Probe - The flue gas was extracted with a quartz probe. Heating was provided if the probe temperature dropped below 230 F. The probe had a 90° bend and was pointed in the direction of the flow.

- Quartz Filter - A glass fiber filter was used to remove particulate from the gas stream. The filter was mounted on a glass frit inside a quartz filter housing. The complete filter set-up was housed inside a small heated oven, which was used to maintain filter temperatures at 230°F.

- Sample transport - The gas sample was transported into the dilution system by means of a heated Teflon sample line. Sample temperatures within the Teflon line were kept at 230°F. The Teflon line was fitted with stainless steel fittings. Stainless steel fittings were used to avoid leakage problems that accompany Teflon and quartz fittings. Contact with the steel was minimized to reduce the loss of NO_x species.

- Dilution System - The sample gas was diluted with nitrogen at constant pressure and

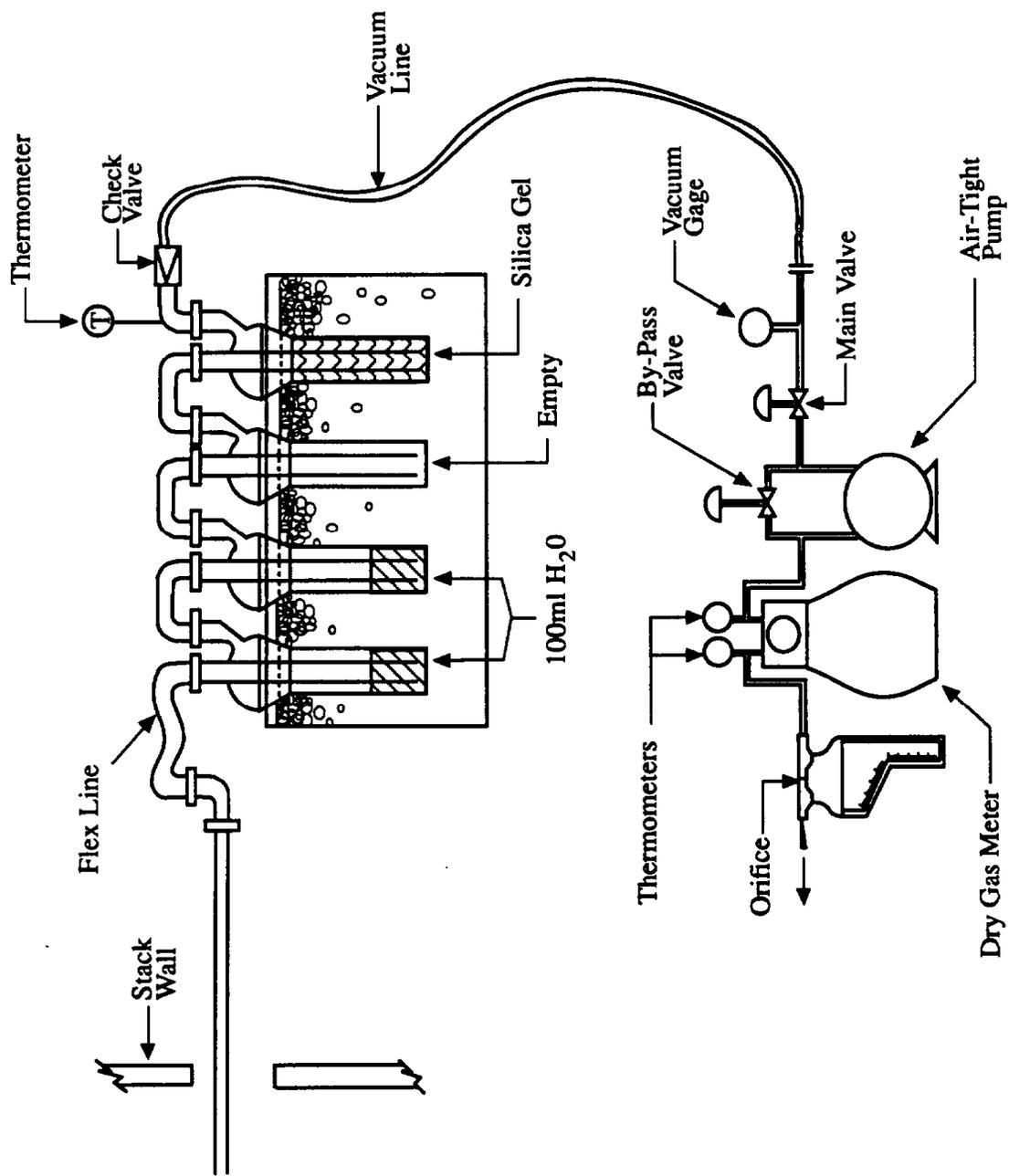


Figure 4-1. CARB Method 4 Moisture Train.

temperature. The system was calibrated before each test run to produce the appropriate dilution ratio. To maintain the dilution ratio throughout the test, sample and nitrogen flow rates and system temperatures and pressures were maintained at their values recorded during the calibration. A post test calibration check also was conducted. CO₂ also was monitored in the diluted gases during the test. This concentration was compared to the pretest stack CO₂ measurement.

Sample Bags - Sample bags consisted of 12 liter Tedlar bags. The bags were filled with 10 liters of diluted stack gas.

Analysis - GC/MS with cryogenic trapping.

The probe was placed in the sample stream and the downstream end of the probe was connected to a heated sample line. The opposite end of the heated sample line was connected to the filter which was connected to the dilution system. Nitrogen was introduced to produce the appropriate dilution ratio. The diluted sample gas was directed to a tedlar bag and a CO₂ analyzer. Flow to the tedlar bag was monitored using a rotameter. Three 30 minute integrated Tedlar bag samples were taken and analyzed for speciated hydrocarbons (see Table 4-2) using GC/MS. Diluted sample gas also was passed to a CO₂ analyzer. This CO₂ reading was compared to the pretest undiluted CO₂ reading to ensure that the appropriate dilution ratio was maintained.

Analysis

The analysis procedures were based on EPA TO-14. Samples collected in air bags were kept in cardboard boxes to avoid any possible light-induced photochemical-reactions. Upon receipt at the laboratory, the tag data on bags were properly recorded and Lab-IDs were assigned. A bag was then connected to the GC analytical system. During the analysis, the VOCs were concentrated by collection in a cryogenically-cooled trap. The cryogen was then removed and the temperature of the trap raised. The VOC's originally collected in the trap were re-volatilized and sent through a moisture control module (MCM). The MCM removes moisture from the stream to prevent plugging in the GC column. After the VOCs passed through the MCM, they were separated on a GC column, then detected by a MS detector.

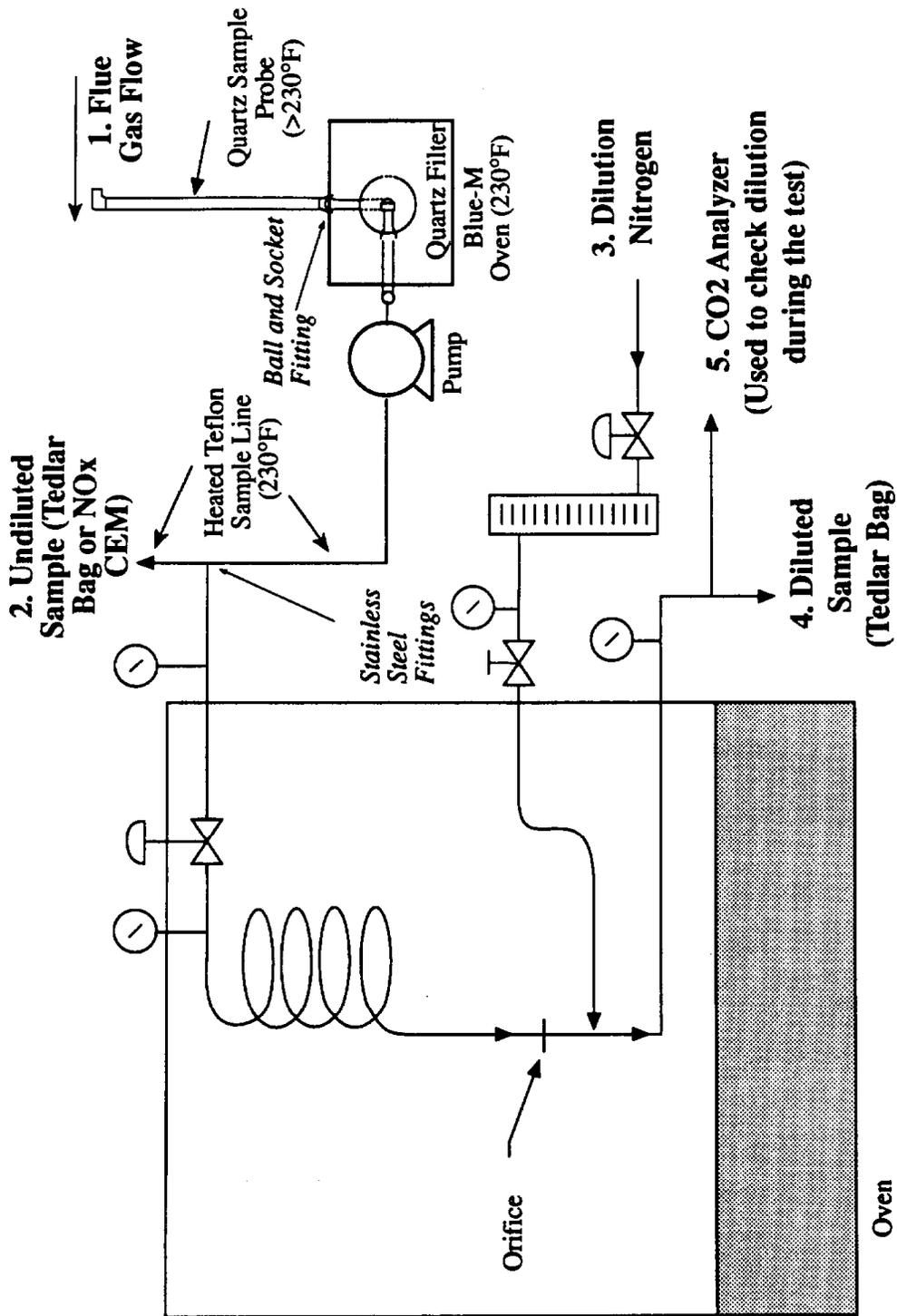


Figure 4-2. Dilution system for VOC sampling.

from the standard deviation of each analyte concentration by multiplying it with 3.14. In this report, practical quantitation limits (PQLs) have been provided. The PQL is defined as the lowest level that can be reliably determined within specified accuracy during routine lab operation conditions. PQLs are generally 2 to 5 times higher than the MDL.

4.2.4 Modified CARB Method 422 (Undiluted Sample)

As discussed in section 4.1, CARB method 422 was modified to include an extended target analyte list. The complete list of undiluted sample target substances is shown in Table 4-2. The undiluted sampling and analysis procedures are described in detail in the following sections.

Sampling

The sampling system is illustrated in Figure 4-2 and key components are described in Section 4.2.3. To collect the undiluted sample, a stream was split off the sampling system before the dilution system and captured in a tedlar bag. A water knockout was used to prevent condensation in the bag. The flow rate was monitored using a rotameter. Three 30 minute integrated Tedlar bag samples were taken and analyzed for speciated hydrocarbons (see Table 4-2) using a GC/FID.

Analysis

Samples collected in air bags were kept in cardboard boxes to avoid any possible light-induced photochemical-reactions. Upon receipt at the laboratory, tag data on the bags was properly recorded and Lab-IDs were assigned. A bag was then connected to the GC analytical system. After the VOCs were separated on the GC column, they were detected by a FID.

Except where noted, the system was calibrated using standards for the substances listed in Table 4-2. The calibration procedure included: a.) BFB tune: within limits; b.) instrument blank: no contamination; and c.) three point calibration. Substances without standards were quantified using the following equation.

$$C = (A_x C_{is} D) / (A_{is} R F V_x)$$

A_x - Response of the analyte being measured

C_{is} - Volume of internal standard added (10⁻⁶ L)

Except where noted, the system was calibrated using standards for the substances listed in Table 4-2. The calibration procedure included: a.) BFB tune: within limits; b.) instrument blank: no contamination; and c.) three point calibration. Substances without standards were quantified using the following equation.

$$C = (A_x C_{is} D) / (A_{is} RF V_s)$$

- A_x - Response of the analyte being measured
- C_{is} - Volume of internal standard added (10⁻⁶ L)
- D - Dilution factor
- A_{is} - Response of internal standard
- RF - Response factor for a similar analyte
- V_s - Volume of sample

I. Instruments Used

1. GC/MSD: HP-5890A/5971A, 1991
2. GC/MSD Data System: HP QS/2, 1991
3. Recorder/Integrator: Perkin-Elmer 1020, 1991
4. Nutech VOC Autosampler/3550A Cryogenic Concentrator.

II. QA/QC of Sample Analysis

Before analyzing the samples, a mid point calibration check was performed to check if the system was within the initial calibration range. Comparing with the initial response factor, the relative percentage deviation of each response factor in the calibration check should be less than 25%. An instrument blank was also run to check if there was contamination in the sampling system and the detection system. Three-day holding time was strictly enforced.

III. Detection Limit Procedures

SW846 revision 1 (July 1992) was used to determine the method detection limit (MDL). MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. 7 replicate spikes at concentrations 3 to 5 times of estimated detection limits were analyzed. MDL is then calculated

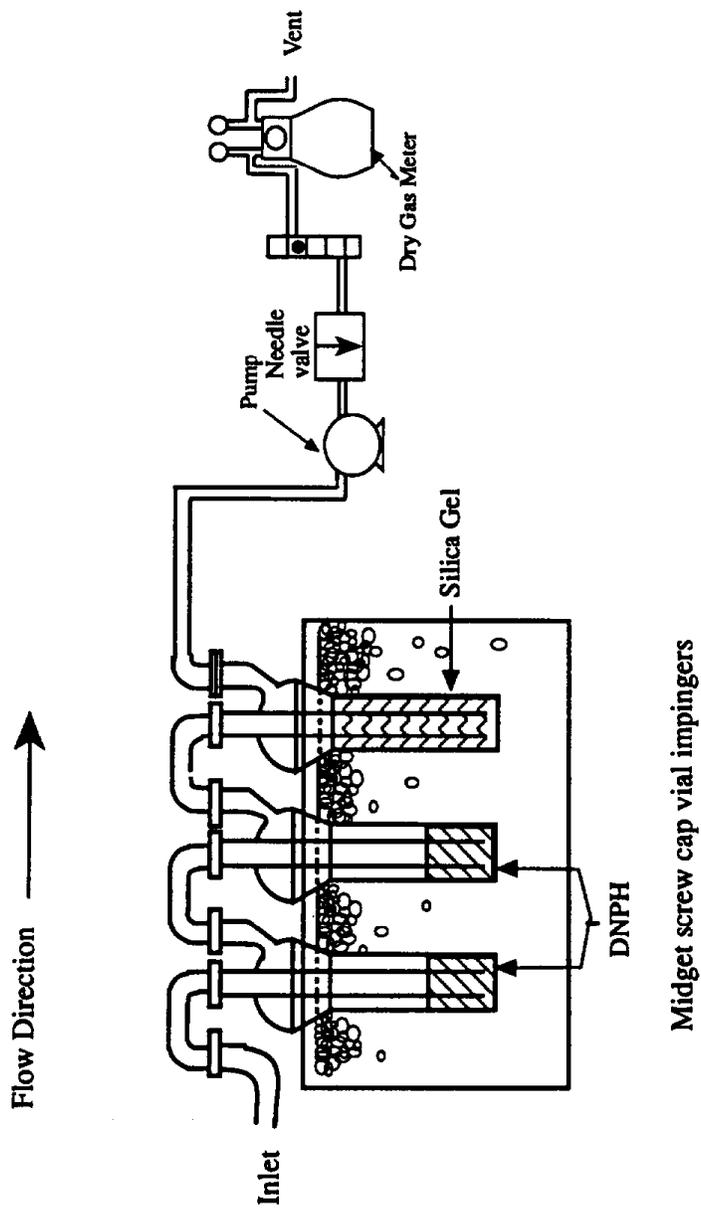


Figure 4-3. CARB 430 sampling system.

- D - Dilution factor
- A_{is} - Response of internal standard
- RF - Response factor for a similar analyte
- V_s - Volume of sample

I. Instruments Used

1. GC/FID: Perkin-Elmer 8500, 1989 (or HP 5890A, 1992)
2. Recorder/Integrator: Perkin-Elmer 1020, 1991

II. QA/QC of Sample Analysis

Before analyzing samples, a mid point calibration check was performed to check if the system was within the initial calibration range. Comparing with the initial response factor, the relative percentage deviation of each response factor in the calibration check should be less than 25%. An instrument blank was also run to check if there was contamination in the sampling system and the detection system. Three-day holding time was strictly enforced.

III. Detection Limit Procedures

SW846 revision 1 (July 1992) was used to determine the method detection limit (MDL). MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. 7 replicate spikes at concentrations 3 to 5 times of estimated detection limits were analyzed. MDL is then calculated from the standard deviation of each analyte concentration by multiplying it with 3.14. In this report, practical quantitation limits (PQLs) have been provided. The PQL is defined as the lowest level that can be reliably determined within specified accuracy during routine lab operation conditions. PQLs are generally 2 to 5 times higher than the MDL.

4.2.5 CARB Method 430 Aldehydes and Ketones

Principles of CARB 430 were utilized for the sampling of aldehydes and ketones. A diagram of the sampling system is shown in Figure 4-3. The key components for this sampling system include:

- Probe - The probe was constructed of stainless steel. During

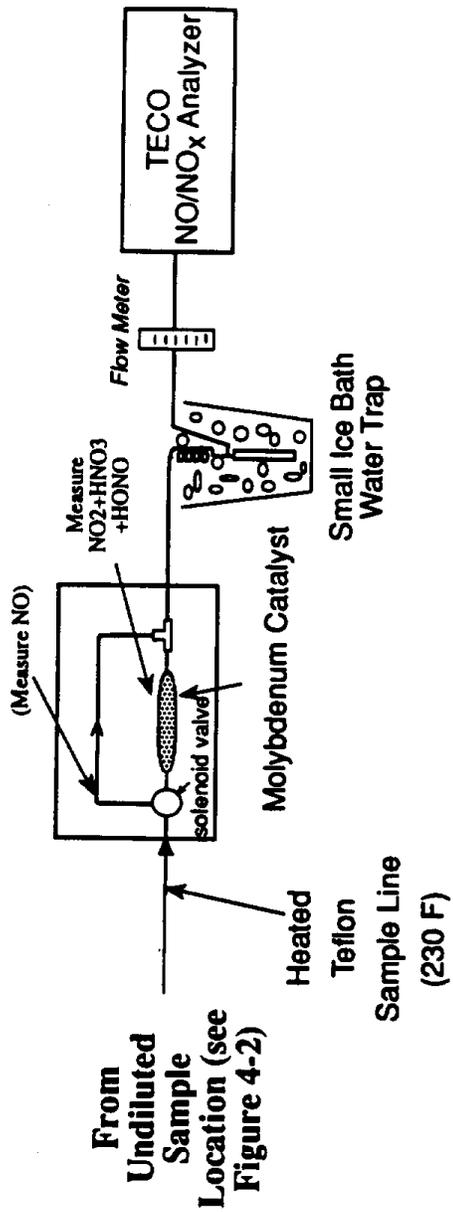


Figure 4-4. NO_x speciation sampling equipment.

the test the probe was heated above the dew point of the sample gas.

- | | | |
|----------------|---|--|
| Sample Line | - | The line was constructed of Teflon tubing. |
| Impingers | - | Three glass midget impingers were connected in series. The first two impingers contained 10 ml of impinger solution and the third was empty. The impinger system was placed in an ice water bath during testing. |
| Impinger Soln. | - | Dilute solution of 2,4-Dinitrophenylhydrazine (DNPH). |
| Analysis | - | Organo-chloride extraction High-pressure liquid chromatography (HPLC). Methanol/water was used with the extended analyte list. This permitted the separation of acetone and acrolein as well as acetone and propanol |

After the system was assembled and leak checked, the probe was placed into the sample stream. The sample gas was drawn into the train at the maximum rate of 0.5 liters/min for one hour. A field extraction was performed to prevent decay of the sample during transport to the lab.

4.2.6 Emission Monitoring of NO and NO_x

One of the objectives of this project was to quantify NO_x species including NO and NO₂. To accomplish this objective, the sampling apparatus illustrated in Figure 4-4 was utilized. This apparatus and the procedures discussed below have been used successfully to monitor NO and NO₂ in previous programs¹.

NO and NO_x were monitored at the undiluted sample location (see Figure 4-2). The NO₂ concentration is the difference between the total NO_x and NO readings. The dilution system, sample probe, quartz filter, and sample transport are described in section 4.4.3. Additional key equipment and features of the NO and NO_x sample procedures are as follows:

Refinery Gas Process Heater (Site G)

The exhaust gas for the refinery process heater at Site G is collected into a common manifold and is exhausted to atmosphere through three individual exhaust stacks (see Figure 3-1g). Since only one stack had sample ports, all of the sampling was conducted at this stack. The total mass rate of each detected target analyte was determined by multiplying emission rates from the single stack by three.

Section 4 References

- (1) Evans A.B., Pont J.N., Moyeda D.K., and England G.C., "Emissions Sampling Protocol for Measuring NO/NO_x in the presence of High Concentrations of NO₂", Western States Meeting Salt Lake City, Utah, March 1993.

- Molybdenum Catalyst - This catalyst was used to convert NO₂ to NO for detection by the chemiluminescent analyzer. The catalyst was located before the chiller to reduce the loss of NO₂ due to condensation and low temperature reactions in the chiller and sample line¹.
- Chiller - The molybdenum catalyst was followed by a low-volume water trap which consisted of a spiral-formed stainless steel tube with a condensate-catching reservoir on the bottom.
- NO_x analysis - Levels of NO were measured using a chemiluminescent analyzer.

The system described above was operated by placing the probe in the stack. Then the sample gas was passed through the catalyst to convert NO₂ to NO resulting in a total NO_x reading. After ten one minute NO_x readings were recorded on the data acquisition system (DAS), the catalyst was bypassed providing a total NO reading. Ten one minute NO readings were then recorded on the DAS. This process was repeated until six ten minute periods of NO and NO_x readings were recorded. The total NO₂ concentration was then determined by subtracting the average of all NO readings from the average of all NO_x readings.

4.2.7 Sampling Modifications

Site specific modifications to the sampling plan described in sections 4.1.1 through 4.1.7 are presented in this section.

Refinery Gas Process Heater (Site B)

The exhaust gas for the refinery process heater at Site B is collected into a common manifold and is exhausted to atmosphere through two individual exhaust stacks (see Figure 3-1b). Since only one stack had sample ports, all of the sampling was conducted at this stack. The total mass rate of each detected target analyte was determined by multiplying emission rates from the single stack by two.

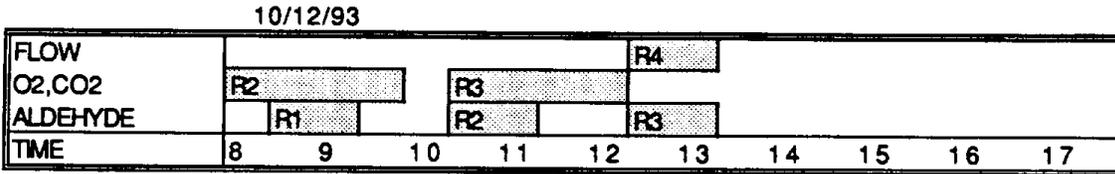
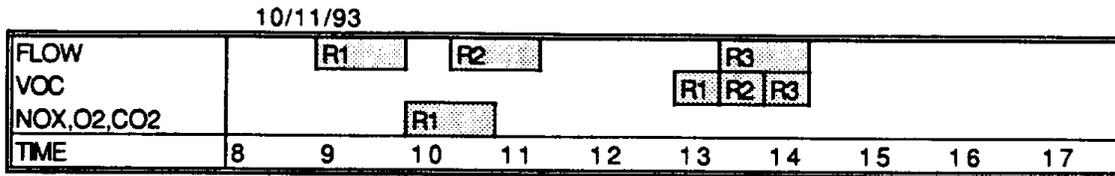


Figure 5-1a. Landfill gas IC engine (uncontrolled) test chronology.

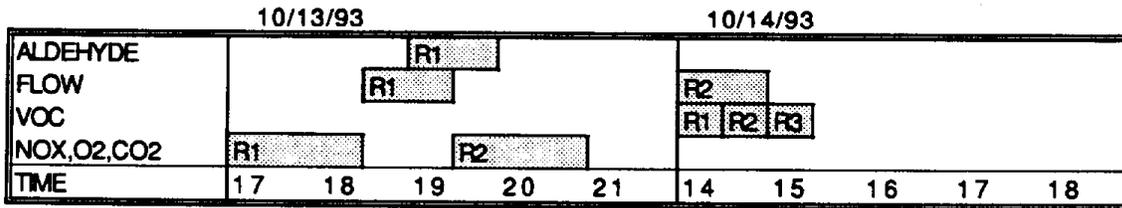


Figure 5-1b. Refinery gas process heater (low NOx burners) test chronology.

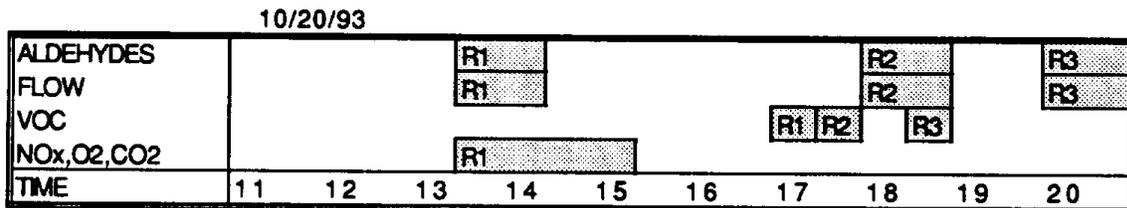


Figure 5-1c. Natural gas steam generator (low NOx Burners/Exhaust Gas Recirculation) test chronology.

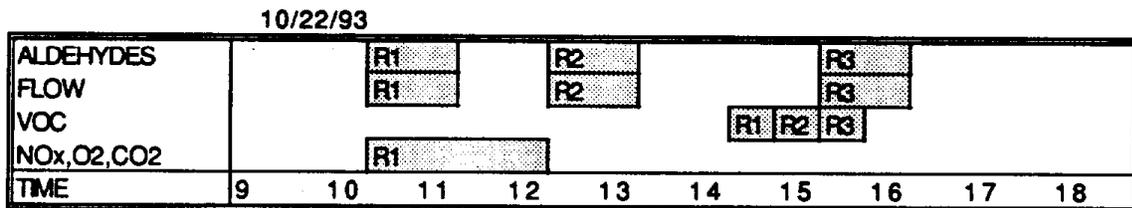


Figure 5-1d. Field gas IC engine (uncontrolled) test chronology.

5.0 TEST RESULTS

This section presents run specific results and source averages for the NO_x and VOC samples collected and analyzed during this program. Key results from the QA/QC program are discussed as they relate to the quality of the test results. Section 6.0 includes a complete discussion of QA/QC results. Section 5.1 presents the sampling schedule at each source. Process operation during each test is described in Section 5.2. Section 5.3 and 5.4 present results from the VOC and NO_x sampling activities.

5.1 Sampling Schedule

The sampling schedule for each source is given in figures 5-1(a-h). The sampling activities at most of the sources included:

- Three one hour CARB 430 (aldehyde/ketone) runs,
- Three half hour tedlar bag (VOC) runs,
- An hour and a half to two hour NO_x run, and
- Three one hour moisture/velocity determination runs.

The only deviations from this schedule occurred at the landfill gas IC engine where four one hour moisture/velocity runs and two additional O₂/CO₂ CEM runs were conducted. In addition, only a single aldehyde sample was collected at the first process heater tested. Three samples could not be collected because the glassware and reagents prepared by the lab were lost during transport. Only two velocity traverses were conducted because of the reduced aldehyde sampling program.

Since only two sample ports were available at each of the sources, simultaneous operation of all sample collection systems was not possible. In general, two to three samples were collected at a time as shown in figures 5-1(a-h). At most sources, the aldehyde and flow samples were collected simultaneously. The VOC samples were usually collected during the second or third aldehyde run and the NO_x CEM was usually operated during the first aldehyde run or on the first day of testing. At six of the sources, the VOC and aldehyde samples were collected on the same day. However, due to the allowed sampling time, the VOC and aldehyde samples at the landfill gas IC engine and the first refinery gas process had to be collected on different days. Because the VOC and aldehyde samples were not collected simultaneously at any of the sources over all three runs, run specific speciation profiles were not developed at any of the sources. Instead, the source averages for each detected VOC and aldehyde were used to generate a single speciation profile for each source.

In the following subsections, results are identified by their run number. The reader should consult figures 5-1(a-h) to determine the time relation of each result to other results.

5.2 Process Operation

During each of the tests, it was requested that the operation of the source be typical. To characterize the operation of each source during the testing, key operational parameters were collected. These parameters are summarized in this subsection. Table 5-1 summarizes heat input rates to each unit based on the fuel flow and heating value and based on the fuel F-Factor and stack flow rate and oxygen concentration. The sample runs corresponding to each listed heat input rate also are provided in the table. Parameters which are not simultaneous with the listed sample runs are enclosed in parentheses. The percent difference between the heat input based on the flue flow and the F-Factor are provided in the last column. The second refinery process heater tested had the best agreement between the two calculations while the landfill gas IC engine had the worst. Since the emission factors provided in Section 5.3 were based on the heat input rate computed from the fuel flow, the larger the difference in the heat input calculations the greater the uncertainty in the computed emission factors.

Table 5-2 summarizes the stack gas flow, temperature and moisture, and the dilution ratio. This ratio is expressed as the total volume of nitrogen added to each liter of stack gas sampled. The stack gas was diluted with nitrogen to prevent condensation in the tedlar bags and reduce the rate of NO₂ reactions with olefins. The dilution ratio increased the analytical detection limit from 5 ppbv to as high as 61 ppbv. The natural gas IC engine had the highest dilution ratio and therefore the largest detection limit. Increased dilution at the natural gas IC engine was necessary because of the high moisture content of the stack gases. It should be noted that only one of the two stacks at the refinery process heater with low NO_x burners and one of the three stacks at the refinery process heater with selective catalytic reduction were sampled. Total flow rates were determined by multiplying the single stack rates by the total number of stacks at each site. This estimating procedure increases uncertainty of the emission rates of detected substances and the emission factors presented in Section 5.3. However, the speciation profiles will not be affected unless significant stratification was present in the system. The stack flow rate at the utility boiler also was estimated because only a single traverse could be conducted due to a flow obstruction. This obstruction should not affect the VOC and NO_x concentrations or profiles.

Fuel concentration profiles, heating values, and calculated F-Factors are provided in Table 5-

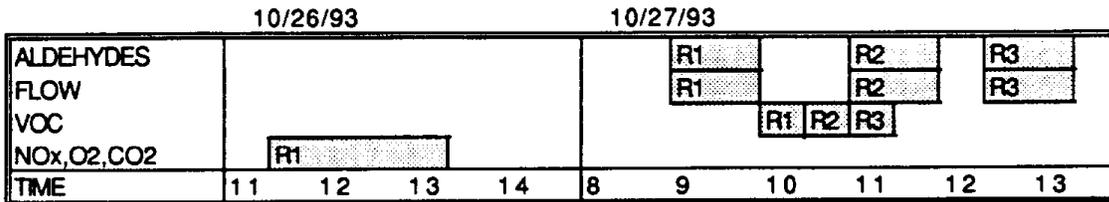


Figure 5-1e. Natural gas IC engine (selective catalytic reduction) test chronology.

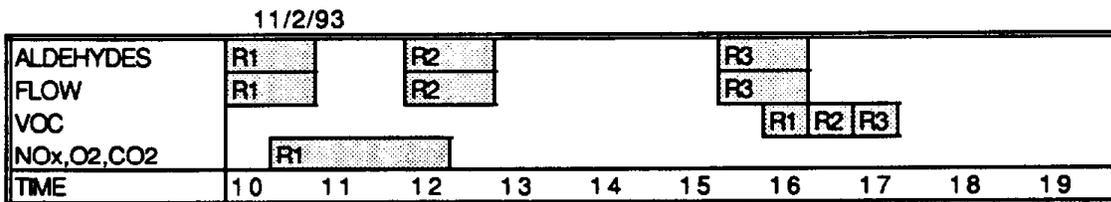


Figure 5-1f. Natural gas turbine (selective catalytic reduction/CO catalyst) test chronology.

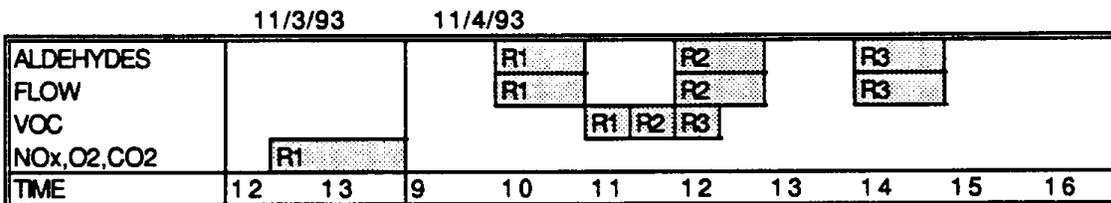


Figure 5-1g. Refinery gas process heater (selective catalytic reduction) test chronology.

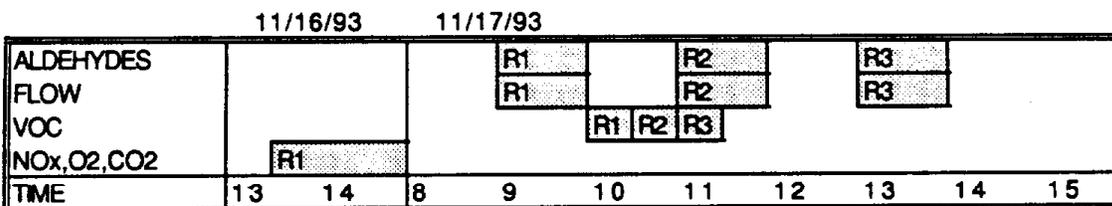


Figure 5-1h. Natural gas utility boiler (uncontrolled) test chronology.

TABLE 5-2. TRAIN PARAMETERS AND REQUIRED DILUTION RATIO.

Parameter	Internal Combustion Engine				Gas Turbine Natural Gas SCR/ CO Catalyst	Process Heater		Steam Generator Natural Gas LNB EGR	Utility Boiler Natural Gas No Control
	Landfill		Field			Refinery Gas	Refinery Gas		
	Gas	No Control	Gas	No Control					
Stack Gas Flow (dscfm)									
Run 1	5985	285	626	567000	30273	37400	9290	32400	
Run 2	5960	271	730	567000	35305	32600	9093	32200	
Run 3	5878	253	645	558000	na	32600	9804	31900	
Average	5941	270	667	564000	32789	34200	9396	32167	
Stack Moisture (%)									
Run 1	12%	17%	19%	11%	11%	15%	17%	13%	
Run 2	10%	15%	18%	11%	12%	17%	17%	13%	
Run 3	13%	16%	19%	10%	na	17%	16%	12%	
Average	12%	16%	19%	11%	12%	16%	17%	13%	
Stack Temperature (F)									
Run 1	874	569	969	339	454	339	347	223	
Run 2	878	605	963	339	482	329	347	223	
Run 3	877	573	987	339	na	333	331	223	
Average	876	582	973	339	468	334	342	223	
Dilution Ratio									
All Runs	7.5	8.9	10.2	4.9	5.4	8.3	8.9	7.7	

LNB - Low NOx Burner
 SCR - Selective Catalytic Reduction
 EGR - Exhaust Gas Recirculation

TABLE 5-1. PROCESS HEAT INPUT RATES.

DEVICE/GROUP/SUBSTANCE	HEAT INPUT CALCULATION							PD (%)
	Based on Fuel Flow			Based on F-Factor				
	Fuel Flow (scfm)	Heating Value (Btu/cf)	Heat Input (MMBtu/hr)	F-Factor (dscf/MMBtu)	Stack Flow (dscfm)	Oxygen (%)	Heat Input (MMBtu/hr)	
Landfill Gas IC Engine								
Uncontrolled								
VOC R1,R2, and R3	688	(1000)	41	(8729)	5878	(8.5)	24	52
Aldehyde/Ketone R1	702	(1000)	42	(8729)	(5838)	(8.4)	(24)	54
Aldehyde/Ketone R2	695	(1000)	42	(8729)	(5838)	(8.4)	(24)	53
Aldehyde/Ketone R3	679	(1000)	41	(8729)	5838	(8.4)	24	51
Refinery Gas Process Heater								
Low NOx Burner								
VOC R1 and R2	2136	(1700)	218	(8508)	60546	(9.9)	226	-4
VOC R3	2510	(1700)	256	(8508)	60546	(9.9)	226	12
Aldehyde/Ketone R1	2214	(1700)	226	(8508)	70610	(9.9)	264	-15
Natural Gas Steam Generator								
Low NOx Burner								
Exhaust Gas Recirculation								
VOC R1,R2, and R3	847	(990)	50	(8058)	(9093)	(2.5)	(60)	-17
Aldehyde/Ketone R1	861	(990)	51	(8058)	9289	2.5	61	-17
Aldehyde/Ketone R2	847	(990)	50	(8058)	9093	(2.5)	60	-17
Aldehyde/Ketone R3	864	(990)	51	(8058)	9805	(2.5)	64	-22
Field Gas IC Engine								
Uncontrolled								
VOC R1,R2, and R3	na	na	na	(8648)	(253)	(2.5)	(1.5)	na
Aldehyde/Ketone R1	na	na	na	(8648)	285	2.5	1.7	na
Aldehyde/Ketone R2	na	na	na	(8648)	272	(2.5)	1.7	na
Aldehyde/Ketone R3	na	na	na	(8648)	253	(2.5)	1.5	na
Natural Gas IC Engine								
Selective Catalytic Reduction								
VOC R1,R2, and R3	59	(1000)	3.5	(8560)	(730)	(0.0)	(5.1)	-36
Aldehyde/Ketone R1	54	(1000)	3.2	(8560)	626	(0.0)	4.4	-30
Aldehyde/Ketone R2	59	(1000)	3.5	(8560)	730	(0.0)	5.1	-36
Aldehyde/Ketone R3	78	(1000)	4.7	(8560)	645	(0.0)	4.5	3
Natural Gas Turbine								
Selective Catalytic Reduction								
CO Catalyst								
VOC R1,R2, and R3	14746	(1100)	973	(8419)	(558428)	(14.0)	(1323)	-30
Aldehyde/Ketone R1	15331	(1100)	1012	(8419)	567392	(14.0)	1344	-28
Aldehyde/Ketone R2	15117	(1100)	998	(8419)	567392	(14.0)	1344	-30
Aldehyde/Ketone R3	14746	(1100)	973	(8419)	558428	(14.0)	1323	-30
Refinery Gas Process Heater								
Selective Catalytic Reduction								
VOC R1 and R2	7017	(1400)	589	(10083)	(97803)	(1.1)	(551)	7
VOC R3	7050	(1400)	592	(10083)	97803	(1.1)	551	7
Aldehyde/Ketone R1	6866	(1400)	577	(10083)	112131	(1.1)	631	-9
Aldehyde/Ketone R2	7033	(1400)	591	(10083)	97803	(1.1)	551	7
Aldehyde/Ketone R3	6833	(1400)	574	(10083)	97755	(1.1)	550	4
Natural Gas Utility Boiler								
Uncontrolled								
VOC R1,R2, and R3	(1900)	(1000)	(114)	(8480)	(32181)	(5.0)	(173)	-41
Aldehyde/Ketone R1	(1900)	(1000)	(114)	(8480)	32350	(5.0)	174	-42
Aldehyde/Ketone R2	(1900)	(1000)	(114)	(8480)	32181	(5.0)	173	-41
Aldehyde/Ketone R3	(1900)	(1000)	(114)	(8480)	31929	(5.0)	172	-41

() - Not Simultaneous with emission measurements.

TABLE 5-3. FUEL ANALYSES.

SUBSTANCE	CONCENTRATION (Volume, %)										
	Natural Gas			Field Gas			Refinery Gas		Landfill Gas		TEOR
	Internal Combustion Engine (SCR)	Gas Turbine (SCR/CO Catalyst)	Steam Generator (LNB, EGR)	Utility Boiler (Uncontrolled)	Internal Combustion Engine (Uncontrolled)	Process Heater (LNB)	Process Heater (SCR)	Internal Combustion Engine (Uncontrolled)	Steam Generator (LNB, EGR)		
VOCs											
Methane	95	89	73	90	69	34	42	94	10		
Ethane	2	3.5	4.4	3.8	11	17	17	2.8	0.12		
Propane	0.36	1.9	1.6	0.65	11	23	19	0.76	0.046		
Isobutane	0.042	0.27	0.44	0.064	1.3	5.8	2.4	0.096	0.008		
Butane	0.066	1.6	0.75	0.075	2.4	3.4	5.1	0.14	0.14		
Neopentane	0.001	0.002	0.004	0.001	0.002	0.004	0.005	ND	0.005		
Isopentane	0.021	0.11	0.31	0.022	0.31	0.7	1	0.044	0.004		
n-Pentane	0.018	0.095	0.29	0.017	0.18	0.42	0.93	0.035	0.004		
Ethylene	ND	0.57	ND	ND	ND	6.6	6.2	ND	ND		
Propene	ND	ND	ND	ND	ND	0.001	0.001	0.001	0.001		
1-Butene	ND	ND	ND	ND	ND	ND	ND	ND	ND		
cis-2-Butene	ND	0.036	ND	ND	ND	ND	0.35	ND	ND		
trans-2-Butene	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Cyclopentane	ND	ND	0.083	ND	0.016	ND	ND	ND	ND		
Ethyne	ND	ND	ND	ND	0.001	0.027	ND	ND	ND		
C6+	0.069	0.14	1.4	0.074	0.057	0.48	0.86	0.075	0.32		
Unknown C4						0.083	0.45				
Unknown C5											
Others		0.025									
Oxygen	0.16	0.015	0.48	0.64	0.036	0.84	0.044	0.19	0.36		
Nitrogen	1.2	1.3	2.2	3.4	0.66	7	3.3	0.93	1.1		
Carbon Monoxide	ND	ND	ND	ND	ND	0.55	1	ND	ND		
Carbon Dioxide	1.4	1	15	1.1	4	0.16	0.15	1.2	88		
Heating Value (Btu/cf)	1000	1100	990	1000	1300	1700	1400	1000	120		
F-Factor (discf/MMBtu)	8560	8419	8058	8480	8648	8508	10083	8729	NA		
Specific Gravity	0.59	0.64	0.81	0.61	0.81	1.1	0.89	0.59	1.4		

ND - Not Detected
 SCR - Selective Catalytic Reduction
 LNB - Low NOx Burner
 EGR - Exhaust Gas Recirculation

3. The profiles include hydrocarbons which could not be identified. It should be noted that a small quantity of refinery gas was burned at the gas turbine. This fuel was not sampled and a specific profile is not provided in Table 5-3. However, the refinery gas profile for the refinery process heater with low NO_x burners can be used to represent to the gas turbine refinery gas since these sources were located at the same facility. As expected, most of the natural gases burned had similar profiles. The natural gas burned at the steam generator did have a lower methane concentration because of its high carbon dioxide content. The landfill gas had a comparable profile to the natural gas source profiles. The field gas and refinery gases had higher concentrations of C₂ through C₄ hydrocarbons than the other fuels. Fuel VOC profiles calculated using weight fractions are provided in Table 5-4. These profiles do not include oxygen, nitrogen, carbon monoxide or carbon dioxide.

5.3 Volatile Organic Compound Emissions

One of the key objectives of this program was to develop complete VOC speciation profiles for gas fired combustion sources. To achieve this objective, over 100 VOCs were included on the target analyte list as shown in Table 4-2. While all of these substances were included on the target list, only a few compounds were detected. A total of 21 different substances were detected at one or more of the sources during the program. This section presents profiles (section 5.3.1), concentrations on a weight and volume percent basis, and emission factors (section 5.3.2) for these substances.

A complete list of actual detection limits, accounting for dilution and moisture, is provided in Table 5-5. The actual detection limits ranged from 27 to 61 ppbv, dry for C₄ and heavier substances and from 550 to 600 ppbv, dry for C₃ and lighter substances. Analytical detection limits were 5 ppbv for C₄ and heavier and 500 ppbv for C₃ and lighter substances. Volume II provides a complete listing of analytical detection limits for each source. The analytical and actual detection limits differed significantly for C₄ and heavier substances because these substances were diluted up to 10 to 1 (see Table 5-2) to provide greater stability in the sample matrix. To reduce the impact of dilution on the detection limits for C₄ and heavier substances, the diluted samples were concentrated. Detection limits for light hydrocarbons were an order of magnitude greater than heavier hydrocarbons because preconcentration was not available on the GC/FID system used to quantify C₃ and lighter hydrocarbons. A GC/MS system was used to quantify C₄ and heavier hydrocarbons. The injection volume for the GC/FID system was increased to lower the analytical detection limit from 1 ppmv to 0.5 ppmv.

TABLE 5-5. TEDLAR BAG SAMPLING DETECTION LIMITS.

SUBSTANCE	DETECTION LIMIT (ppbv, dry)							
	Internal Combustion Engine			Gas Turbine	Process Heater		Steam Generator	Utility Boiler
	Landfill Gas	Field Gas	Natural Gas	Natural Gas	Refinery Gas	Refinery Gas	Natural Gas	Natural Gas
	No Control	No Control	SCR	SCR/CO Catalyst	LNB	SCR	LNB EGR	No Control
<i>Paraffins (C1-C6)</i>								
Methane	580	600	600	550	570	600	600	580
Ethane	580	600	600	550	570	600	600	580
Propane	580	600	600	550	570	600	600	580
n-Butane	43	53	61	27	31	50	53	44
Isobutane [2-methylpropane]	43	53	61	27	31	50	53	44
n-Pentane	43	53	61	27	31	50	53	44
Isopentane [2-methylbutane]	43	53	61	27	31	50	53	44
Neopentane [2,2-dimethylpropane]	43	53	61	27	31	50	53	44
n-Hexane	43	53	61	27	31	50	53	44
2-methylpentane	43	53	61	27	31	50	53	44
3-methylpentane	43	53	61	27	31	50	53	44
2,2-dimethylbutane	43	53	61	27	31	50	53	44
2,3-dimethylbutane	43	53	61	27	31	50	53	44
<i>Olefins (C2-C5)</i>								
Ethene	580	600	600	550	570	600	600	580
Propene	580	600	600	550	570	600	600	580
1-Butene	43	53	61	27	31	50	53	44
cis-2-Butene	43	53	61	27	31	50	53	44
trans-2-Butene	43	53	61	27	31	50	53	44
2-methylpropene	43	53	61	27	31	50	53	44
1-Pentene	43	53	61	27	31	50	53	44
cis-2-Pentene	43	53	61	27	31	50	53	44
trans-2-Pentene	43	53	61	27	31	50	53	44
2-methyl-2-Butene	43	53	61	27	31	50	53	44
2-methyl-1-Butene	43	53	61	27	31	50	53	44
3-methyl-1-Butene	43	53	61	27	31	50	53	44
<i>Acetylenes (C2-C5)</i>								
Ethyne	580	600	600	550	570	600	600	580
Propyne	580	600	600	550	570	600	600	580
1-Butyne	43	53	61	27	31	50	53	44
2-Butyne	43	53	61	27	31	50	53	44
1-Pentyne	43	53	61	27	31	50	53	44
2-Pentyne	43	53	61	27	31	50	53	44

TABLE 5-4. FUEL VOC PROFILES.

SUBSTANCE	PROFILE (Weight Fraction of Total Organic Gas)									
	Natural Gas		Field Gas			Refinery Gas		Landfill Gas		TEOR
	Internal Combustion Engine (SCR)	Gas Turbine (SCR/CO Catalyst)	Steam Generator (LNB, EGR)	Utility Boiler (Uncontrolled)	Internal Combustion Engine (Uncontrolled)	Process Heater (LNB)	Process Heater (SCR)	Internal Combustion Engine (Uncontrolled)	Steam Generator (LNB, EGR)	
Methane	0.9439	0.8064	0.7346	0.9004	0.5079	0.1873	0.2337	0.9134	0.8059	
Ethane	0.0373	0.0595	0.0830	0.0713	0.1518	0.1756	0.1774	0.0510	0.0181	
Propane	0.0098	0.0473	0.0443	0.0179	0.2227	0.3484	0.2908	0.0203	0.0102	
Isobutane	0.0015	0.0089	0.0161	0.0023	0.0347	0.1158	0.0484	0.0034	0.0023	
Butane	0.0024	0.0526	0.0274	0.0027	0.0640	0.0679	0.1029	0.0049	0.0409	
Neopentane	0.0000	0.0001	0.0002	ND	0.0001	0.0001	0.0001	ND	0.0018	
Isopentane	0.0009	0.0045	0.0140	0.0010	0.0103	0.0174	0.0250	0.0019	0.0015	
n-Pentane	0.0008	0.0039	0.0131	0.0008	0.0060	0.0104	0.0233	0.0015	0.0015	
Ethylene	ND	0.0090	ND	ND	ND	0.0636	0.0604	0.0000	ND	
cis-2-Butene	ND	0.0012	ND	ND	ND	ND	0.0069	0.0000	ND	
Cyclopentane	ND	0.0000	ND	ND	0.0005	ND	ND	0.0000	ND	
Ethyne	ND	ND	ND	ND	0.0000	0.0002	0.0000	0.0000	ND	
C6+	0.0031	0.0057	0.0634	0.0033	0.0019	0.0119	0.0215	0.0000	0.0001	
Unknown C4						0.0014		0.0033		
Unknown C5		0.0008					0.0094			

ND - Not Detected

SCR - Selective Catalytic Reduction

LNB - Low NOx Burner

EGR - Exhaust Gas Recirculation

TABLE 5-5. TEDLAR BAG SAMPLING DETECTION LIMITS.

SUBSTANCE	DETECTION LIMIT (ppbv, dry)							
	Internal Combustion Engine			Gas Turbine	Process Heater		Steam Generator	Utility Boiler
	Landfill Gas	Field Gas	Natural Gas	Natural Gas	Refinery Gas	Refinery Gas	Natural Gas	Natural Gas
	No Control	No Control	SCR	SCR/ CO Catalyst	LNB	SCR	LNB EGR	No Control
<i>Chlorinated Hydrocarbons (Continued)</i>								
1,1,2-Trichloroethane	43	53	61	27	31	50	53	44
Tetrachloroethene	43	53	61	27	31	50	53	44
Ethylene Dibromide	43	53	61	27	31	50	53	44
Ethylene Dichloride	43	53	61	27	31	50	53	44
Chlorobenzene	43	53	61	27	31	50	53	44
1,1,2,2-Tetrachloroethane	43	53	61	27	31	50	53	44
1,3-Dichlorobenzene	43	53	61	27	31	50	53	44
1,4-Dichlorobenzene	43	53	61	27	31	50	53	44
Chlorotoluene	43	53	61	27	31	50	53	44
1,2-Dichlorobenzene	43	53	61	27	31	50	53	44
1,2,4-Trichlorobenzene	43	53	61	27	31	50	53	44
Hexachlorobutadiene	43	53	61	27	31	50	53	44
trans-1,2-Dichloroethene	43	53	61	27	31	50	53	44
1,1,1,2-Tetrachloroethane	43	53	61	27	31	50	53	44
<i>Carbon Disulfide</i>	43	53	61	27	31	50	53	44
<i>1,3 - Butadiene</i>	43	53	61	27	31	50	53	44
<i>Propadiene</i>	43	53	61	27	31	50	53	44

LNB - Low NOx Burner

SCR - Selective Catalytic Reduction

EGR - Exhaust Gas Recirculation

TABLE 5-5. TEDLAR BAG SAMPLING DETECTION LIMITS.

SUBSTANCE	DETECTION LIMIT (ppbv, dry)							
	Internal Combustion Engine			Gas Turbine	Process Heater		Steam Generator	Utility Boiler
	Landfill Gas	Field Gas	Natural Gas	Natural Gas	Refinery Gas	Refinery Gas	Natural Gas	Natural Gas
	No Control	No Control	SCR	SCR/CO Catalyst	LNB	SCR	LNB EGR	No Control
<i>Aromatics</i>								
Benzene	43	53	61	27	31	50	53	44
Toluene	43	53	61	27	31	50	53	44
Ethyl Benzene	43	53	61	27	31	50	53	44
m-Xylene	43	53	61	27	31	50	53	44
p-Xylene	43	53	61	27	31	50	53	44
o-Xylene	43	53	61	27	31	50	53	44
Styrene	43	53	61	27	31	50	53	44
1,3,5-Trimethylbenzene	43	53	61	27	31	50	53	44
1,2,4-Trimethylbenzene	43	53	61	27	31	50	53	44
Phenol	43	53	61	27	31	50	53	44
Naphthalene	43	53	61	27	31	50	53	44
<i>Naphthenes</i>								
Cyclopropane	43	53	61	27	31	50	53	44
Cyclobutane	43	53	61	27	31	50	53	44
Cyclopentane	43	53	61	27	31	50	53	44
Cyclohexane	43	53	61	27	31	50	53	44
<i>Ethers</i>								
MTBE	43	53	61	27	31	50	53	44
Dimethyl Ether	43	53	61	27	31	50	53	44
Ethyl Methyl Ether	43	53	61	27	31	50	53	44
Diethyl Ether	43	53	61	27	31	50	53	44
Ethyl Propyl Ether	43	53	61	27	31	50	53	44
Dipropyl Ether	43	53	61	27	31	50	53	44
<i>Chlorinated Hydrocarbons</i>								
Chloromethane	43	53	61	27	31	50	53	44
Bromomethane	43	53	61	27	31	50	53	44
Chloroethane	43	53	61	27	31	50	53	44
1,1-Dichloroethene	43	53	61	27	31	50	53	44
Methylene Chloride	43	53	61	27	31	50	53	44
1,1-Dichloroethane	43	53	61	27	31	50	53	44
cis-1,2-Dichloroethene	43	53	61	27	31	50	53	44
Chloroform	43	53	61	27	31	50	53	44
1,1,1-Trichloroethane	43	53	61	27	31	50	53	44
Carbon Tetrachloride	43	53	61	27	31	50	53	44
1,2-Dichloroethane	43	53	61	27	31	50	53	44
Trichloroethene	43	53	61	27	31	50	53	44
1,2-Dichloropropane	43	53	61	27	31	50	53	44
cis-1,3-Dichloropropene	43	53	61	27	31	50	53	44
trans-1,3-Dichloropropene	43	53	61	27	31	50	53	44

TABLE 5-6. EMISSION VOC PROFILES
 (Only substances detected at one or more sources listed. See Table 5-5 for complete listing of over 100 target substances and detection limits).

SUBSTANCE	PROFILE (Weight Fraction of Total Organic Gas)			
	Landfill Gas	Field Gas	Natural Gas	SCR
	No Control	No Control		
Methane (a)	0.9468	0.4564	0.8592	
Ethane (a)	0.0205	0.1218	0.0581	
Propane (a)	0.0041	0.1237	0.0125	
Ethene (a)	0.0202	0.1132	0.0357	
Propene (a)	0.0042	0.0354	0.0040	
Ethyne (a)	ND	0.1348	0.0118	
1,3-Butadiene (b)	0.0002	0.0017	ND	
Benzene (a)	0.0003	0.0017	0.0003	
Toluene (a)	0.0006	{0.0010}	0.0008	
m,p-Xylenes (a)	ND	0.0004	ND	
Formaldehyde	{0.0020}	{0.0078}	{0.0168}	
Acetaldehyde	{0.0005}	{0.0015}	{0.0005}	
Acrolein	0.0002	0.0003	0.0002	
Propanal (a)	0.0000	0.0001	0.0001	
Acetone (a)	{0.0001}	{0.0001}	{0.0002}	
Crotonaldehyde (a)	0.0000	ND	0.0001	
Isobutyraldehyde (a)	0.0000	ND	ND	
Methyl Ethyl Ketone (a)	0.0001	0.0001	ND	
Total Weight Fraction	1.0000	1.0000	1.0000	
Detection Limit Ratio (c)	0.0079	0.0096	0.0099	

SCR - Selective Catalytic Reduction

(a) - Full ARB QA/QC standards were not applied to these results.

(b) - Matrix spike recovery less than 70% (See Table 6-4 and 6-6 for listing of recoveries).

(c) - Ratio of the sum of detection limits in ppbw,dry for nondetected substances to the sum of detections in ppbw,dry for detected substances.

98 - Average of detected and nondetected runs. 1/2 detection limit used for nondetected runs as specified in AB2588.

99 - All runs below the detection limit. No value reported as specified in AB2588.

() - Field blank corrected.

{ } - Field blank > 20% of sample value.

To ensure that all VOCs were quantified, the lab was instructed to report any peaks which were not attributable to the target analytes. As noted in Section 5.1, run specific profiles could not be calculated because the aldehyde and tedlar bag samples could not be collected simultaneously. As outlined in CARB Method 430, the aldehyde/ketone detections were blank corrected if the sample to blank ratio exceeded 5. Corrected aldehyde/ketone results are enclosed in parentheses in the results presentation. If the sample to blank ratio was less than 5, the value reported was termed the "reporting limit" and was equal to 5 times the blank level. Aldehyde/ketone results at the reporting limit are given in italic. The hydrocarbon and aromatic results were not corrected. These results are enclosed in { } if the field blank exceeded 20% of the sample value. 1,3-Butadiene results are not available for the refinery process heater with selective catalytic reduction and the utility boiler because of an equipment failure. Only a single aldehyde/ketone run was conducted at the refinery process heater with low NOx burners because the reagent and glassware were lost during transport from the lab.

5.3.1 VOC Profiles

Table 5-6 lists emission VOC profiles for the IC Engine sources. Profiles were not generated for the other sources because the sensitivity of the analysis procedures was not sufficient. Additional discussion of the accuracy of the profiles is provided later in this section. The IC engine profiles were developed by averaging the run specific weight fractions for each VOC target analyte at each source. As specified in AB2588 (see Air Toxics "Hot Spots" Information and Assessment Act of 1987 as adopted on June 10, 1993), 1/2 the detection limit was used when averaging detected and nondetected weight fractions. These averages are noted as 98. Averages were not calculated when all weight fractions for a target analyte at a source were at the detection limit, as specified in AB2588. These averages are noted as 99 and the value is given as ND. Next the total weight fraction of detected VOCs in the stack gas at each source was calculated by summing the average VOC weight fractions for each detected target analyte. The average VOC weight fractions for each detected target analyte were then divided by the total weight fraction of detected VOCs in the stack gas to generate the profiles in Table 5-6. The values are provided to four digits as specified in the ARB Speciation Manual dated July, 1989.

It is important to note the method of generating the profiles assumes that VOCs which were not detected in any of the runs do not contribute to the profile. This assumption can generate significant error if the sum of detection limits for nondetected substances is on the same order of magnitude as the sum of detections. The detection limit ratios, defined as the ratio of the sum of detection limits in parts per billion weight dry (ppbw,dry) for nondetected substances to the sum of

deviation (RSD) also are provided in the tables. The RSD provides an indication of the precision of the sampling and analysis procedures as well as the variability in the source emissions. 1/2 detection limits have been provided in the tables. Run specific emission factors are provided in Tables 5-9(a-h). The emission factors are expressed as lbs of substance emitted per trillion Btu of fuel burned.

The VOC concentrations in Tables 5-7(a-h) show that methane was the most prevalent VOC in the exhaust gases from each source. In addition, the reciprocating IC engines have more detections than the other sources. These devices have more detections because of the higher levels of total organic gases present. Reciprocating IC engines generally have total organic gas emissions on the order of 1000 ppmv while the external combustion sources have total organic gas emissions on the order of 10 ppmv. External combustion sources have lower total organic gas emissions because they have longer residence times which provide for increased mixing and combustion. Because the total organic gas emissions are lower for the external combustion sources and the gas turbine, the levels of the VOCs also are lower resulting in fewer detections as observed in Tables 5-7(a-h).

1,3-Butadiene was only detected at the landfill and field gas IC engines. It should be noted that the hold time for the natural gas IC engine exceeded two hours. Over this time period, significant decay in 1,3-Butadiene levels may have occurred resulting in the nondetection observed.

Aromatics were detected at each of the sources except refinery gas process heater with low NO_x burners and the utility boiler. Of the aromatics toluene, was the most commonly detected, while benzene was only detected at the IC engines. Formaldehyde and acetaldehyde were detected at each of the sources. However, at all sources except the IC engines detections were close to the blank levels and the reporting limit (five times the blank level) was reported at some sources. C3 and C4 aldehydes also were detected at some of the sources. Acetone also was detected at all of the sources.

5.4 NO_x Speciation

Another key objective of the program was to speciate NO_x emissions from each source. Species measured include NO and NO_x. NO₂ was determined by difference of the NO_x and NO measurements. Table 5-10 summarizes the O₂, CO₂, and NO_x speciation results for each source. The type of NO_x control device at each source, 7% O₂ corrected NO, NO₂ and NO_x concentrations, and NO to NO_x ratio are also provided in Table 5-10. Most of the sources except

detections in ppbw,dry for detected substances, were 0.0079, 0.0096, and 0.0099 for the landfill, field, and natural gas IC engines, respectively. These detection limit ratios are low indicating the detection limit treatment procedures have little influence on the IC Engine profiles. For the other sources, the detection limit ratios were 0.86 (utility boiler), 0.96 (process heater with LNB), 1.1 (gas turbine), 1.8 (steam generator), and 2.5 (process heater with SCR). For these sources, the assumptions described above may result in significant error. The detection limits had a significant impact on the uncertainty as indicated by the detection limit ratio of the external combustion sources and gas turbine VOC emissions profiles because:

- 1.) these devices have low total organic emissions, from 1 to 10 ppmv. Low total organic emission levels require very sensitive analysis techniques especially for C1 through C3 hydrocarbons. These techniques were beyond the scope of the program; and
- 2.) the extensive list of target analytes, over 100, yielded a large number of nondetected substances. One of the goals of the program was to quantify all VOCs in the emissions. Because of this goal, many substances were included on the target list even though there was a low probability of their presence in the emissions.

Because of the high uncertainty of the profiles for the external combustion sources and the gas turbine, no profiles were presented for these sources.

The IC engine profiles in Table 5-6 indicate that methane was the most prevalent VOC in the exhaust gases from each source. The field gas IC engine had the lowest percentage of methane and the highest percentage of C2 and C3 hydrocarbons. This is not surprising since this source also had the highest percentage of C2 and C3 hydrocarbons in the fuel. The fuel and emissions profiles for the landfill gas and natural gas IC engine also are similar. This indicates that the VOC profile changes little as a result of the combustion process at least for IC Engines. This is expected since IC Engines have short residence times and it is expected that some fuel will escape the engine without being exposed to combustion conditions.

5.3.2 VOC Emission Concentrations and Emission Factors

Tables 5-7(a-h) and 5-8(a-h) list run specific VOC concentrations in parts per billion weight dry and parts per billion volume dry at each of the sources. The tables are listed in the order the devices were tested. The same notations are used to indicate blank corrected data, data at the reporting limit, and results which had high blank levels. The source average and relative standard

TABLE 5-7a. VOC WEIGHT CONCENTRATION LANDFILL GAS INTERNAL COMBUSTION ENGINE (UNCONTROLLED)*

SUBSTANCE	CONCENTRATION (ppbw, dry)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	730000	740000	640000	700000	7.3
<u>Ethane</u>	15000	14000	16000	15000	5.3
<u>Propane</u>	4000	3000	2200	3100	29
<u>Ethene</u>	13000	16000	16000	15000	12
<u>Propene</u>	3800	2600	2900	3100	19
<u>Ethyne</u>	ND	ND	ND	ND	ND
<u>1,3-Butadiene</u>	200	a	NA	190	14
<u>Hexane</u>	ND	ND	ND	ND	ND
<u>Benzene</u>	62	62	62	62	99
<u>Toluene</u>	220	270	270	250	10
<u>Ethyl Benzene</u>	450	450	480	460	3.3
<u>m,p-Xylenes</u>	ND	ND	ND	ND	ND
<u>Phenol</u>	76	76	76	76	99
<u>Formaldehyde</u>	ND	ND	ND	ND	ND
<u>Acetaldehyde</u>	68	68	68	68	99
<u>Acrolein</u>	(90)	(1900)	(2400)	(1500)	83
<u>Propanal</u>	(460)	(360)	(280)	(370)	25
<u>Acetone</u>	180	170	150	170	11
<u>Crotonaldehyde</u>	28	22	17	22	26
<u>Isobutyraldehyde</u>	(110)	77	75	(88)	23
<u>Methyl Ethyl Ketone</u>	33	25	24	27	17
	ND	7.9	ND	4.5	65
	71	2.8	74	49	82

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 a - Average of run 2 diluted and undiluted bags.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 () - Field blank corrected.
 Italic - Reporting limit.
 {} - Field blank > 20% of sample value.

the natural gas IC engine operated fuel lean as indicated by the stack oxygen levels. The natural gas IC engine, however, was operated fuel rich. Overall, the IC engines had the highest NO_x concentrations. The natural gas utility boiler also had a high NO_x concentration. Sources with NO_x control devices had lower NO_x emission concentrations. These sources also had the lowest ratio of NO to NO_x. NO_x emissions from sources without NO_x control were almost entirely composed of NO.

Figures 5-2(a-h) present NO and NO_x concentrations at each source as a function of the sample time. These figures illustrate the variability in source operation as well as the difference between NO and NO_x emission concentrations. The sources with SCR, figures 5-2e, f and g, have the most visible difference.

TABLE 5-7c. VOC WEIGHT CONCENTRATION NATURAL GAS STEAM GENERATOR (LOW NOX BURNERS, EXHAUST GAS RECIRCULATION)*^.

SUBSTANCE	CONCENTRATION (ppbw, dry)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	2500	2500	2300	2400	4.6
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	300	300	300	ND	ND
<u>Butane</u>	440	440	440	99	ND
<u>Ethene</u>	280	280	280	99	ND
<u>Propene</u>	420	420	420	99	ND
<u>Ethyne</u>	260	260	260	99	ND
<u>1,3-Butadiene</u>	5.9	5.9	5.9	99	ND
<u>Hexane</u>	76	1400	1400	98	80
<u>Benzene</u>	ND	69	69	99	ND
<u>Toluene</u>	420	260	330	340	24
<u>Ethyl Benzene</u>	94	94	94	99	ND
<u>m,p-Xylenes</u>	410	94	94	200	92
<u>Phenol</u>	1600	83	83	600	150
<u>Formaldehyde</u>	45	46	50	47	5.3
<u>Acetaldehyde</u>	38	39	2.7	26	78
<u>Acrolein</u>	3	2.8	2.7	ND	ND
<u>Propanal</u>	3	2.8	2.7	99	ND
<u>Acetone</u>	150	150	170	160	5.3
<u>Crotonaldehyde</u>	3	2.8	2.7	99	ND
<u>Isobutyraldehyde</u>	3	2.8	2.7	99	ND
<u>Methyl Ethyl Ketone</u>	3	2.8	2.7	99	ND

< - Sum of detected and nondetected fractions.

() - Field blank corrected.

ND - Not detected (1/2 detection limit given for runs).

Italic - Reporting limit .

98 - Average of detected and nondetected.

{ } - Field blank > 20% of sample value.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

^Because of the high uncertainty in results, no speciation profiles were developed for this source.

TABLE 5-7b. VOC WEIGHT CONCENTRATION REFINERY GAS PROCESS HEATER (LOW NOX BURNERS)*^A.

SUBSTANCE	CONCENTRATION (ppbw, dry)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	6700	5500	5800	6000	11
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	ND	ND	ND	99	ND
<u>Ethene</u>	ND	ND	ND	99	ND
<u>Propene</u>	ND	ND	ND	99	ND
<u>Ethyne</u>	ND	ND	ND	99	ND
<u>1,3-Butadiene</u>	ND	ND	ND	99	ND
<u>Hexane</u>	ND	ND	ND	99	ND
<u>Benzene</u>	ND	ND	ND	99	ND
<u>Toluene</u>	ND	ND	ND	99	ND
<u>Ethyl Benzene</u>	ND	ND	ND	99	ND
<u>m,p-Xylenes</u>	ND	ND	ND	99	ND
<u>Phenol</u>	ND	ND	ND	99	ND
<u>Formaldehyde</u>	(40)	49	49	ND	ND
<u>Acetaldehyde</u>	48			(40)	48
<u>Acrolein</u>	ND	ND		99	ND
<u>Propanal</u>	ND	ND		99	ND
<u>Acetone</u>	<	16		98	16
<u>Crotonaldehyde</u>	ND	2.4		99	ND
<u>Isobutyraldehyde</u>	ND	2.4		99	ND
<u>Methyl Ethyl Ketone</u>	ND	2.4		99	ND

< - Sum of detected and nondetected fractions.

ND - Not detected (1/2 detection limit given for runs).

98 - Average of detected and nondetected.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

^Because of the high uncertainty in results, no speciation profiles were developed for this source.

() - Field blank corrected.

Italic - Reporting limit.

{ } - Field blank > 20% of sample value.

TABLE 5-7e. VOC WEIGHT CONCENTRATION NATURAL GAS INTERNAL COMBUSTION ENGINE
(SELECTIVE CATALYTIC REDUCTION)*.

SUBSTANCE	CONCENTRATION (ppbw, dry)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	700000	690000	650000	680000	3.4
<u>Ethane</u>	48000	47000	43000	46000	5.2
<u>Propane</u>	9800	9900	10000	9900	1.1
<u>Ethene</u>	27000	30000	29000	28000	5.7
<u>Propene</u>	3200	2900	3300	3100	6
<u>Ethyne</u>	9400	9400	9200	9300	1.6
<u>1,3-Butadiene</u>	ND	ND	ND	ND	ND
<u>Hexane</u>	88	88	88	88	99
<u>Benzene</u>	220	250	220	230	7.9
<u>Toluene</u>	560	640	640	610	7.1
<u>Ethyl Benzene</u>	ND	ND	ND	ND	ND
<u>m,p-Xylenes</u>	ND	ND	ND	ND	ND
<u>Phenol</u>	96	96	96	96	ND
<u>Formaldehyde</u>	(12000)	(14000)	(14000)	(13000)	11
<u>Acetaldehyde</u>	(360)	(330)	(400)	(360)	10
<u>Acrolein</u>	(130)	(100)	(220)	(150)	41
<u>Propanal</u>	<	ND	<	69	72
<u>Acetone</u>	140	(130)	140	(140)	5.7
<u>Crotonaldehyde</u>	<	ND	<	58	47
<u>Isobutyraldehyde</u>	ND	ND	ND	ND	ND
<u>Methyl Ethyl Ketone</u>	21	38	38	ND	ND

< - Sum of detected and nondetected fractions.

ND - Not detected (1/2 detection limit given for runs).

98 - Average of detected and nondetected.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

() - Field blank corrected.

Italic - Reporting limit.

{ } - Field blank > 20% of sample value.

TABLE 5-7d. VOC WEIGHT CONCENTRATION FIELD GAS INTERNAL COMBUSTION ENGINE
(UNCONTROLLED)*.

SUBSTANCE	CONCENTRATION (ppbw, dry)			RSD (%)
	R1	R2	R3	
<u>Methane</u>	310000	310000	310000	0.41
<u>Ethane</u>	84000	83000	84000	0.88
<u>Propane</u>	86000	82000	87000	3.2
<u>Ethene</u>	110000	59000	60000	41
<u>Propene</u>	25000	23000	25000	4.5
<u>Ethyne</u>	58000	110000	110000	32
<u>1,3-Butadiene</u>	1200	1100	NA	8.3
<u>Hexane</u>	ND	78	78	ND
<u>Benzene</u>	650	1600	1300	40
<u>Toluene</u>	{570}	{800}	{770}	18
<u>Ethyl Benzene</u>	ND	96	96	ND
<u>m,p-Xylenes</u>	270	270	270	0
<u>Phenol</u>	ND	85	85	ND
<u>Formaldehyde</u>	(1200)	(5800)	(9000)	73
<u>Acetaldehyde</u>	(740)	(1400)	(1000)	32
<u>Acrolein</u>	<	280	260	65
<u>Propanal</u>	42	<	78	43
<u>Acetone</u>	(55)	(110)	(53)	46
<u>Crotonaldehyde</u>	ND	ND	31	ND
<u>Isobutyraldehyde</u>	ND	ND	31	ND
<u>Methyl Ethyl Ketone</u>	61	120	110	34

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 () - Field blank corrected.
 Italic - Reporting limit.
 {} - Field blank > 20% of sample value.

TABLE 5-7g. VOC WEIGHT CONCENTRATION REFINERY GAS PROCESS HEATER (SELECTIVE CATALYTIC REDUCTION)**.

SUBSTANCE	CONCENTRATION (ppbw, dry)					RSD (%)
	R1	R2	R3	Average		
<u>Methane</u>	{2200}	{2800}	{2400}	{2500}		12
<u>Ethane</u>	ND	ND	ND	99	ND	ND
<u>Propane</u>	300	300	300	ND	ND	ND
<u>Ethene</u>	ND	ND	ND	99	ND	ND
<u>Propene</u>	440	440	440	99	ND	ND
<u>Ethyne</u>	280	280	280	99	ND	ND
<u>1,3-Butadiene</u>	ND	ND	ND	99	ND	ND
<u>Hexane</u>	420	420	420	99	ND	ND
<u>Benzene</u>	260	260	260	99	ND	ND
<u>Toluene</u>	NA	NA	NA	NA	ND	ND
<u>Ethyl Benzene</u>	71	71	71	99	ND	ND
<u>m,p-Xylenes</u>	65	65	65	99	ND	ND
<u>Phenol</u>	460	430	210	370	36	36
<u>Formaldehyde</u>	ND	ND	ND	99	ND	ND
<u>Acetaldehyde</u>	88	88	88	98	230	54
<u>Acrolein</u>	320	280	88	99	ND	ND
<u>Propanal</u>	78	78	78	99	ND	ND
<u>Acetone</u>	67	65	78	70	10	10
<u>Crotonaldehyde</u>	43	41	50	45	10	10
<u>Isobutyraldehyde</u>	2.6	2.6	3.3	99	ND	ND
<u>Methyl Ethyl Ketone</u>	2.6	2.6	3.3	99	ND	ND
	2.6	2.6	3.3	98	11	130
	2.6	5.8	3.3	99	ND	ND
	2.6	5.3	3.3	98	3.9	43
				98	3.7	37

< - Sum of detected and nondetected fractions.

ND - Not detected (1/2 detection limit given for runs).

98 - Average of detected and nondetected.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

^Because of the high uncertainty in results, no speciation profiles were developed for this source.

() - Field blank corrected.

Italic - Reporting limit.

{ } - Field blank > 20% of sample value.

TABLE 5-7f. VOC WEIGHT CONCENTRATION NATURAL/REFINERY GAS TURBINE (SELECTIVE CATALYTIC REDUCTION/CO CATALYST)**^.

SUBSTANCE	CONCENTRATION (ppbw, dry)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	4500	4500	4000	4300	6.9
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	280	280	280	ND	ND
<u>Ethene</u>	410	410	410	99	ND
<u>Propene</u>	260	260	260	99	ND
<u>Ethyne</u>	400	400	400	99	ND
<u>1,3-Butadiene</u>	240	240	240	99	ND
<u>Hexane</u>	3.1	3.1	3.1	99	ND
<u>Benzene</u>	40	40	40	99	ND
<u>Toluene</u>	36	36	36	99	ND
<u>Ethyl Benzene</u>	200	42	200	98	62
<u>m,p-Xylenes</u>	49	49	49	99	ND
<u>Phenol</u>	49	49	120	98	55
<u>Formaldehyde</u>	43	43	43	99	ND
<u>Acetaldehyde</u>	47	48	47	48	1.6
<u>Acrolein</u>	41	42	41	41	1.6
<u>Propanal</u>	3.6	3.7	3.6	99	ND
<u>Acetone</u>	3.6	3.7	3.6	99	ND
<u>Crotonaldehyde</u>	3.6	3.7	42	98	130
<u>Isobutyraldehyde</u>	3.6	3.7	3.6	99	ND
<u>Methyl Ethyl Ketone</u>	3.6	3.7	3.6	99	ND

< - Sum of detected and nondetected fractions. () - Field blank corrected.

ND - Not detected (1/2 detection limit given for runs). Italic - Reporting limit.

98 - Average of detected and nondetected. {} - Field blank > 20% of sample value.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

^Because of the high uncertainty in results, no speciation profiles were developed for this source.

TABLE 5-8a. VOC VOLUME CONCENTRATION LANDFILL GAS INTERNAL COMBUSTION ENGINE (UNCONTROLLED)*

SUBSTANCE	CONCENTRATION (ppbv, dry)				RSD (%)
	RI	R2	R3	Average	
<u>Methane</u>	1400000	1400000	1200000	1300000	7.3
<u>Ethane</u>	15000	14000	16000	15000	5.3
<u>Propane</u>	2700	2000	1500	2100	29
<u>Ethene</u>	14000	17000	17000	16000	12
<u>Propene</u>	2700	1900	2100	2200	19
<u>Ethyne</u>	ND	ND	290	ND	ND
<u>1,3-Butadiene</u>	110	99	NA	100	7.8
<u>Hexane</u>	22	ND	22	ND	ND
<u>Benzene</u>	86	100	100	98	10
<u>Toluene</u>	150	150	160	150	3.3
<u>Ethyl Benzene</u>	22	ND	22	ND	ND
<u>m,p-Xylenes</u>	22	ND	22	ND	ND
<u>Phenol</u>	22	ND	22	ND	ND
<u>Formaldehyde</u>	(90)	(1900)	(2400)	(1500)	83
<u>Acetaldehyde</u>	(310)	(240)	(190)	(250)	25
<u>Acrolein</u>	97	<	<	89	11
<u>Propanal</u>	14	<	8.6	11	26
<u>Acetone</u>	(57)	40	39	(45)	23
<u>Crotonaldehyde</u>	<	11	<	12	17
<u>Isobutyraldehyde</u>	14	<	10	12	17
<u>Methyl Ethyl Ketone</u>	1.1	<	1.2	1.9	65
	30	ND	31	21	82

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 a - Average of run 2 diluted and undiluted bags.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 () - Field blank corrected.
 Italic - Reporting limit.
 {} - Field blank > 20% of sample value.

TABLE 5-7h. VOC WEIGHT CONCENTRATION NATURAL GAS UTILITY BOILER (UNCONTROLLED)**^.

SUBSTANCE	CONCENTRATION (ppbw, dry)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	{8700}	{8700}	{8700}	{8700}	
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	ND	ND	ND	99	ND
<u>Ethene</u>	ND	ND	ND	99	ND
<u>Propene</u>	ND	ND	ND	99	ND
<u>Ethyne</u>	ND	ND	ND	99	ND
<u>1,3-Butadiene</u>	NA	NA	NA	NA	ND
<u>Hexane</u>	ND	ND	ND	99	ND
<u>Benzene</u>	ND	ND	ND	99	ND
<u>Toluene</u>	ND	ND	ND	99	ND
<u>Ethyl Benzene</u>	ND	ND	ND	99	ND
<u>m,p-Xylenes</u>	ND	ND	ND	99	ND
<u>Phenol</u>	ND	ND	ND	99	ND
<u>Formaldehyde</u>	(76)	(43)	33	(51)	45
<u>Acetaldehyde</u>	34	(58)	31	(41)	36
<u>Acrolein</u>	ND	ND	ND	99	ND
<u>Propanal</u>	9.3	45	2.5	98	120
<u>Acetone</u>	17	36	2.5	98	91
<u>Crotonaldehyde</u>	2.8	32	2.5	98	140
<u>Isobutyraldehyde</u>	ND	ND	ND	99	ND
<u>Methyl Ethyl Ketone</u>	14	<	2.5	98	88

< - Sum of detected and nondetected fractions.

() - Field blank corrected.

ND - Not detected (1/2 detection limit given for runs).

Italic - Reporting limit.

98 - Average of detected and nondetected.

{ } - Field blank > 20% of sample value.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

^Because of the high uncertainty in results, no speciation profiles were developed for this source.

TABLE 5-8c. VOC VOLUME CONCENTRATION NATURAL GAS STEAM GENERATOR (LOW NOX BURNERS, EXHAUST GAS RECIRCULATION)*^.

SUBSTANCE	CONCENTRATION (ppbv, dry)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	4700	4700	4300	4600	4.6
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	300	300	300	ND	ND
<u>Ethene</u>	300	300	300	99	ND
<u>Propene</u>	300	300	300	99	ND
<u>Ethyne</u>	300	300	300	99	ND
<u>1,3-Butadiene</u>	3.3	3.3	3.3	99	ND
<u>Hexane</u>	27	490	490	98	80
<u>Benzene</u>	27	ND	ND	99	ND
<u>Toluene</u>	140	85	110	110	24
<u>Ethyl Benzene</u>	27	ND	ND	99	ND
<u>m,p-Xylenes</u>	120	27	27	57	92
<u>Phenol</u>	520	27	27	190	150
<u>Formaldehyde</u>	45	46	50	47	5.3
<u>Acetaldehyde</u>	26	26	1.9	18	78
<u>Acrolein</u>	1.6	ND	ND	ND	ND
<u>Propanal</u>	1.5	ND	1.4	ND	ND
<u>Acetone</u>	79	80	87	82	5.3
<u>Crotonaldehyde</u>	1.3	ND	1.2	ND	ND
<u>Isobutyraldehyde</u>	1.2	ND	1.2	ND	ND
<u>Methyl Ethyl Ketone</u>	1.2	ND	1.2	ND	ND

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 ^Because of the high uncertainty in results, no speciation profiles were developed for this source.

() - Field blank corrected.
 Italic - Reporting limit.
 {} - Field blank > 20% of sample value.

TABLE 5-8b. VOC VOLUME CONCENTRATION REFINERY GAS PROCESS HEATER (LOW NOX BURNERS)*^.

SUBSTANCE	CONCENTRATION (ppbv, dry)					RSD (%)
	R1	R2	R3	Average		
<u>Methane</u>	12000	10000	11000	11000	11	
<u>Ethane</u>	ND	ND	ND	99	ND	
<u>Propane</u>	280	280	280	99	ND	
<u>Ethene</u>	280	280	280	99	ND	
<u>Propene</u>	280	280	280	99	ND	
<u>Ethyne</u>	280	280	280	99	ND	
<u>1,3-Butadiene</u>	2.8	2.8	2.8	99	ND	
<u>Hexane</u>	15	15	15	99	ND	
<u>Benzene</u>	15	15	15	99	ND	
<u>Toluene</u>	15	15	15	99	ND	
<u>Ethyl Benzene</u>	15	15	15	99	ND	
<u>m,p-Xylenes</u>	15	15	15	99	ND	
<u>Phenol</u>	15	15	15	99	ND	
<u>Formaldehyde</u>	(39)			(39)		
<u>Acetaldehyde</u>	32			32		
<u>Acrolein</u>	1.5			99	ND	
<u>Propanal</u>	1.5			99	ND	
<u>Acetone</u>	<			98	8	
<u>Crotonaldehyde</u>	1			99	ND	
<u>Isobutyraldehyde</u>	1			99	ND	
<u>Methyl Ethyl Ketone</u>	1			99	ND	

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 ^Because of the high uncertainty in results, no speciation profiles were developed for this source.

TABLE 5-8e. VOC VOLUME CONCENTRATION NATURAL GAS INTERNAL COMBUSTION ENGINE
(SELECTIVE CATALYTIC REDUCTION)*.

SUBSTANCE	CONCENTRATION (ppbv, dry)					RSD (%)
	R1	R2	R3	Average		
<u>Methane</u>	130000	130000	120000	130000		3.4
<u>Ethane</u>	48000	46000	43000	46000		5.2
<u>Propane</u>	6700	6800	6800	6700		1.1
<u>Ethene</u>	28000	32000	31000	30000		5.7
<u>Propene</u>	2200	2100	2400	2200		6
<u>Ethyne</u>	11000	11000	11000	11000		1.6
<u>1,3-Butadiene</u>	ND	0.84	ND	0.84	99	ND
<u>Hexane</u>	ND	30	ND	30	99	ND
<u>Benzene</u>	85	97	85	89		7.9
<u>Toluene</u>	180	210	210	200		7.1
<u>Ethyl Benzene</u>	ND	30	ND	30	99	ND
<u>m,p-Xylenes</u>	ND	30	ND	30	99	ND
<u>Phenol</u>	ND	30	ND	30	99	ND
<u>Formaldehyde</u>	(12000)	(14000)	(14000)	(13000)		11
<u>Acetaldehyde</u>	(250)	(220)	(270)	(250)		10
<u>Acrolein</u>	(71)	(55)	(120)	(82)	98	41
<u>Propanal</u>	<	ND	<	35	98	72
<u>Acetone</u>	22	20	65	35		5.7
<u>Crotonaldehyde</u>	73	(66)	73	(71)		47
<u>Isobutyraldehyde</u>	<	ND	<	25	98	ND
<u>Methyl Ethyl Ketone</u>	ND	16	ND	16	99	ND
	ND	16	ND	16	99	ND

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 () - Field blank corrected.
 Italic - Reporting limit.
 {} - Field blank > 20% of sample value.

TABLE 5-8d. VOC VOLUME CONCENTRATION FIELD GAS INTERNAL COMBUSTION ENGINE (UNCONTROLLED)*.

SUBSTANCE	CONCENTRATION (ppbv, dry)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	580000	580000	580000	580000	0.41
<u>Ethane</u>	83000	82000	82000	82000	0.88
<u>Propane</u>	57000	55000	59000	57000	3.2
<u>Ethene</u>	120000	62000	63000	82000	41
<u>Propene</u>	17000	16000	18000	17000	4.5
<u>Ethyne</u>	66000	120000	130000	110000	32
<u>1,3-Butadiene</u>	670	600	NA	640	8.3
<u>Hexane</u>	27	27	27	ND	ND
<u>Benzene</u>	250	590	500	450	40
<u>Toluene</u>	{180}	{260}	{250}	{230}	18
<u>Ethyl Benzene</u>	27	27	27	ND	ND
<u>m,p-Xylenes</u>	75	75	75	75	0
<u>Phenol</u>	27	27	27	ND	ND
<u>Formaldehyde</u>	(1200)	(5700)	(8900)	(5300)	73
<u>Acetaldehyde</u>	(490)	(950)	(670)	(700)	32
<u>Acrolein</u>	<	150	140	100	65
<u>Propanal</u>	22	54	40	39	43
<u>Acetone</u>	(28)	(57)	(27)	(37)	46
<u>Crotonaldehyde</u>	ND	ND	ND	ND	ND
<u>Isobutyraldehyde</u>	ND	ND	ND	ND	ND
<u>Methyl Ethyl Ketone</u>	25	51	46	41	34

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 () - Field blank corrected.
 Italic - Reporting limit.
 {} - Field blank > 20% of sample value.

TABLE 5-8g. VOC VOLUME CONCENTRATION REFINERY GAS PROCESS HEATER (SELECTIVE CATALYTIC REDUCTION)*^.

SUBSTANCE	CONCENTRATION (ppbv, dry)					RSD (%)
	R1	R2	R3	Average		
<u>Methane</u>	{4100}	{5200}	{4600}	{4600}		12
<u>Ethane</u>	ND	ND	ND	99	ND	ND
<u>Propane</u>	300	300	300	99	ND	ND
<u>Ethene</u>	300	300	300	99	ND	ND
<u>Propene</u>	300	300	300	99	ND	ND
<u>Ethyne</u>	300	300	300	99	ND	ND
<u>1,3-Butadiene</u>	NA	NA	NA	NA	NA	ND
<u>Hexane</u>	25	25	25	99	ND	ND
<u>Benzene</u>	25	25	25	99	ND	ND
<u>Toluene</u>	150	140	70	99	120	36
<u>Ethyl Benzene</u>	25	25	25	99	ND	ND
<u>m,p-Xylenes</u>	90	80	25	98	65	54
<u>Phenol</u>	25	25	25	99	ND	ND
<u>Formaldehyde</u>	67	65	78		70	10
<u>Acetaldehyde</u>	29	28	34		30	10
<u>Acrolein</u>	1.4	1.4	1.8	99	ND	ND
<u>Propanal</u>	1.3	1.4	1.7	99	ND	ND
<u>Acetone</u>	1.3	1.5	1.7	98	5.9	130
<u>Crotonaldehyde</u>	1.1	1.1	1.4	99	ND	ND
<u>Isobutyraldehyde</u>	1.1	<	1.4	98	1.6	43
<u>Methyl Ethyl Ketone</u>	1.1	<	1.4	98	1.6	37

< - Sum of detected and nondetected fractions.

() - Field blank corrected.

ND - Not detected (1/2 detection limit given for runs).

Italic - Reporting limit .

98 - Average of detected and nondetected.

{ } - Field blank > 20% of sample value.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

^Because of the high uncertainty in results, no speciation profiles were developed for this source.

TABLE 5-8f. VOC VOLUME CONCENTRATION NATURAL/REFINERY GAS TURBINE (SELECTIVE CATALYTIC REDUCTION/CO CATALYST)**A.

SUBSTANCE	CONCENTRATION (ppbv, dry)				RSD (%)
	R1	R2	R3	Average	
Methane	8300	8100	7300	7900	6.9
Ethane	ND	ND	ND	99	ND
Propane	ND	ND	ND	99	ND
Ethene	ND	ND	ND	99	ND
Propene	ND	ND	ND	99	ND
Ethyne	ND	ND	ND	99	ND
1,3-Butadiene	ND	ND	ND	99	ND
Hexane	ND	ND	ND	99	ND
Benzene	ND	ND	ND	99	ND
Toluene	ND	ND	ND	98	62
Ethyl Benzene	ND	ND	ND	99	ND
m,p-Xylenes	ND	ND	ND	98	55
Phenol	ND	ND	ND	99	ND
Formaldehyde	46	47	46	46	1.6
Acetaldehyde	27	28	27	27	1.6
Acrolein	ND	ND	ND	99	ND
Propanal	ND	ND	ND	99	ND
Acetone	ND	ND	ND	98	130
Crotonaldehyde	ND	ND	ND	99	ND
Isobutyraldehyde	ND	ND	ND	99	ND
Methyl Ethyl Ketone	ND	ND	ND	99	ND

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 ^Because of the high uncertainty in results, no speciation profiles were developed for this source.

() - Field blank corrected.
 Italic - Reporting limit.
 {} - Field blank > 20% of sample value.

TABLE 5-9a. VOC EMISSION FACTORS LANDFILL GAS INTERNAL COMBUSTION ENGINE (UNCONTROLLED)*.

SUBSTANCE	EMISSION FACTOR (lb/TBtu)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	490000	490000	430000	470000	7.3
<u>Ethane</u>	10000	9600	11000	10000	5.3
<u>Propane</u>	2600	2000	1500	2000	29
<u>Ethene</u>	8600	11000	11000	10000	12
<u>Propene</u>	2500	1700	2000	2100	19
<u>Ethyne</u>	ND	ND	ND	ND	ND
<u>1,3-Butadiene</u>	130	120	NA	130	7.1
<u>Hexane</u>	ND	41	ND	ND	ND
<u>Benzene</u>	150	180	180	170	10
<u>Toluene</u>	300	300	320	300	3.3
<u>Ethyl Benzene</u>	ND	ND	ND	ND	ND
<u>m,p-Xylenes</u>	ND	ND	ND	ND	ND
<u>Phenol</u>	ND	45	ND	ND	ND
<u>Formaldehyde</u>	(58)	(1200)	(1600)	(960)	84
<u>Acetaldehyde</u>	(300)	(230)	(190)	(240)	23
<u>Acrolein</u>	120	110	98	110	9.2
<u>Propanal</u>	<	14	<	15	24
<u>Acetone</u>	<	50	50	(57)	22
<u>Crotonaldehyde</u>	<	16	<	18	16
<u>Isobutyraldehyde</u>	ND	5.2	ND	2.9	65
<u>Methyl Ethyl Ketone</u>	46	1.8	50	33	82

< - Sum of detected and nondetected fractions.

() - Field blank corrected.

ND - Not detected (1/2 detection limit given for runs).

Italic - Reporting limit.

98 - Average of detected and nondetected.

{ } - Field blank > 20% of sample value.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

a - Average of run 2 diluted and undiluted bags.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

TABLE 5-8h. VOC VOLUME CONCENTRATION NATURAL GAS UTILITY BOILER (UNCONTROLLED)**^

SUBSTANCE	CONCENTRATION (ppbv, dry)					RSD (%)
	R1	R2	R3	Average		
<u>Methane</u>	{16000}	{16000}	{16000}	{16000}		
<u>Ethane</u>	ND	ND	ND	99	ND	ND
<u>Propane</u>	290	290	290	99	ND	ND
<u>Ethene</u>	290	290	290	99	ND	ND
<u>Propene</u>	290	290	290	99	ND	ND
<u>Ethyne</u>	290	290	290	99	ND	ND
<u>1,3-Butadiene</u>	NA	NA	NA	NA	ND	ND
<u>Hexane</u>	ND	22	22	99	ND	ND
<u>Benzene</u>	ND	22	22	99	ND	ND
<u>Toluene</u>	ND	22	22	99	ND	ND
<u>Ethyl Benzene</u>	ND	22	22	99	ND	ND
<u>m,p-Xylenes</u>	ND	22	22	99	ND	ND
<u>Phenol</u>	ND	22	22	99	ND	ND
<u>Formaldehyde</u>	(75)	(42)	(42)	99	(50)	45
<u>Acetaldehyde</u>	23	(39)	(39)	99	(28)	36
<u>Acrolein</u>	ND	ND	1.3	99	ND	ND
<u>Propanal</u>	4.7	23	1.3	98	9.6	120
<u>Acetone</u>	8.8	19	1.3	98	9.5	91
<u>Crotonaldehyde</u>	1.2	14	1.1	98	5.3	140
<u>Isobutyraldehyde</u>	ND	<	1	99	ND	ND
<u>Methyl Ethyl Ketone</u>	5.8	<	12	98	6.4	88

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 ^Because of the high uncertainty in results, no speciation profiles were developed for this source.

TABLE 5-9c. VOC EMISSION FACTORS NATURAL GAS STEAM GENERATOR (LOW NOX BURNERS, EXHAUST GAS RECIRCULATION)*^.

SUBSTANCE	EMISSION FACTOR (lb/TBtu)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	2100	2100	2000	2100	4.6
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	ND	ND	ND	99	ND
<u>Ethene</u>	ND	ND	ND	99	ND
<u>Propene</u>	ND	ND	ND	99	ND
<u>Ethyne</u>	ND	ND	ND	99	ND
<u>1,3-Butadiene</u>	ND	ND	ND	99	ND
<u>Hexane</u>	65	1200	1200	98	80
<u>Benzene</u>	ND	ND	ND	99	ND
<u>Toluene</u>	360	220	280	290	24
<u>Ethyl Benzene</u>	ND	ND	ND	99	ND
<u>m,p-Xylenes</u>	350	80	80	98	92
<u>Phenol</u>	1400	71	71	98	150
<u>Formaldehyde</u>	39	39	45	41	8.6
<u>Acetaldehyde</u>	32	33	2.5	23	77
<u>Acrolein</u>	ND	ND	ND	98	ND
<u>Propanal</u>	ND	ND	ND	99	ND
<u>Acetone</u>	130	2.4	2.5	99	ND
<u>Crotonaldehyde</u>	ND	130	150	140	8.6
<u>Isobutyraldehyde</u>	ND	2.4	2.5	99	ND
<u>Methyl Ethyl Ketone</u>	ND	2.4	2.5	99	ND
	ND	2.4	2.5	99	ND

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 ^Because of the high uncertainty in results, no speciation profiles were developed for this source.

TABLE 5-9b. VOC EMISSION FACTORS REFINERY GAS PROCESS HEATER (LOW NOX BURNERS)*^.

SUBSTANCE	EMISSION FACTOR (lb/TBtu)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	8600	7000	6300	7300	16
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	ND	370	310	ND	ND
<u>Ethene</u>	ND	540	460	99	ND
<u>Propene</u>	ND	340	290	99	ND
<u>Ethyne</u>	ND	510	440	99	ND
<u>1,3-Butadiene</u>	ND	320	270	99	ND
<u>Hexane</u>	ND	6.6	5.6	99	ND
<u>Benzene</u>	ND	57	48	99	ND
<u>Toluene</u>	ND	51	44	99	ND
<u>Ethyl Benzene</u>	ND	61	52	99	ND
<u>m,p-Xylenes</u>	ND	70	60	99	ND
<u>Phenol</u>	ND	70	60	99	ND
<u>Formaldehyde</u>	ND	70	70	99	ND
<u>Acetaldehyde</u>	(57)			(57)	
<u>Acrolein</u>	68			68	
<u>Propanal</u>	ND	4.1		99	ND
<u>Acetone</u>	ND	4.2		99	ND
<u>Crotonaldehyde</u>	<	23		98	23
<u>Isobutyraldehyde</u>	ND	3.4		99	ND
<u>Methyl Ethyl Ketone</u>	ND	3.5		99	ND
<u>Methyl Ethyl Ketone</u>	ND	3.5		99	ND

< - Sum of detected and nondetected fractions.

ND - Not detected (1/2 detection limit given for runs).

98 - Average of detected and nondetected.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

^Because of the high uncertainty in results, no speciation profiles were developed for this source.

() - Field blank corrected.

Italic - Reporting limit .

() - Field blank > 20% of sample value.

TABLE 5-9e. VOC EMISSION FACTORS NATURAL GAS INTERNAL COMBUSTION ENGINE
(SELECTIVE CATALYTIC REDUCTION)*.

SUBSTANCE	EMISSION FACTOR (lb/TBtu)					RSD (%)
	R1	R2	R3	Average		
<u>Methane</u>	590000	580000	560000	580000		3.4
<u>Ethane</u>	41000	40000	37000	39000		5.2
<u>Propane</u>	8300	8400	8500	8400		1.1
<u>Ethene</u>	23000	25000	24000	24000		5.7
<u>Propene</u>	2700	2500	2800	2700		6
<u>Ethyne</u>	8000	8000	7800	7900		1.6
<u>1,3-Butadiene</u>	ND	ND	ND	ND	99	ND
<u>Hexane</u>	ND	ND	ND	ND	99	ND
<u>Benzene</u>	190	220	190	200		7.9
<u>Toluene</u>	480	540	540	520		7.1
<u>Ethyl Benzene</u>	ND	ND	ND	ND	99	ND
<u>m,p-Xylenes</u>	ND	ND	ND	ND	99	ND
<u>Phenol</u>	ND	ND	ND	ND	99	ND
<u>Formaldehyde</u>	(8400)	(9700)	(8400)	(8800)		8.2
<u>Acetaldehyde</u>	(270)	(220)	(240)	(240)		9.2
<u>Acrolein</u>	(96)	(70)	(130)	(100)	98	32
<u>Propanal</u>	<	ND	<	44	98	62
<u>Acetone</u>	100	(87)	85	(92)	98	11
<u>Crotonaldehyde</u>	<	ND	<	37	98	38
<u>Isobutyraldehyde</u>	ND	ND	ND	ND	99	ND
<u>Methyl Ethyl Ketone</u>	ND	ND	ND	ND	99	ND

< - Sum of detected and nondetected fractions.

ND - Not detected (1/2 detection limit given for runs).

98 - Average of detected and nondetected.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

() - Field blank corrected.

Italic - Reporting limit .

{ } - Field blank > 20% of sample value.

TABLE 5-9d. VOC EMISSION FACTORS FIELD GAS INTERNAL COMBUSTION ENGINE (UNCONTROLLED)*.

SUBSTANCE	EMISSION FACTOR (lb/TBtu)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	180000	180000	180000	180000	0.41
<u>Ethane</u>	49000	48000	49000	49000	0.88
<u>Propane</u>	50000	48000	51000	49000	3.2
<u>Ethene</u>	67000	34000	35000	45000	41
<u>Propene</u>	14000	13000	15000	14000	4.5
<u>Ethyne</u>	34000	63000	64000	54000	32
<u>1,3-Butadiene</u>	720	640	NA	680	8.3
<u>Hexane</u>	ND	ND	ND	ND	ND
<u>Benzene</u>	380	900	770	680	40
<u>Toluene</u>	{330}	{460}	{440}	{410}	18
<u>Ethyl Benzene</u>	ND	ND	ND	ND	ND
<u>m,p-Xylenes</u>	160	160	160	160	0
<u>Phenol</u>	ND	ND	ND	ND	ND
<u>Formaldehyde</u>	(800)	(3600)	(5200)	(3200)	70
<u>Acetaldehyde</u>	(480)	(880)	(580)	(650)	32
<u>Acrolein</u>	<	180	150	120	64
<u>Propanal</u>	28	<	45	47	42
<u>Acetone</u>	(36)	(70)	<	(46)	47
<u>Crotonaldehyde</u>	ND	ND	ND	ND	ND
<u>Isobutyraldehyde</u>	ND	ND	ND	ND	ND
<u>Methyl Ethyl Ketone</u>	40	78	65	61	31

< - Sum of detected and nondetected fractions.

() - Field blank corrected.

ND - Not detected (1/2 detection limit given for runs).

Italic - Reporting limit.

98 - Average of detected and nondetected.

{ } - Field blank > 20% of sample value.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

TABLE 5-9g. VOC EMISSION FACTORS REFINERY GAS PROCESS HEATER (SELECTIVE CATALYTIC REDUCTION)**.

SUBSTANCE	EMISSION FACTOR (lb/TBtu)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	{1700}	{2100}	{1900}	{1900}	12
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	230	230	230	99	ND
<u>Ethene</u>	340	340	340	99	ND
<u>Propene</u>	220	220	220	99	ND
<u>Ethyne</u>	330	330	320	99	ND
<u>1,3-Butadiene</u>	200	200	200	99	ND
<u>Hexane</u>	NA	NA	NA	NA	ND
<u>Benzene</u>	55	55	55	99	ND
<u>Toluene</u>	50	50	50	99	ND
<u>Ethyl Benzene</u>	360	330	160	280	37
<u>m,p-Xylenes</u>	68	68	68	99	ND
<u>Phenol</u>	250	220	68	98	54
<u>Formaldehyde</u>	60	60	60	99	ND
<u>Acetaldehyde</u>	61	50	62	57	11
<u>Acrolein</u>	39	32	40	37	11
<u>Propanal</u>	2.3	2	2.6	99	ND
<u>Acetone</u>	2.3	2	2.6	99	ND
<u>Crotonaldehyde</u>	2.3	22	2.6	98	130
<u>Isobutyraldehyde</u>	2.3	2	2.6	99	ND
<u>Methyl Ethyl Ketone</u>	2.3	4.5	2.6	98	37
	2.3	4.1	2.6	98	31

< - Sum of detected and nondetected fractions.
 ND - Not detected (1/2 detection limit given for runs).
 98 - Average of detected and nondetected.
 99 - Average not calculated when all runs < detection limit (see AB2588)
 *See Table 5-5 for complete list of target VOCs and detection limits.
 Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).
 ^Because of the high uncertainty in results, no speciation profiles were developed for this source.

TABLE 5-9f. VOC EMISSION FACTORS NATURAL/REFINERY GAS TURBINE (SELECTIVE CATALYTIC REDUCTION/CO CATALYST)*^.

SUBSTANCE	EMISSION FACTOR (lb/TBtu)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	12000	12000	10000	11000	6.9
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	740	740	740	ND	ND
<u>Ethene</u>	ND	ND	ND	99	ND
<u>Propene</u>	1100	1100	1100	99	ND
<u>Ethyne</u>	690	690	690	99	ND
<u>1,3-Butadiene</u>	ND	ND	ND	99	ND
<u>Hexane</u>	1000	1000	1000	99	ND
<u>Benzene</u>	640	640	640	99	ND
<u>Toluene</u>	8	8	8	99	ND
<u>Ethyl Benzene</u>	100	100	100	99	ND
<u>m,p-Xylenes</u>	94	94	94	99	ND
<u>Phenol</u>	530	110	530	98	62
<u>Formaldehyde</u>	130	130	130	99	ND
<u>Acetaldehyde</u>	130	130	310	98	55
<u>Acrolein</u>	110	110	110	99	ND
<u>Propanal</u>	120	130	120	120	1.7
<u>Acetone</u>	100	110	110	110	1.7
<u>Crotonaldehyde</u>	9.2	9.5	9.5	99	ND
<u>Isobutyraldehyde</u>	9.2	9.5	9.5	99	ND
<u>Methyl Ethyl Ketone</u>	9.2	9.5	9.5	98	140
	9.2	9.5	9.5	99	ND
	9.2	9.5	9.5	99	ND
	9.2	9.5	9.5	99	ND

< - Sum of detected and nondetected fractions. () - Field blank corrected.

ND - Not detected (1/2 detection limit given for runs). Italic - Reporting limit.

98 - Average of detected and nondetected. {} - Field blank > 20% of sample value.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

^Because of the high uncertainty in results, no speciation profiles were developed for this source.

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TABLE 5-9h. VOC EMISSION FACTORS NATURAL GAS UTILITY BOILER (UNCONTROLLED)*^.

SUBSTANCE	EMISSION FACTOR (lb/TBtu)				RSD (%)
	R1	R2	R3	Average	
<u>Methane</u>	{11000}	{11000}	{11000}	{11000}	
<u>Ethane</u>	ND	ND	ND	99	ND
<u>Propane</u>	380	380	380	99	ND
<u>Ethene</u>	ND	ND	ND	99	ND
<u>Propene</u>	560	560	560	99	ND
<u>Ethyne</u>	350	350	350	99	ND
<u>1,3-Butadiene</u>	ND	ND	ND	99	ND
<u>Hexane</u>	530	530	530	99	ND
<u>Benzene</u>	330	330	330	99	ND
<u>Toluene</u>	NA	NA	NA	NA	ND
<u>Ethyl Benzene</u>	84	84	84	99	ND
<u>m,p-Xylenes</u>	76	76	76	99	ND
<u>Phenol</u>	89	89	89	99	ND
<u>Formaldehyde</u>	100	100	100	99	ND
<u>Acetaldehyde</u>	100	100	100	99	ND
<u>Acrolein</u>	91	91	91	99	ND
<u>Propanal</u>	(99)	(56)	43	(66)	45
<u>Acetone</u>	44	(76)	40	(53)	36
<u>Crotonaldehyde</u>	3.7	3.2	3.3	99	ND
<u>Isobutyraldehyde</u>	12	58	3.3	98	120
<u>Methyl Ethyl Ketone</u>	23	47	3.3	98	90
	3.7	42	3.3	98	140
	3.7	3.2	3.3	99	ND
	18	39	3.3	98	88

< - Sum of detected and nondetected fractions.

ND - Not detected (1/2 detection limit given for runs).

98 - Average of detected and nondetected.

99 - Average not calculated when all runs < detection limit (see AB2588)

*See Table 5-5 for complete list of target VOCs and detection limits.

Underline - Full ARB QA/QC standards were not applied to these substances (see Section 6).

^Because of the high uncertainty in results, no speciation profiles were developed for this source.

() - Field blank corrected.

Italic - Reporting limit .

{ } - Field blank > 20% of sample value.

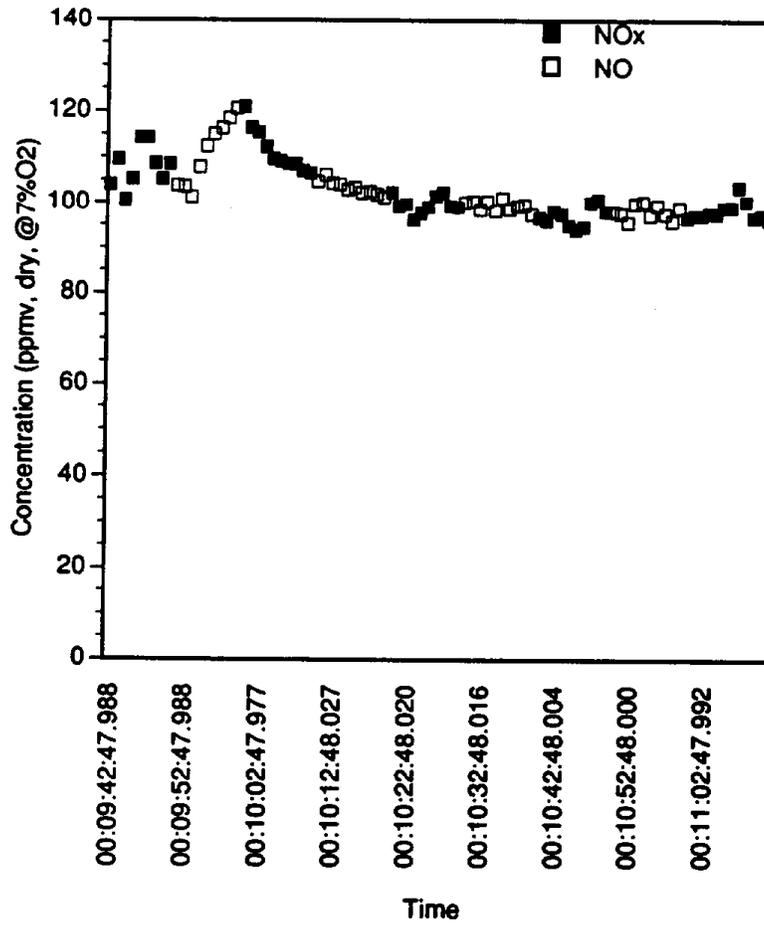


Figure 5-2a. NO/NOx profile Landfill Gas ICE.

TABLE 5-10. CONTINUOUS EMISSION MONITORING RESULTS.

DEVICE	APC Device	O2 % %, Dry	CO2 % %, Dry	NO ppmv, Dry	NOx ppmv, Dry	NO ppmv, Dry 7%O2	NOx ppmv, Dry 7%O2	NO2 (1) ppmv, Dry 7%O2	NO/NOx Ratio (%)
RICE									
Landfill Gas	None	8.3	10.7	93.4	93.2	102.7	102.5	-0.2	100
Field Gas	None	2.5	8.9	499.9	494.0	375.5	377.0	1.5	100
Natural Gas	SCR	0.0	11.9	116.6	137.6	77.6	91.6	14.0	85
Gas Turbine									
Natural Gas	SCR/CO Catalyst	14.0	4.0	7.5	8.7	15.1	17.5	2.4	86
Process Heater									
Refinery Gas	LNB	9.9	6.9	23.1	23.7	29.2	29.8	0.7	98
Refinery Gas	SCR	1.6	12.2	11.6	12.3	8.4	8.9	0.6	94
Steam Generator									
Natural Gas	LNB,EGR	2.5	12.9	23.1	23.2	17.5	17.6	0.1	99
Utility Boiler									
Natural Gas	None	5.0	9.2	103.2	103.2	90.3	90.2	-0.1	100

(1) Difference between NOx and NO measurements.

RICE - Reciprocating Internal Combustion Engine.

APC - Air Pollution Control

EGR - Exhaust Gas Recirculation

LNB - Low NOx Burner

SCR - Selective Catalytic Reduction

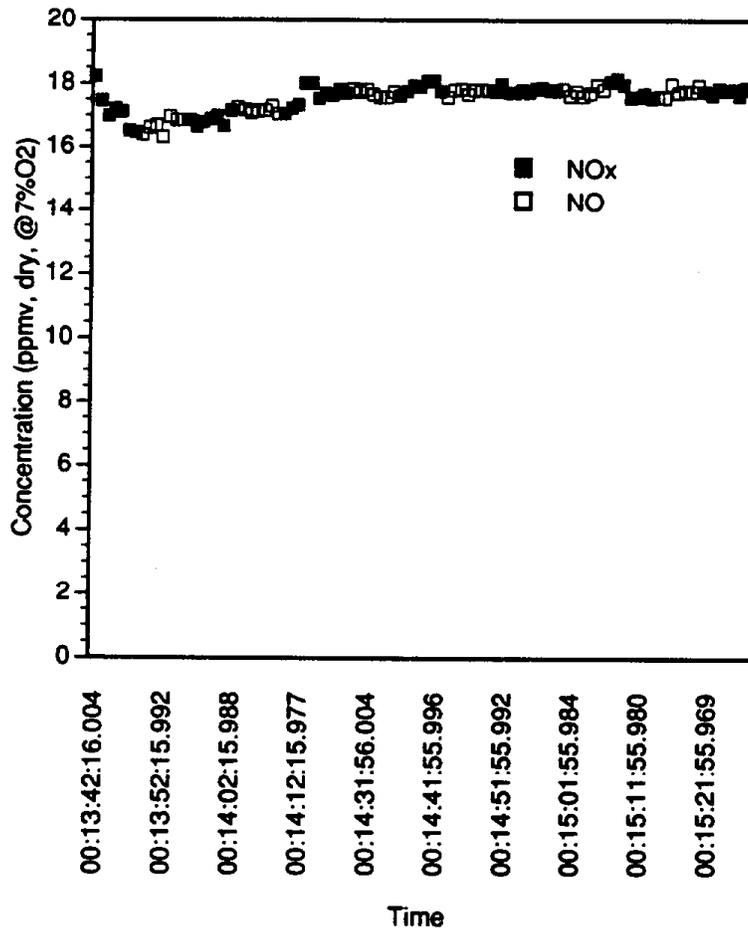


Figure 5-2c. NO/NOx profile NG Steam Generator.

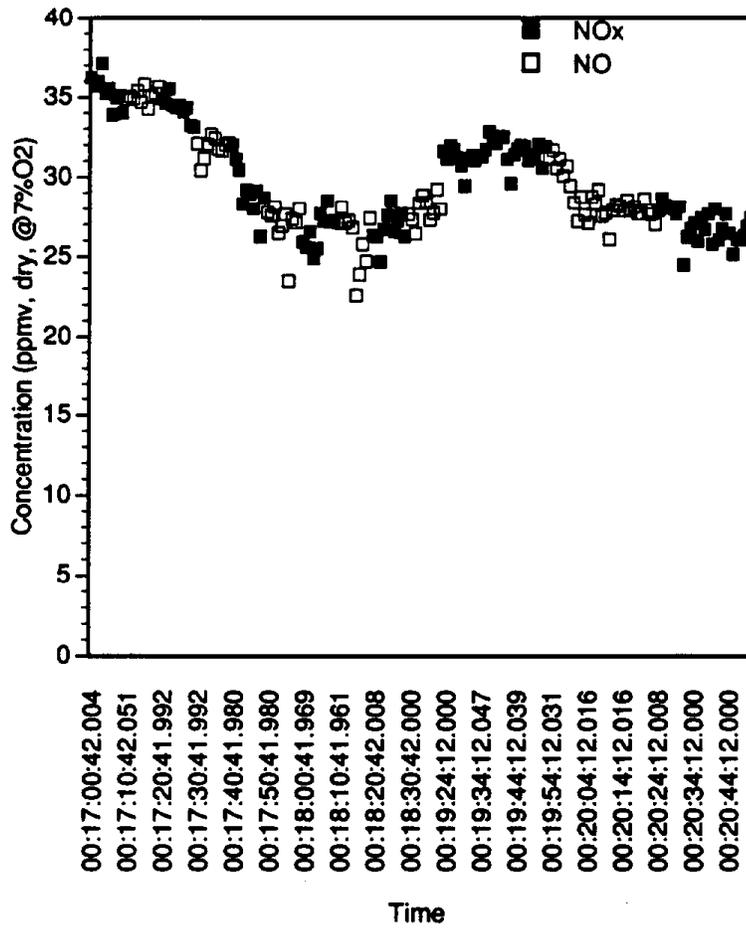


Figure 5-2b. NO/NOx profile RFG Process Heater.

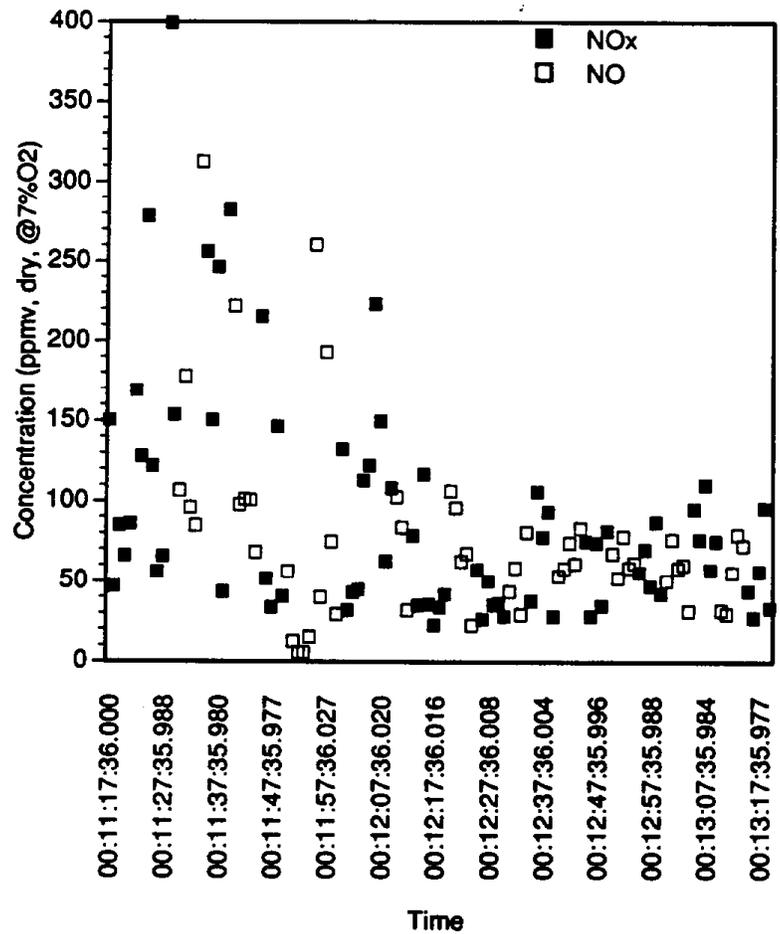


Figure 5-2e. NO/NOx profile NG ICE.

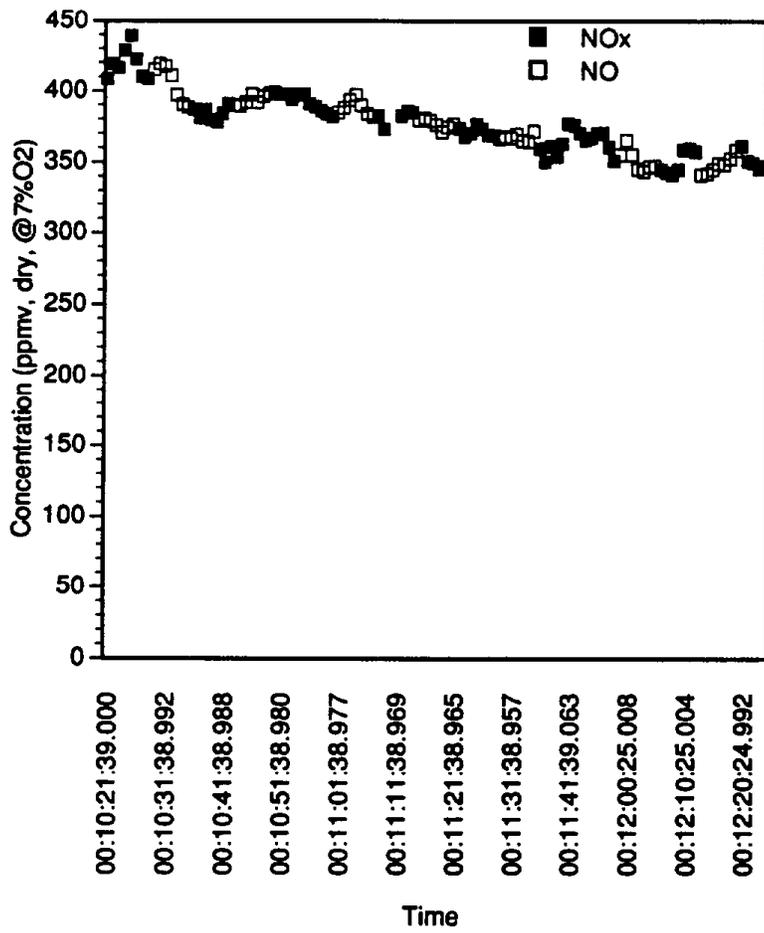


Figure 5-2d. NO/NOx profile Field Gas ICE.

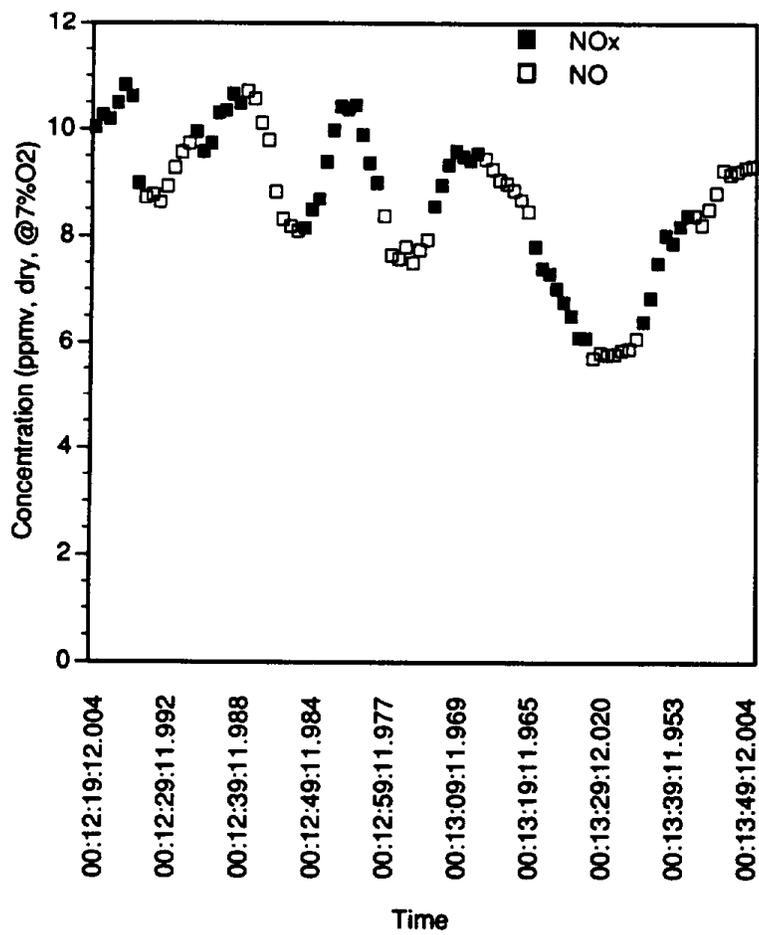


Figure 5-2g. NO/NOx profile RFG Process Heater.

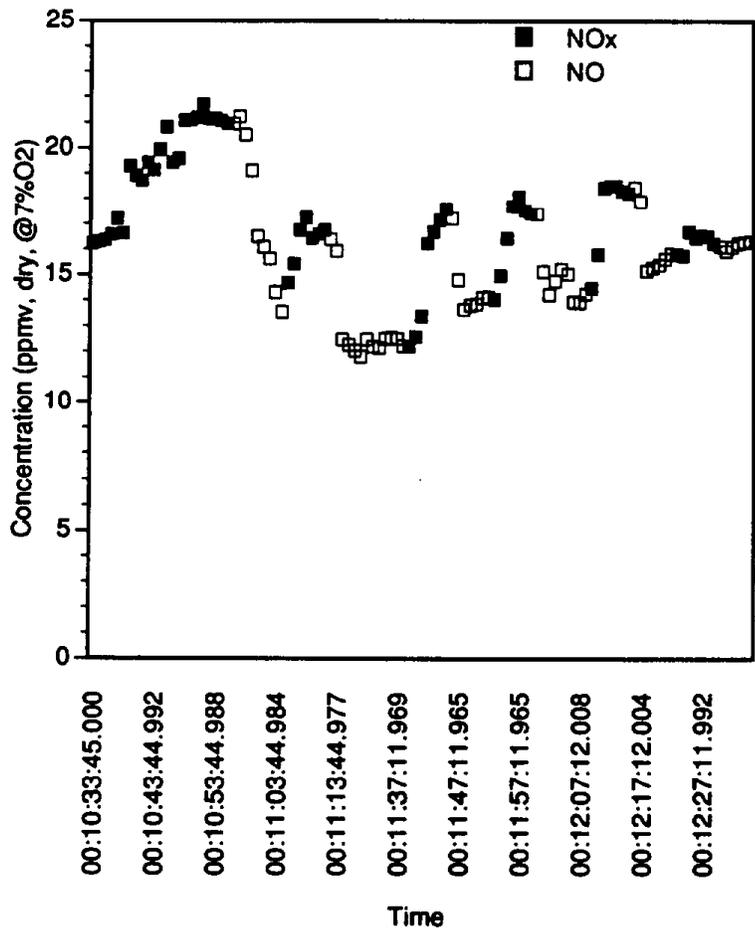


Figure 5-2f. NO/NOx profile NG/RFG Gas Turbine.

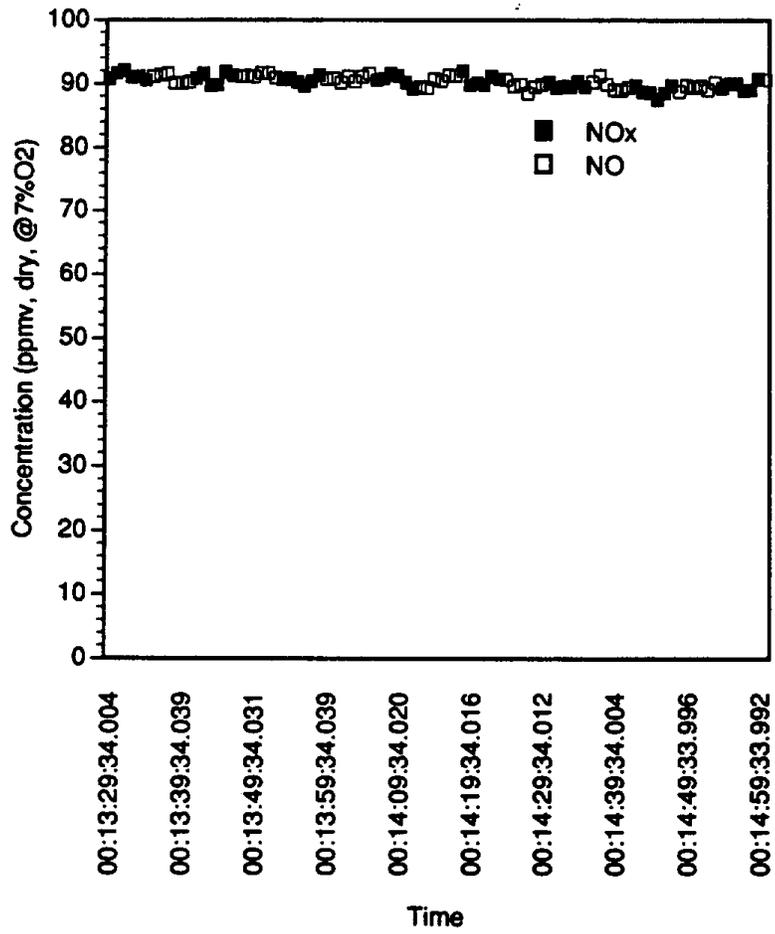


Figure 5-2h. NO/NOx profile NG Utility Boiler.

Precision	A measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Precision is best expressed in terms of the standard deviations. Various measures of precision exist depending upon the "prescribed similar conditions."
Completeness	A measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal conditions.

These DQOs are used to support decisions concerning test validity and adequacy with respect to the program goals. Table 6-1 lists the major tests performed in this program, refers to the sampling and analysis procedure, and the DQOs for that procedure. The DQOs are based on the following information sources:

- (1) Prior knowledge of the measurement system employed;
- (2) Method validation studies using replicates, spikes, standards, calibrations, recoveries, etc.;
- (3) Laboratory operating practices.

To ensure that the DQOs were met, a series of Data Quality Indicators (DQIs) were calculated based on QC checks conducted during the program. A detailed discussion and presentation of primary QC checks is provided in sections 6.2 through 6.7. DQIs for each method are listed in Table 6-1. DQOs are not available for most of the species quantified by Modified CARB 422 because little validation work has been conducted to date. The precision DQO was satisfied for 1,3-Butadiene, however, the accuracy was below the DQO. The 1,3-Butadiene recovery may have been low due to reactions occurring in the matrix spike sample. The accuracy of the olefins was comparable, biased high, to 1,3-Butadiene while the precision of the alkanes, olefins, and aromatics was low. 1,3-Butadiene measurements could not be obtained from the last two facilities due to an equipment failure and the resulting completeness was 71%.

In general, the precision and accuracy of the standard CARB 430 results, formaldehyde, acetaldehyde and acrolein, was excellent. Little precision and accuracy information was available for the remaining aldehydes and ketones because these substances were not spiked and only low levels were obtained from the field samples. The completeness objective was not satisfied for the

6.0 QUALITY ASSURANCE

Quality assurance encompasses the organization and program within which quality control (QC) activities are performed. Quality control activities are those which accompany testing, engineering and other procedures to provide control of data quality, and quantify the quality of data resulting from those procedures.

Each source test performed included a quality assurance (QA) program which incorporated the principles and requirements given in the test protocol. Implementation of this quality assurance program for each source test was paramount to the success of the program and the resultant data base of VOC and NO_x profiles.

The importance of the quality assurance program which was performed with each source test is three-fold. First, the QA program assured higher quality, more reliable test results than may have been obtained otherwise. Second, the QA program provided a means to determine the level of data quality. Third, only by following a sound QA program will the test results be valid for a wide range of uses including emission estimation, regulatory development, and ozone modeling.

This section presents results from and describes the following elements of the QA program.

- Data quality objectives and Indicators
- Calibration Procedures, Frequency, and Corrective Action
- Internal QC Checks, Frequency, and Corrective Action

6.1 Data Quality Objectives and Indicators

Data quality objectives (DQO) are either qualitative or quantitative statements defining the quality of data needed to support the program goals. The objectives are expressed in terms of accuracy, precision, and completeness. These terms are defined below:

Accuracy The degree of agreement of a measurement (or an average of measurements) of a parameter, X, with an accepted reference or true value, T. It is usually expressed as the difference between the two values, X-T, or the difference as a percentage, $100 (X-T)/T$. It is also sometimes expressed as a ratio, X/T. Accuracy is a measure of the bias in a method.

CARB 430 results because only one sample was collected from the refinery process heater (B) because the glassware and reagents from the lab were lost during transport.

The precision, accuracy and completeness objectives were satisfied for all of the CARB 100 results. The NO_x species had the lowest accuracy and precision.

6.2 Sample Location QC Checks

Table 6-2 summarizes the stack diameter, number of ports and sample points, and the upstream and downstream disturbance distances for each source. Acceptance limits for the stack diameter, and downstream and upstream disturbance distances are provided below.

- Stack diameter >12 inch.
- Downstream Disturbance Distance > 2D
- Upstream Disturbance Distance > 0.5D

The field and natural gas IC engines both had stack diameters less than 12 inches due to the small capacity of these sources. While these sources did not have acceptable stack diameters, the VOC profiles are still valid since they do not depend on the method 1 and 2 results. The emission factors and mass rates for these sources do depend on the method 1 and 2 results and may be impacted by the size of the stack. The natural gas utility boiler only had a single port so perpendicular traverses of the stack could not be made. Once again, the CARB method 1 and 2 results do not impact the VOC profiles. However, since the emission rates and emission factors do depend on the velocity of the stack gases they may be impacted by the fact that two traverses could not be conducted.

6.3 Continuous Emission Monitoring System QC Checks

During the testing program, calibration checks were conducted for the analyzer and the complete CEM system (sampling system and analyzer) before and after each test. These checks were conducted to determine the error of the analyzer and complete system before and after the test and the drift of the analyzer and complete system during the tests. Analyzer drifts at zero-, mid-, and high-span levels are illustrated in Figure 6-1. Analyzer drift is expressed as the difference between the final and initial analyzer calibration checks normalized by the full span value. The

TABLE 6-1. DATA QUALITY OBJECTIVES AND INDICATORS FOR CRITICAL MEASUREMENTS.

Measurement	Accuracy		Precision		Completeness	
	DQO	DOI	DQO	DOI	DQO	DOI
CARB 422 (1,2)						
Alkanes	-	-	-	40.2	100	100
Olefins	-	139	-	66.1	100	100
Aromatics	-	-	-	46	100	100
1,3-Butadiene	100+/-20	62	<20	5.6	100	71
CARB 430 (3,4)						
Formaldehyde	100+/-30	80.5	<30	8.9	100	92
Acetaldehyde	100+/-30	73.5	<30	6.5	100	92
Acrolein	100+/-30	92.5	<30	6.2	100	92
Propanal	-	-	-	19.1	100	92
Acetone	-	-	-	44.1	100	92
Crotonaldehyde	-	-	-	-	100	92
Isobutyraldehyde	-	-	-	-	100	92
Methyl Ethyl Ketone	-	-	-	-	100	92
CARB 100 (5,6)						
Oxygen	+/-5	-.44 to 0.44	<5	0.4	90	100
Carbon Dioxide	+/-5	-.89 to .67	<5	0.3	90	100
Oxides of Nitrogen	+/-5	-2 to 2.6	<5	2.3	90	100

1) Accuracy indicated using trip spike recoveries. 1,3-Butadiene based on matrix spike.

2) Precision indicated using three sets of field duplicate recoveries at the first source.

1,3-Butadiene precision based on calibrations.

3) Accuracy indicated using field spike recoveries at each source.

4) Precision indicated using laboratory duplicates on field samples from each source.

5) Accuracy based on midspan checks through complete system at each source.

6) Precision based on replicate midspan checks through complete system at each source.

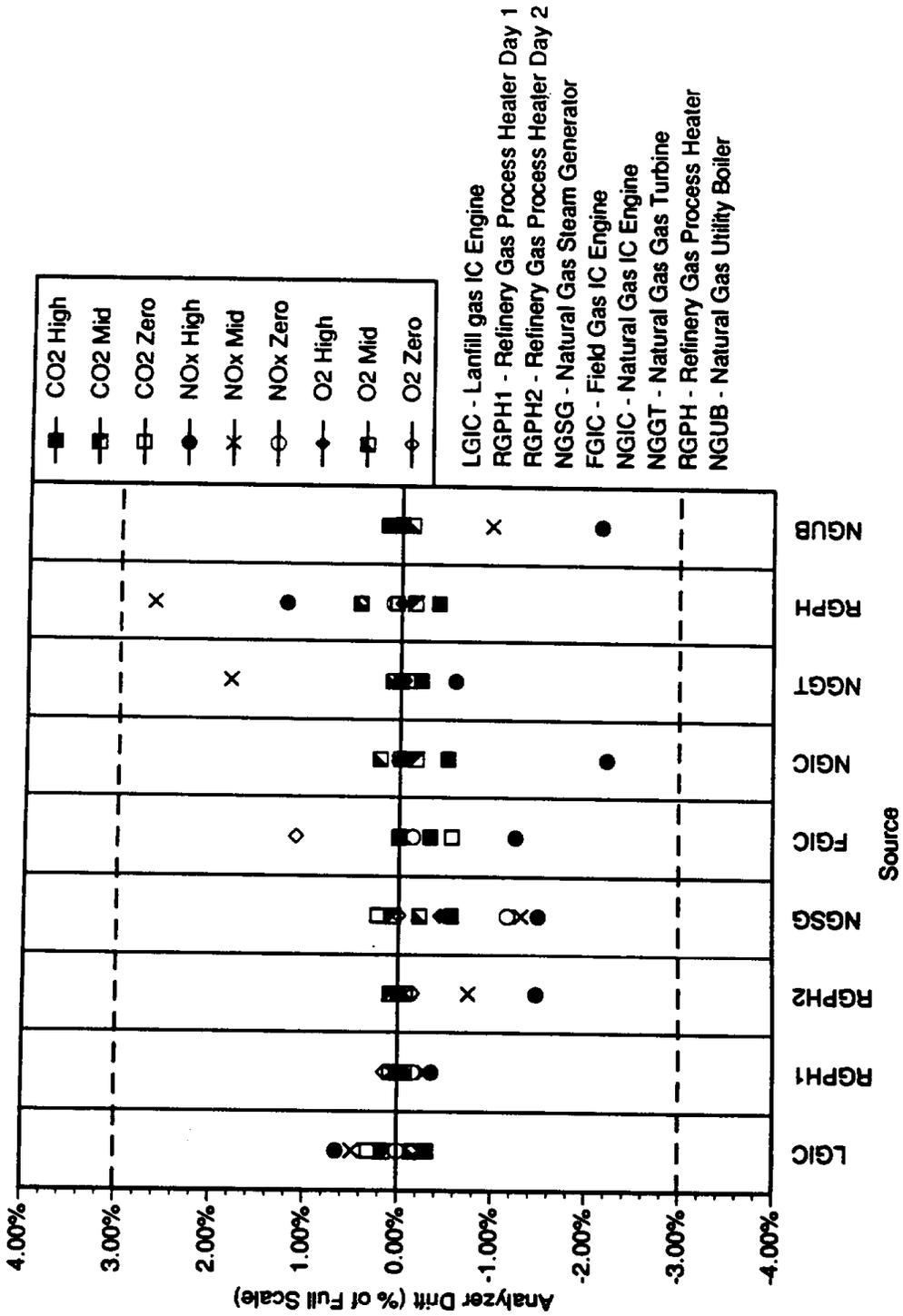


Figure 6-1. Analyzer drift checks.

TABLE 6-2. SAMPLE POINT SUMMARY.

Source	Stack Diameter (inches)	Number of Ports	Number of Sample Points	Upstream Disturbance Distance (Diameters)	Downstream Disturbance Distance (Diameters)
Landfill Gas IC Engine	17.5	2	16	2.5	3
Refinery Gas Process Heater	98	2	12	2	7
Natural Gas Steam Generator	35	2	16	2	5
Field Gas IC Engine	6*	2	8	6	4
Natural Gas IC Engine	9*	2	12	1.9	6.7
Natural Gas Turbine	180	4	12	7	8
Refinery Gas Process Heater	66	2	16	2	4
Natural Gas Utility Boiler	96	1**	10**	2	2

*Stack diameter less than 12 inches due to size of the source.

**Only a single port so only one traverse of stack could be conducted.

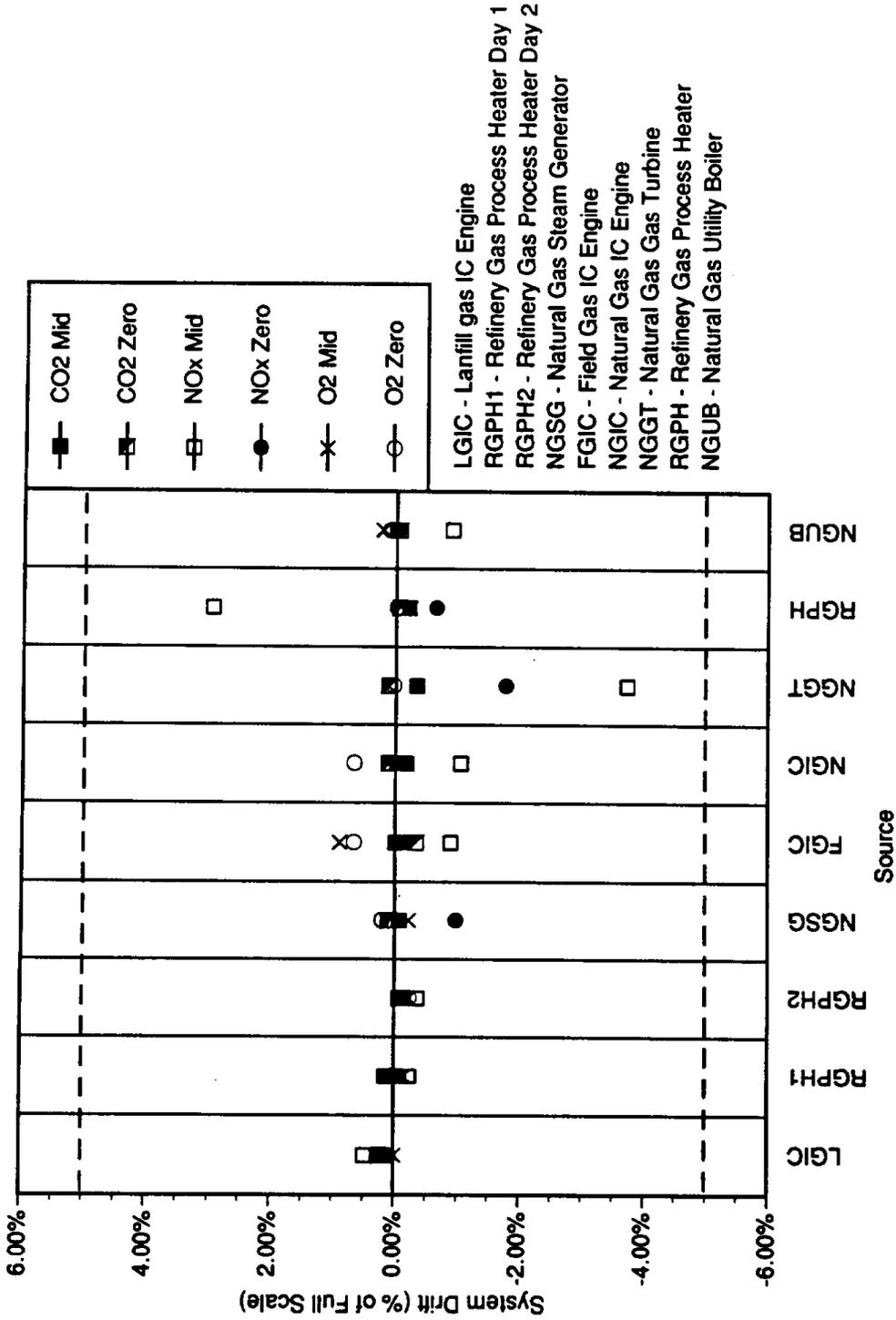


Figure 6-2. System drift checks.

acceptance limit is +/- 3%. All of the analyzer drifts satisfy this objective.

System drifts at zero- and mid-span levels are illustrated in Figure 6-2. System drift is expressed as the difference between the final and initial system calibration checks normalized by the full span value. During the system calibration checks, known concentrations of target substances were injected into the sampling system and analyzers. The acceptance limit for system drift is +/- 5%. All of the system drifts satisfied this objective.

Zero- and mid-span system errors are summarized Figures 6-3. System error is expressed as the difference between the final system calibration check and the calibration gas value (true value) normalized by the full span value. The acceptance limit is +/- 5%. All of the system errors satisfy this objective.

6.4 CARB Method 430 QC Checks

Several QC checks were conducted in the field and lab to ensure the quality of the results. Key checks included the collection and analysis of field, lab and trip blanks and spikes, replicate analysis of field samples, and the monitoring of extraction and analysis hold times. Results from all of these QC checks except hold times are summarized in the following sections. Hold times are summarized in section 6.7.

6.4.1 Blank Results.

Field, lab, and trip blank results are summarized in Table 6-3 for each source and substance quantified. The field blank is used to indicate interferences in field and laboratory procedures. The field blanks were prepared by assembling a complete sampling train and conducting a leak check. The train was then recovered and sent to the lab for analysis. Three field blanks were prepared per source. If the ratio of the sample to field blank detection was greater than 5, the sample detection was corrected using the field blank detection. If the sample to field blank detection ratio was less than 5, 5 times the blank level, reporting limit, was reported. Table 6-3 shows that the IC engine formaldehyde and acetaldehyde sample to field blank ratios were all well in excess of 5. These results were corrected and are of high quality. Most of the detections at the other sources had lower sample to field blank ratios and are of lower quality. The field blank to sample ratios at the natural gas steam generator, natural gas turbine, second refinery gas process heater were close to 1. Detections for these sources are a result of interferences.

TABLE 6-3. ALDEHYDE/KETONE BLANK SUMMARY.

Device/Substance	Field Blank (ng/ml)			Lab Blank (ng/ml)	Trip Blank (ng/ml)	Sample to Field Blank Ratio					
	Run 1	Run 2	Run 3			Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Landfill Gas IC Engine											
Formaldehyde	14	< 13	< 21	ND 10		C 12	C 210	C 272			
Acetaldehyde	19	16	17	ND 10		C 50	C 37	C 30			
Acrolein	ND 11	ND 11	ND 11	ND 10		NA NA	NA NA	NA NA			
Propanal	ND 11	ND 11	ND 11	ND 10		NA NA	NA NA	NA NA			
Acetone	25	29	27	17		C 9	FL 5	FL 5			
Crotonaldehyde	ND 11	ND 11	ND 11	ND 10		NA NA	NA NA	NA NA			
Isobutyraldehyde	ND 11	ND 11	ND 11	ND 10		NA NA	NA NA	NA NA			
Methyl Ethyl Ketone	< 14	37	< 29	70		FL 1	NA NA	FL 1			
Refinery Gas Process Heater											
Formaldehyde	14			ND 10	ND 10	C 6					
Acetaldehyde	16			ND 10	19	FL 1					
Acrolein	ND 11			ND 10	ND 10	NA NA					
Propanal	ND 11			ND 10	ND 10	NA NA					
Acetone	ND 11			73	43	NA NA					
Crotonaldehyde	ND 11			ND 10	ND 10	NA NA					
Isobutyraldehyde	ND 11			ND 10	ND 10	NA NA					
Methyl Ethyl Ketone	ND 11			ND 10	ND 10	NA NA					
Natural Gas Steam Generator											
Formaldehyde	< 13	19	16	ND 10	20	FL 1	FL 3	FL 1			
Acetaldehyde	< 13	< 14	13	ND 10	10	FL 1	FL 1	NA NA			
Acrolein	ND 11	ND 11	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			
Propanal	ND 11	ND 11	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			
Acetone	123	22	14	ND 10	14	FL 0.2	FL 1	FL 0.3			
Crotonaldehyde	ND 11	ND 11	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			
Isobutyraldehyde	ND 11	ND 11	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			
Methyl Ethyl Ketone	ND 11	ND 11	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			
Field Gas IC Engine											
Formaldehyde	ND 10	10	< 13	ND 10	11	C 190	C 878	C 1324			
Acetaldehyde	ND 10	12	ND 11	ND 10	ND 10	C 118	C 222	C 153			
Acrolein	ND 10	ND 10	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			
Propanal	ND 10	ND 10	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			
Acetone	ND 10	< 21	< 17	22	16	C 7	C 13	C 6			
Crotonaldehyde	ND 10	ND 10	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			
Isobutyraldehyde	ND 10	ND 10	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			
Methyl Ethyl Ketone	ND 10	ND 10	ND 11	ND 10	ND 10	NA NA	NA NA	NA NA			

ND - Not detected

<-Detected in either the first or second impinger blank.

RL-Field blank ratio < 5. 5 times the field blank level must be used as the reporting limit.

C-Field blank ratio > 5. The field blank can be used to correct the sample data.

NA-Field blank ratio not calculated because either the field blank or sample value was not detected.

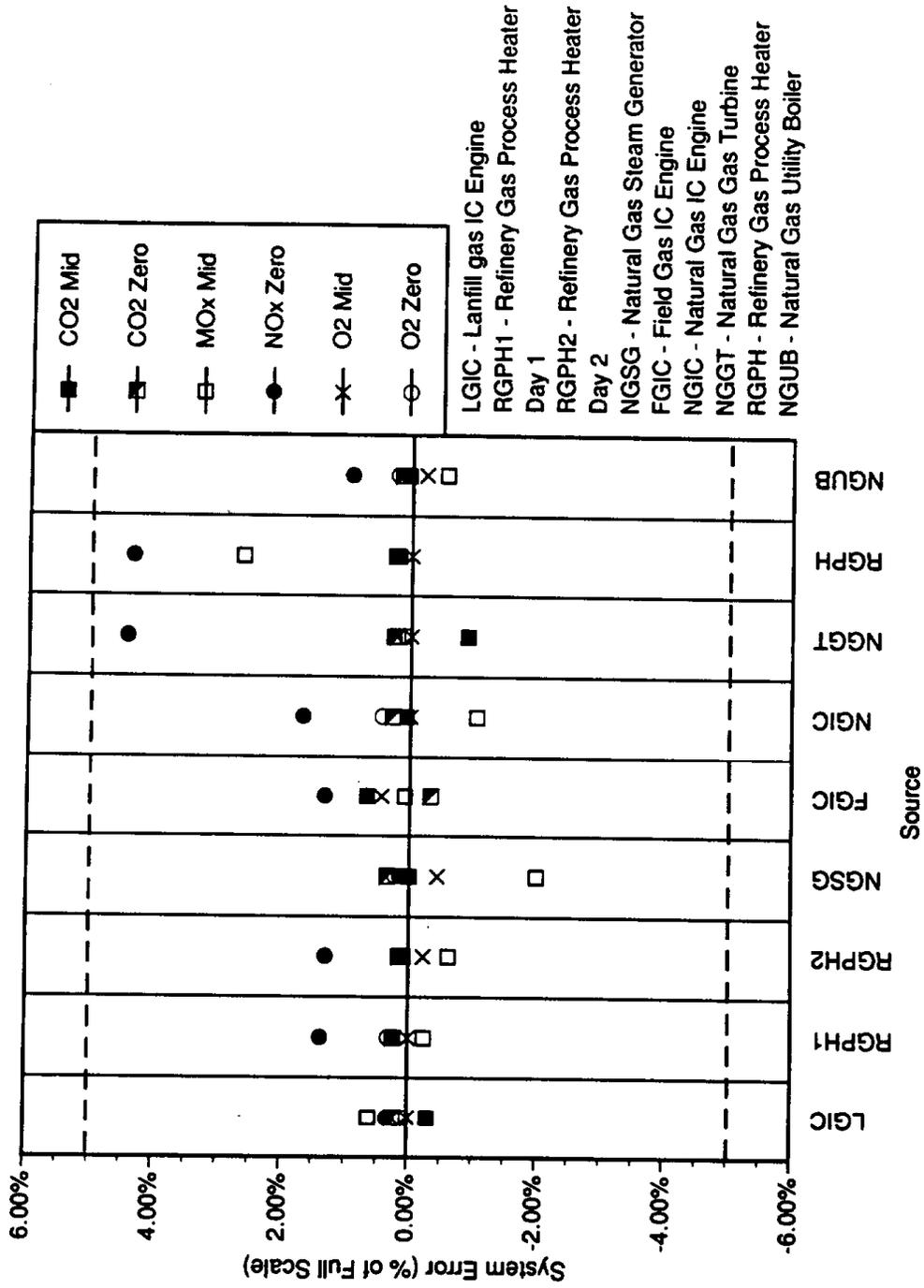


Figure 6-3. Final system error checks.

Lab blank results also are summarized in Table 6-3. Lab blanks are prepared in the laboratory and are used to indicate interferences in the laboratory procedures. If the lab blank level is comparable to the field blank level, the lab is most likely the source of the interference. Table 6-3 shows that acetone was the only significant contaminant in the laboratory procedures. The acetone detections at the IC engines may have been a result of the laboratory procedures.

In addition to the lab and field blanks, trip blanks also were collected and analyzed. These blanks are prepared in the lab, delivered to the test site, and returned to the lab for analysis. If the field blank level is comparable to the trip blank level it is likely that the interference occurred in the transport and/or laboratory procedures. Table 6-3 illustrates that some of the interferences at each source resulted during sample transport.

6.4.2 Spike Results

Matrix, lab, and trip spike are summarized in Table 6-4 for each source and substance quantified. The matrix spike is used to indicate interferences resulting from the sample matrix. Matrix spikes were prepared by adding known quantities of target substances to the sample matrix. The sample was then analyzed and the percent recovery was determined as the ratio of the sample detection to the spike quantity. A low recovery indicates that the target substance is either held up in the sample matrix or is depleted through reactions with the sample matrix. Table 6-3 provides matrix spike recoveries for formaldehyde, acetaldehyde, and acrolein for each source. The other substances are not standard target analytes and were not spiked. All of the recoveries were acceptable except for the IC Engines. For these sources, percent recoveries could not be measured due to the high sample background level. Corresponding laboratory and trip spike recoveries for these samples, however, were acceptable. The laboratory spikes were prepared by adding known quantities of target substances to reagents prepared in the laboratory. These spikes were used to assess the laboratory procedures. The trip spikes were prepared by adding known quantities of target substances to reagents prepared in the laboratory. These reagents were then sent to the field and back to the laboratory for analysis. The trip spike is used to determine if the target substances decay during transport.

6.4.3 Duplicate Results.

Replicate analyses on the field samples also were conducted during the program to assess the precision of the analytical procedures. One set of run samples was analyzed in duplicate for each site. These results are provided in Table 6-4. This table shows sample detections for the

TABLE 6-3. ALDEHYDE/KETONE BLANK SUMMARY (Continued).

Device/Substance	Field Blank (ng/ml)			Lab Blank (ng/ml)	Trip Blank (ng/ml)	Sample to Field Blank Ratio		
	Run 1	Run 2	Run 3			Run 1	Run 2	Run 3
Natural Gas IC Engine								
Formaldehyde	ND 10	ND 10	< 13	ND 10	100	C 1303	C 1850	C 1574
Acetaldehyde	13	< 10	< 11	ND 10	ND 10	C 41	C 42	C 44
Acrolein	ND 10	ND 10	< 12	ND 10	ND 10	C 16	C 15	C 27
Propanal	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Acetone	27	< 37	< 42	16	46	FL 2	C 8	FL 3
Crotonaldehyde	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Isobutyraldehyde	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Methyl Ethyl Ketone	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Natural Gas Turbine								
Formaldehyde	< 17	ND 10	ND 10	ND 10	ND 10	FL 1	FL 3	FL 1
Acetaldehyde	< 12	ND 10	< 10	ND 10	17	FL 1	FL 2	FL 2
Acrolein	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Propanal	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Acetone	ND 10	< 13	ND 10	ND 10	ND 10	NA NA	NA NA	FL 1
Crotonaldehyde	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Isobutyraldehyde	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Methyl Ethyl Ketone	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Refinery Gas Process Heater								
Formaldehyde	< 37	< 22	ND 10	ND 10	38	FL 1	FL 1	FL 1
Acetaldehyde	< 13	17	13	ND 10	14	FL 1	FL 2	FL 1
Acrolein	ND 9	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Propanal	ND 9	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Acetone	ND 9	< 11	ND 10	ND 10	ND 10	NA NA	FL 1	NA NA
Crotonaldehyde	ND 9	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Isobutyraldehyde	ND 9	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Methyl Ethyl Ketone	ND 9	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Natural Gas Utility Boiler								
Formaldehyde	10	< 14	< 11	ND 10	11	C 12	C 8	FL 5
Acetaldehyde	10	< 11	< 11	ND 10	ND 10	FL 4	C 11	FL 2
Acrolein	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Propanal	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Acetone	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Crotonaldehyde	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Isobutyraldehyde	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA
Methyl Ethyl Ketone	ND 10	ND 10	ND 10	ND 10	ND 10	NA NA	NA NA	NA NA

ND - Not detected

<-Detected in either the first or second impinger blank.

RL-Field blank ratio < 5. 5 times the field blank level must be used as the reporting limit.

C-Field blank ratio > 5. The field blank can be used to correct the sample data.

NA-Field blank ratio not calculated because either the field blank or sample value was not detected.

TABLE 6-4. ALDEHYDE/KETONE SPIKE AND DUPLICATE RESULTS.

Device/Substance	Spike (% Recovery)			Duplicate		
	Lab	Trip	Matrix	Value 1 (ug)	Value 2 (ug)	APD (%)
Natural Gas IC Engine						
Formaldehyde	107	91	0*	330	330	0.0
Acetaldehyde	95	95	0*	6.9	6.7	2.9
Acrolein	104	NS	0*	2.7	2.6	3.8
Propanal	NS	NS	NS	ND 1.1	ND 1.1	0.0
Acetone	NS	NS	NS	1.6	1.5	6.5
Crotonaldehyde	NS	NS	NS	ND 1.1	ND 1.1	0.0
Isobutyraldehyde	NS	NS	NS	ND 1.1	ND 1.1	0.0
Methyl Ethyl Ketone	NS	NS	NS	ND 1.1	ND 1.1	0.0
Natural Gas Turbine						
Formaldehyde	107	112	95	0.1	0.1	0.0
Acetaldehyde	93	105	87	0.15	0.15	0.0
Acrolein	109	NS	109	ND 0.1	ND 0.1	0.0
Propanal	NS	NS	NS	ND 0.1	ND 0.1	0.0
Acetone	NS	NS	NS	ND 0.1	ND 0.1	0.0
Crotonaldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Isobutyraldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Methyl Ethyl Ketone	NS	NS	NS	ND 0.1	ND 0.1	0.0
Refinery Gas Process Heater						
Formaldehyde	102	96	79	0.11	0.12	8.7
Acetaldehyde	91	91	67	0.23	0.19	19.0
Acrolein	106	NS	97	ND 0.1	ND 0.1	0.0
Propanal	NS	NS	NS	ND 0.1	ND 0.1	0.0
Acetone	NS	NS	NS	ND 0.1	ND 0.1	0.0
Crotonaldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Isobutyraldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Methyl Ethyl Ketone	NS	NS	NS	ND 0.1	ND 0.1	0.0
Natural Gas Utility Boiler						
Formaldehyde	95	75	88	1.8	1.5	18.2
Acetaldehyde	94	70	81	0.64	0.61	4.8
Acrolein	82	NS	102	ND 0.1	ND 0.1	0.0
Propanal	NS	NS	NS	0.23	0.19	19.0
Acetone	NS	NS	NS	0.68	0.17	120.0
Crotonaldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Isobutyraldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Methyl Ethyl Ketone	NS	NS	NS	0.44	0.3	37.8

ND - Not detected

NS - Not spiked

*Percent recovery could not be measured due to high level sample background.

TABLE 6-4. ALDEHYDE/KETONE SPIKE AND DUPLICATE RESULTS.

Device/Substance	Spike (% Recovery)			Duplicate		
	Lab	Trip	Matrix	Value 1 (ug)	Value 2 (ug)	APD (%)
Landfill Gas IC Engine						
Formaldehyde	82		69	0.21	0.2	4.9
Acetaldehyde	73		41	0.24	0.23	4.3
Acrolein	98		78	0.61	0.56	8.5
Propanal	NS		NS	ND 0.1	ND 0.1	0.0
Acetone	NS		NS	ND 0.1	ND 0.1	0.0
Crotonaldehyde	NS		NS	ND 0.1	ND 0.1	0.0
Isobutyraldehyde	NS		NS	ND 0.1	ND 0.1	0.0
Methyl Ethyl Ketone	NS		NS	0.22	0.14	44.4
Refinery Gas Process Heater						
Formaldehyde	82	93	80	0.16	0.14	13.3
Acetaldehyde	79	104	77	0.14	0.14	0.0
Acrolein	75	NS	94	ND 0.1	ND 0.1	0.0
Propanal	NS	NS	NS	ND 0.1	ND 0.1	0.0
Acetone	NS	NS	NS	ND 0.1	ND 0.1	0.0
Crotonaldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Isobutyraldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Methyl Ethyl Ketone	NS	NS	NS	ND 0.1	ND 0.1	0.0
Natural Gas Steam Generator						
Formaldehyde	83	97	72	0.13	0.11	16.7
Acetaldehyde	83	91	88	0.15	0.13	14.3
Acrolein	85	NS	75	ND 0.1	ND 0.1	0.0
Propanal	NS	NS	NS	ND 0.1	ND 0.1	0.0
Acetone	NS	NS	NS	ND 0.1	0.1	0.0
Crotonaldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Isobutyraldehyde	NS	NS	NS	ND 0.1	ND 0.1	0.0
Methyl Ethyl Ketone	NS	NS	NS	ND 0.1	ND 0.1	0.0
Field Gas IC Engine						
Formaldehyde	101	95	0*	44	40	9.5
Acetaldehyde	84	100	0*	16	15	6.5
Acrolein	99	NS	0*	ND 0.6	ND 0.6	0.0
Propanal	NS	NS	NS	0.8	0.66	19.2
Acetone	NS	NS	NS	1.8	1.7	5.7
Crotonaldehyde	NS	NS	NS	ND 0.6	ND 0.6	0.0
Isobutyraldehyde	NS	NS	NS	ND 0.6	ND 0.6	0.0
Methyl Ethyl Ketone	NS	NS	NS	1.2	1.3	8.0

ND - Not detected.

NS - Not spiked.

*Percent recovery could not be measured due to high level sample background.

TABLE 6-5. VOC FIELD BLANK RESULTS*.

Substance	Field Blank Concentration (ppbv)		
	Field Gas IC Engine	Refinery Gas Process Heater (G)	Natural Gas Utility Boiler
Toluene	8 (21)	6 (12)	NA
Methane	NA	1400 (3800)	4300 (14000)

*Only those compounds which were detected are listed.

() - Average sample value

two analyses conducted on each sample. The absolute percent difference (APD) expressed as the absolute difference between the two analyses normalized by the average of the two analyses. The acceptance limit for the APD is 30 or less. All of the APDs satisfy this objective except for methyl ethyl ketone at the landfill gas IC engine and utility boiler, and acetone at the utility boiler. These results are imprecise because the sample detections are very close to the analytical detection limit. Under these conditions, the precision of laboratory analyses are known to be low.

6.5 Modified CARB Method 422 QC Checks

Several QC checks were conducted in the field and lab to ensure the quality of the results. Key checks included the collection and analysis of field blanks, trip and matrix spikes, stability tests, collection of duplicate samples, and the monitoring of analysis hold times. Results from all of these QC checks except hold times are summarized in the following sections. Hold times are presented in section 6.7.

6.5.1 Field Blank Results.

Field blank results for detected substances are summarized in Table 6-5 for each source. The field blank is used to indicate interferences in field and laboratory procedures. The field blanks were prepared by assembling the sampling system and conducting a leak check with nitrogen through the complete system. The tedlar bag was then sent to the lab for analysis. One field blank was prepared per source. If the ratio of the field blank to sample detection was greater than 0.2, the sample detection was noted in the results section. Table 6-5 shows that of the 100 plus target substances, only toluene and methane were detected in the field blanks at three of the sources. At the field gas IC Engine and refinery gas process heater with selective catalytic reduction, the toluene field blank levels were 38 and 50% of the sample detections, respectively. At the refinery gas process heater with selective catalytic reduction and utility boiler, the methane field blank levels were 36 and 30% of the sample detections, respectively. All of these results were noted as having high field blank levels in the results section.

6.5.2 Spike Results

Matrix and trip blank spike recoveries are summarized in Table 6-6 for each source and selected substances including olefins and 1,3-Butadiene. Matrix spikes are used to indicate interferences resulting from the sample matrix. The matrix spike was prepared by adding a known amount of target substance to the sample matrix. The sample was then analyzed and the percent

recovery was determined as the ratio of the sample detection to the spike quantity. A low recovery indicates that the target substance is either held up in the sample matrix or is depleted through reactions with the sample matrix. A high or low spike recovery may also indicate problems occurring in the analytical procedures. The impact of matrix on sample recovery was only assessed for 1,3-Butadiene. The matrix spike recovery for 1,3-Butadiene was 62 percent. The 1,3-Butadiene recovery may have been low due to reactions occurring in the matrix spike sample. While a matrix spike was not available for the other substance, results from the stability test can be used to assess the impact of sample matrix on olefins. During the stability test the recovery of olefins from a combustion gas matrix was excellent even up to 72 hours (see section 6.5.4).

The trip spikes were prepared by adding known quantities of target substances in the field to a tedlar bag containing nitrogen. This tedlar bag was then sent to the laboratory for analysis. The trip spike is used to determine if the target substances decay during transport or are impacted by the analytical procedures. Table 6-6 shows the level of each substance spiked into the trip sample and the corresponding laboratory detection. The recovery ratio also is provided. All substances spiked into the bag except ethylene, propylene, 2-methylpropene, cis-2-pentene, 1-hexene, 2-hexene, 2-methyl 1-pentene, 4-methyl 1-pentene, 2-methyl 2-pentene, 3-methyl 2-pentene, 4-methyl 2-pentene, and vinyl chloride were detected by the lab. Ethylene and propylene were not detected because the levels spiked were much lower than the analytical detection limit. There is no apparent reason why 2-methylpropene and cis-2-pentene were not detected by the laboratory. The low recoveries indicate that the effective detection limit for these substance may be substantially higher than 5 ppbv. 1-Hexene, 2-hexene, 2-methyl 1-pentene, 4-methyl 1-pentene, 2-methyl 2-pentene, 3-methyl 2-pentene, and 4-methyl 2-pentene also were not detected by the laboratory. Even though these substance were not included on the analytical target list, the laboratory was instructed to identify any unidentified peaks. Since the laboratory did not find any unidentified peaks for the trip spike sample, the effective detection limit for C6 or greater hydrocarbons may have been substantially higher than 5 ppbv. It should be noted that no C6 or greater olefins were detected in the program. Hexane was detected at one of the sources. Only one substance, Methyl Ether, was detected which was not in the spike.

The trip spike recoveries ranged from 34 to 571%. Overall, the recoveries were low, except for 2-Butene and 3-methyl-1-butene, indicating the substances could not be extracted from the matrix, reacted in the bag during transport, or the preconcentration system was not operating as effectively as planned. Trip spike recoveries for 2-Butene and 3-methyl-1-butene were high indicating reaction in the tedlar bag before analysis or interference in the laboratory procedures. It also should be noted that the spike levels were close to the detection limit of the method. The

TABLE 6-6. VOC TRIP SPIKE RESULTS.

Substance	Lab Result (ppbv)	Spike (ppbv)	Lab/Spike (%)
Matrix Spike			
1,3-Butadiene (ARB)	60	96.3	62
Trip Spike			
1,3-Butadiene (APCL)	11	20	55
1,3-Butadiene (ARB)	18	20	90
Ethylene	ND (500)	20	ND
Propylene	ND (500)	19.9	ND
1-Butene	16	20	80
2-Butene (cis & trans)*	96	16.8	571
2-methylpropene	ND (5)	15	ND
1-Pentene	7	20.3	34
2-Pentene (cis & trans)**	9	19.7	46
2-methyl-2-Butene	7	14.5	48
2-methyl-1-Butene	6	15.1	40
3-methyl-1-Butene	18	11.9	151
1-Hexene	NTA	20.6	NTA
2-Hexene	NTA	21	NTA
2-methyl 1-pentene	NTA	15.2	NTA
4-methyl 1-pentene	NTA	15	NTA
2-methyl 2-pentene	NTA	15.1	NTA
3-methyl 2-pentene	NTA	15.1	NTA
4-methyl 2-pentene	NTA	15.1	NTA
Methyl Ether	6	NS	NS
Vinyl Chloride	ND (5)	20	ND
Average			124.0

() - Detection limit

NS - Not spiked

ND - Not detected

NTA - Not on APCL target analyte list.

ARB - Air resource board.

APCL - Applied P&C Laboratories

*Lab result: cis-2-butene 68 ppbv, trans-2-butene 28 ppbv

**Lab result: cis-2-pentene ND 5 ppbv, trans-2-pentene 4 ppbv

TABLE 6-7. VOC FIELD DUPLICATES (LANDFILL GAS FIRED IC ENGINE).

Substance	Concentration (ppbv)												
	Run 1			Run 2			Run 3			APD			
	Diluted	Undiluted		Diluted	Undiluted		Diluted	Undiluted		Run 1	Run 2	Run 3	Average
Methane	892,500	1,190,000		892,500	1,200,000		982,500	1,050,000		28.6	29.4	6.6	21.5
Ethane	16,125	13,200		13,275	12,600		16,800	14,000		19.9	5.2	18.2	14.4
Propane	4,088	2,360		ND	1,780		4,515	1,310		53.6	NA	110.0	81.8
Ethene	12,600	12,100		9,000	14,800		10,275	15,100		4.0	48.7	38.0	30.3
Propene	7,575	2,340		ND	1,620		5,348	1,830		105.6	NA	98.0	101.8
Benzene	75	42		90	62		90	116		56.4	36.8	25.2	39.5
Toluene	126	44		128	78		135	119		96.5	48.5	12.6	52.5
Ethyl Benzene	ND	5		ND	12		ND	ND		NA	NA	NA	NA
m,p-Xylenes	ND	ND		ND	9		ND	12		NA	NA	NA	NA
o-Xylene	ND	ND		ND	5		ND	ND		NA	NA	NA	NA

ND - Not detected

NA - Not available

accuracy of the analytical method is known to decrease near the detection limit. The spike levels should ideally be 5 times higher than the analytical detection limit.

6.5.3 Duplicate Results.

Simultaneous tedlar bag field samples were collected and analyzed at the first source tested. Results for these samples are provided in Table 6-7. This table shows the sample detections for the duplicate samples for each run. The absolute percent difference (APD) is expressed as the absolute difference between the two analyses normalized by the average of the two analyses. It should be noted that while the samples were collected simultaneously, the matrix was different. One sample was diluted while the other was not. While samples were not true duplicates they can still be used to estimate the precision of the sampling and analytical procedures. The precision of methane, ethane, and ethene is excellent. The precision for the remaining substances ranged from 13 to 110%. These results are less precise because the sample detections were close to the analytical detection limit. Under these conditions the precision of laboratory analyses are known to be low.

6.5.4 Stability Test

To determine the effectiveness of the tedlar bag sampling procedures at reducing NO₂ reactions, a stability test was conducted. The stability tested included spiking 1-Butene, 2-Methylpropene, 2-Methyl-1-Butene, and 1,3-Butadiene into bags containing exhaust gases with NO_x levels of 5, 50, 140, and 1400 ppmv. The samples were analyzed at 2, 8, 24, 48, and 72 hours. Only 1,3-Butadiene decayed in the samples. In the high NO_x level bags, the decay rate was quick, < 2 hrs. In the low level NO_x bags, the decay was less. These results indicate that to obtain accurate emissions levels for 1,3-Butadiene, an on-site GC was necessary. However, the tedlar bag sampling procedures were sufficient for the other compounds at least for the matrix and time period examined.

6.6 Fuel Analysis QC Checks

Several QC checks were conducted in the lab to ensure the quality of the fuel analyses. Key checks included method spikes and replicate analyses. These QC checks have been defined in sections 6.4 and 6.5. Spike and replicate results are summarized in Table 6-8. Overall the precision and accuracy of the fuel analyses is excellent.

6.7 Hold Times

Another key aspect of the QC program was the monitoring of extraction and analysis times. It is essential to ensure the correct hold times are maintained or the results may not be valid. In particular, if the proper hold time is exceeded, target substances may decay and be detected at levels less than those actually present in the stack gases. Table 6-9 summarizes hold times for aldehydes/ketones, tedlar bag samples (VOC), and 1,3-Butadiene. The maximum hold times also are provided in the table. All of the samples had acceptable hold times except the VOC samples for the natural gas steam generator. The hold time for the steam generator VOC sample exceeded the limit by 24 hours. This infraction of the hold time should not impact the results because the stability test indicated the target analytes decayed little in 72 hours. It should be noted that the 1,3-Butadiene hold time for the natural gas IC engine exceeded two hours. Over this time period, significant decay in 1,3-Butadiene levels may have occurred resulting in the nondetections observed.

TABLE 6-8. VOC FUEL ANALYSIS DUPLICATE AND METHOD SPIKE(REFINERY GAS PROCESS HEATER)

Substance	Method Spike % Recovery	Duplicate		
		Result 1 (ppbv)	Result 2 (ppbv)	APD
Oxygen	101	0.044	0.044	0.0
Nitrogen	100	3.3	3.3	0.0
Carbon Monoxide	78	1	1	0.0
Methane	91	42	42	0.0
Carbon Dioxide	91	0.15	0.15	0.0
Ethane	90	17	17	0.0
Propane	91	19	19	0.0
Isobutane	91	2.4	2.4	0.0
Butane	92	5.1	5.1	0.0
Neopentane	92	0.005	0.004	22.2
Isopentane	91	1	1	0.0
n-Pentane	91	0.93	0.93	0.0
Ethylene	100	6.2	6.2	0.0
Propene	100	ND 0.001	0.001	0.0
1-Butene	100	ND 0.001	0.001	0.0
cis-2-Butene	100	0.35	0.35	0.0
trans-2-Butene	100	ND 0.001	0.001	0.0
Cyclopentane	100	ND 0.001	0.001	0.0
Ethyne	100	ND 0.001	0.001	0.0
C6+	100	0.86	0.85	1.2
Unknown C5	NA	0.45	0.44	2.2
Heating Value (Btu/cf)	NA	1400	1400	0.0
Specific Gravity	NA	0.89	0.85	4.6

TABLE 6-9. ANALYSIS HOLD TIMES.

Source	Aldehydes/Ketone			VOC			1,3 Butadiene		
	Solution Preparation (1)	Test Date	Extraction Date (2)	Analysis Date (3)	Test Date	Analysis Date (4)	Run 1 Hrs	Run 2 Hrs	Run 3 Hrs
Landfill Gas IC Engine	10/11/93	10/12/93	10/18/93	10/18/93	10/11/93	10/14/93	0.25	0.38	1
Refinery Gas Process Heater	10/11/93	10/13/93	10/20/93	10/21/93	10/14/93	10/17/93	1.5	0.75	1
Natural Gas Steam Generator	10/19/93	10/20/93	10/26/93	10/26/93	10/20/93	10/24/93*	0	0	-
Field Gas IC Engine	10/20/93	10/22/93	10/28/93	10/29/93	10/22/93	10/24/93	0	0	na
Natural Gas IC Engine	10/27/93	10/27/93	10/30/93	11/1/93	10/27/93	10/29/93	2.2	2.2	3.5
Natural Gas Turbine	11/1/93	11/2/93	11/7/93	11/11/93	11/2/93	11/3/93	4	3.5	3
Refinery Gas Process Heater	11/2/93	11/4/93	11/9/93	11/10/93	11/4/93	11/6/93	-	-	-
Natural Gas Utility Boiler	11/15/93	11/17/93	11/19/93	11/24/93	11/17/93	11/19/93	-	-	-

(1) Hold no longer than 2 days.

(2) Extract within 7 days.

(3) Analyze within 30 days.

(4) Analyze within 3 days.

- Not available due to equipment failure

*Out of hold time

**ATTACHMENT 1
CARB 1,3-BUTADIENE RESULTS**

Column Temperature: 50 C
Carrier (air) Flow Rate: 18cc/minute
Sample Loop Flush Time: 10 seconds

Multipoint calibration curves were generated on each testing day. Limits of detection and quantitation as calculated from the multipoint curves are listed in Table 2.

On November 2, 1993 I prepared a matrix spike and trip spike to be submitted for analysis along with the stack samples. Table 3 outlines the compounds included in the spikes and the expected concentrations.

Sampling/Analytical Notes

Landfill Gas IC Engine, 10/11/93: The facility required that we leave the site at 3:30pm. The bag samples were submitted for our analysis late in the afternoon of the 11th. Since samples had to be returned to EER staff at the end of the test day, there was only time for us to run 4 of the 7 samples submitted (Refer to Table 1).

Refinery Gas Process Heater (LNB), 10/14/93: The facility required that ARB staff undergo safety training and wear nomex work suits in order to perform work on-site, at the facility. As we had no nomex suits available we decided to have the bag samples delivered to us for analysis at an off-site location near the facility, the South Coast Air Pollution Control District office in Long Beach. Time constraints again allowed only the analysis of 4 stack samples.

Natural Gas Steam Generator (LNB/EGR), 10/20/93: The undiluted stack samples showed no detectable levels of 1,3-butadiene. Thus the diluted samples were not analyzed.

Field Gas IC Engine, 10/22/93: The Photovac oven heater AC/DC adapter stopped working during the analysis of stack samples. Two samples were successfully run before the malfunction.

Natural Gas IC Engine (SCR), 10/27/93: The 3 undiluted stack samples and the field blank were analyzed and showed no detectable levels of 1,3-butadiene. There were however a number of other unidentified hydrocarbons detected in the samples. The samples also seemed to turn brownish yellow over time (several hours). The Plant Manager apparently was not aware that ARB staff was going to be on-site for the test. He stated that EER and ARB staff had assured him that the facility name and location was to be anonymous. He confiscated a portion of the sample chromatograms and gave me a receipt for them. As of this date we have not received the chromatograms back.

MEMORANDUM

TO: Peter Ouchida, Manager
Testing Section

FROM: Kevin Mongar
Associate Air Pollution Specialist

DATE: January 12, 1994

SUBJECT: 1,3-Butadiene Source Testing

This memo is a summation of the on-site analysis for 1,3-butadiene conducted on Tedlar bag samples collected at the following facilities.

<u>Source ID</u>	<u>Description</u>	<u>Test Date</u>
A	Landfill IC Engine (Uncontrolled)	10/11,12/93
B	Refinery Gas Process Heater (LNB)	10/13,14/93
C	Natural Gas Steam Generator (LNB/EGR)	10/20/93
D	Field Gas IC Engine (Uncontrolled)	10/22/93
E	Natural Gas IC Engine (SCR)	10/27/93
F	Natural Gas Turbine (SCR/CO Catalyst)	11/2/93

LNB - Low NOx Burner
EGR - Exhaust Gas Recirculation
SCR - Selective Catalytic Reduction

The on-site analytical support was requested by ARB's Research Division. The purpose of this request was to provide field support to a private firm, Energy and Environmental Research Corporation (EER), which was working under contract to the ARB. The contract was for the "Development of NOx and VOC Species Profiles for Emissions From Selected Stationary Combustion Sources". The contact person at EER was David Hansell, and Research Division's contract manager for this project was Robert Grant.

EER staff collected exhaust gas samples in Tedlar bags which were delivered to the ARB's on-site gas chromatograph (GC) laboratory for analysis of 1,3-butadiene. A Photovac 10S70 portable gas chromatograph with photoionization detector (PID) was used in the field for the analysis of 1,3-butadiene in Tedlar bag samples. On-site GC was used in this case to provide analyses immediately after sampling. This was necessary due to potential stability problems for 1,3-butadiene in combustion source matrices. The results of the on-site analyses are listed in Table 1. The analysis conditions are listed below.

Columns: fused silica, 10m x 0.52mm ID Al2O3/KCl PLOT with
a 4 inch x 1/8 inch, 6.6% CSP 20M on Carbopack B,
packed backflushable precolumn
Sample Loop: 1cc Teflon

January 12, 1994

TABLE 1

Test Date	Facility	Bag #	Sample	Hours After Sampling	[C] 1,3-Butadiene (ppb)
10/11,12	Source A	1	Diluted ¹	.25	13
"	"	2	Diluted	.38	11
"	"	2	Undiluted	1.00	89
			Field Blank		<2.7
10/14	Source B	1	Diluted	1.50	<5.0
"	"	1	Undiluted	.75	<5.0
"	"	2	Diluted	1.00	<5.0
"	"	2	Undiluted	1.25	<5.0
10/20	Source C	1	Undiluted	0	<5.5
"	"	2	Undiluted	0	<5.5
"	"	3	Undiluted	0	<5.5
10/22	Source D	1	Diluted	0	63
"	"	2	Diluted	0	56
10/27	Source E	1	Undiluted	2.17	<1.4
"	"	2	Undiluted	2.17	<1.4
"	"	3	Undiluted	3.50	<1.4
			Field Blank		<1.4
11/2	Source F	1	Undiluted	4.00	<3.0
"	"	2	Undiluted	3.50	<3.0
"	"	3	Undiluted	3.00	<3.0
"	"		Field Blank		<3.0
"	"		Matrix Spike		60
"	"		Trip Spike		18

¹The diluted sample results have not been corrected for the dilution factor.

January 12, 1994

Natural Gas Turbine (SCR/CO Catalyst), 11/2/93: The GC van was located at the Embassy Suites Hotel for the analyses of samples from this facility. The undiluted stack samples did not contain butadiene at detectable levels and so the diluted samples were not analyzed. David Hansell of EER requested that I prepare and submit to them a trip and matrix spike of a hydrocarbon mix. The compounds included and the concentrations expected in the spikes are outlined in Table 3. Both of these spike samples were analyzed on the Photovac for butadiene prior to delivery to EER staff. The recovery of butadiene in the matrix and trip spikes were 62% and 90% respectively.

Refinery Gas Process Heater (SCR), 11/4/93: The Photovac malfunctioned during this test day before any of the stack samples could be analyzed. The instrument had to be shipped back to the manufacturer for repairs.

TABLE 3

January 12, 1994

Standard	Compound	[C] (ppm) STD	[C] (ppb) Matrix Spike	[C] (ppb) Trip Spike
Scotty II Can Mix #222	Ethylene	99.9	175	20.0
	Propylene	99.3	174	19.9
	1-Butene	100.0	175	20.0
	1-Pentene	101.4	178	20.3
	1-Hexene	102.8	180	20.6
Scotty II Can Mix #4	2-Butene	16.8	147	16.8
	2-Pentene	19.7	173	19.7
	2-Hexene	21.0	184	21.0
Scotty II Can Mix #5	2-Methyl Propene	15.0	131	15.0
	2-Methyl 1-Butene	15.1	131	15.1
	3-Methyl 1-Butene	11.9	104	11.9
	2-Methyl 1-Pentene	15.2	133	15.2
	4-Methyl 1-Pentene	15.0	131	15.0
Scotty II Can Mix #6	2-Methyl 2-Butene	14.5	127	14.5
	2-Methyl 2-Pentene	15.1	132	15.1
	-(cis & trans) 3-Methyl 2-Pentene	14.4	126	15.1
	-(cis & trans) 4-Methyl 2-Pentene	15.8	138	15.8
Scott Marris	1,3-Butadiene	1.0	96.3	20.0
	Vinyl Chloride	1.0	96.3	20.0

