

Research and Development

ENVIRONMENTAL ASSESSMENT OF
A RECIPROCATING ENGINE
RETROFITTED WITH
SELECTIVE CATALYTIC REDUCTION
Volume I. Technical Results

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ENVIRONMENTAL ASSESSMENT OF A RECIPROCATING ENGINE RETROFITTED WITH SELECTIVE CATALYTIC REDUCTION

Volume I: Technical Results

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ABSTRACT

Comprehensive emission measurements and 15-day continuous emission monitoring was performed for a 1,500 kW (2000 hp) gas-fired, fourstroke turbocharged reciprocating engine equipped with an ammonia-based selective catalytic reduction system for NO_x control. Emission reductions were held at about 80 percent using an ammonia-to-NO ratio of about 1.0. NO, levels at the catalyst inlet ranged from 2,200 to 2,600 ppm at an exhaust gas oxygen level of about 11 percent. NOx levels at the catalyst outlet ranged between 65 and 120 ppm. The catalyst had relatively minor effect on CO and particulate emissions, but increased total cyanides by three orders of magnitude (from 7 μ g/dscm to 2.4 mg/dscm) across the catalyst. Total organics decreased about 70 percent from 4.9 mg/dscm to 1.5 mg/dscm. Analyses showed benzene and toluene as the major organic constituents in the catalyst exhaust. Polycyclic aromatics also decreased across the catalyst. The 15-day continuous monitoring tests showed that the catalyst was generally able to maintain NO_x reductions at about 80 percent. Departures from these levels occurred only during brief load surges and ammonia flowrate spikes.

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SECTION 1

INTRODUCTION

This report describes and presents results for a set of environmental assessment tests performed for the Industrial Environmental Research Laboratory/Research Triangle Park (IERL/RTP) of EPA under the Combustion Modification Environmental Assessment (CMEA) program, EPA Contract No. 68-02-3188. The CMEA started in 1976 with a 3-year study, the NO $_{\rm X}$ Control Technology Environmental Assessment (NO $_{\rm X}$ EA, EPA Contract No. 68-02-2160), having the following objectives:

- Identify potential multimedia environmental effects of stationary combustion sources and combustion modification technology
- Develop and document control application guidelines to minimize these effects
- Identify stationary source and combustion modification R&D priorities
- Disseminate program results to intended users

During the first year of the NO_X EA, data and methodologies for the environmental assessment were compiled. Furthermore, priorities for the schedule and level of effort for developing emission data for the various source/fuel/control combinations were identified. This effort revealed major data gaps, particularly for noncriteria pollutants (organic emissions and trace elements) for virtually all combinations of stationary combustion

sources and combustion modification techniques. Consequently, a series of seven environmental field test programs was undertaken to fill these data gaps. The results of these tests are documented in seven individual reports (References 1-1 through 1-7) and in the NO_X EA final report summarizing the entire 3-year effort (Reference 1-8).

The current CMEA program has, as major objectives, the continuation of multimedia environmental field tests initiated in the original NO_X EA program. These new tests, using standardized sampling and analytical procedures (Reference 1-9) are aimed at filling remaining data gaps and addressing the following priority needs:

- Advanced NO_X controls
- Alternate fuels
- Secondary sources
- EPA program data needs
 - -- Residential oil combustion
 - -- Wood firing in residential, commercial, and industrial sources
 - -- High interest emissions determination (e.g., listed and candidate hazardous air-pollutant species)
- Nonsteady-state operations

In California, the South Coast Air Quality Management District (SCAQMD) continues to be in nonattainment of both federal and state NO_2 standards. Reciprocating internal combustion engines (ICE's) in this district are estimated to contribute 14 percent of the NO_X (about 59 Mg/day (65 tons/day)) from all stationary sources and 5.1 percent of the total NO_X emissions in the basin (References 1-10 and 1-11). Furthermore, since acid precipitation in noncoal-burning regions such as the SCAQMD is being increasingly attributed

to NO_X emissions from sources with low stacks, reciprocating ICE's are being viewed as possibly contributing to the acid rain problem.

In 1979, the California Air Resources Board (CARB) proposed a control strategy for ICE's that called for retrofit of these sources with selective and nonselective treatment catalysts (SCR and NSCR, respectively). In keeping with this CARB strategy, the SCAQMD passed rule 1110 calling for demonstration tests of SCR and NSCR technologies for engine NO_X control. Southern California Gas Company (SoCal) has conducted several performance tests to evaluate SCR and NSCR catalysts for their applicability in reducing NO_X from SoCal operated ICE's. However, data on sustained NO_X reduction performance associated with these technologies are currently limited (Reference 1-12). In addition, some potential environmental concerns have been raised. In the case of SCR, for example, the breakthrough of ammonia from the catalyst has been highlighted. For NSCR, the formation of ammonia and cyanide gases are also concerns.

In response to these data requirements and environmental concerns, a lean-burn reciprocating ICE operated by SoCal and retrofitted with a commercially available SCR system was selected for testing under the CMEA program. The objective of the tests was to quantify multimedia emissions (including organics, ammonia, and N_2O) at the inlet and outlet of the SCR catalytic reactor. In addition to these tests, NO_X reduction performance of the SCR was monitored continuously over 15 days under typical operating conditions. A similar field test program was conducted on a rich-burn engine retrofitted with a NSCR reactor. The results of these tests are documented in a separate report (Reference 1-13).

Table 1-1 lists all the tests performed in the CMEA program, outlining the source tested, fuel used, combustion modifications implemented and the level of sampling and analysis performed in each case. Results of these test programs are discussed in separate reports.

TABLE 1-1. COMPLETED TESTS DURING THE CURRENT PROGRAM

Source	Description	Test points unit operation	Sampling protocol	Test collaborator		
Spark-ignited, natural- gas-fueled reciprocating internal combustion engine	Large-bore, 6-cylinder, opposed piston, 186 kW (250 Bhp)/cyl, 900 rpm, Model 38TOS8-1/8	Baseline (pre-NSPS) Increased air-fuel ratio aimed at meeting proposed NSPS of 700 ppm corrected to 15 percent 02 and standard atmospheric conditions	Engine exhaust: SASS Method 5 Gas sample (C ₁ -C ₆ HC) Continuous NO, NO _x , CO, CO ₂ , O ₂ , CH ₄ , TUHC Fuel Lube oil	Fairbanks Morse Division of Colt Industries		
Compression-ignition, diesel-fueled reciprocating internal combustion engine	Large-bore, 6-cylinder opposed piston, 261-kW (350 Bhp)/cyl, 900-rpm, Model 38TDD8-1/8	Baseline (pre-NSPS) Fuel injection retard aimed at meeting pro-posed NSPS of 600 ppm corrected to 15 percent 02 and standard atmospheric conditions	Engine exhaust: SASS Method 8 Method 5 Gas sample (C ₁ -C ₆ HC) Continuous NO, NO _x , CO, CO ₂ , O ₂ , CH ₄ , TUHC Fuel Lube oil	Fairbanks Morse Division of Colt Industries		
Low-NO _X residential condensing heating system furnished by Karlsons Blueburner Systems Ltd. of Canada	Residential hot water heater equipped with M.A.N. low-NO, burner, 0.55 ml/s (0.5 gal/hr) firing capacity, condensing flue gas	Low-NO _x burner design by M.A.N.	Furnace exhaust: SASS Method 8 Method 5 Gas sample (C ₁ -C ₆ HC) Continuous NO, NO _x , CO, CO ₂ , O ₂ , CH ₄ , TUHC Fuel Waste water	New test		
Rocketdyne/EPA low-NO _X residential forced warm air furnace	Residential warm air furnace with modified high pressure burner and firebox, 0.83 ml/s (0.75 gal/hr) firing capacity	Low-NO _x burner design and integrated furnace system	Furnace exhaust: SASS Method 8 Controlled condensation Method 5 Gas sample (C ₁ -C ₆ HC) Continuous NO, NO _x , CO, CO ₂ , O ₂ , CH ₄ , TUHC Fuel	New test		

TABLE 1-1. (continued)

Source	Description	Test points unit operation	Sampling protocol	Test collaborator		
Pulverized coal-fired utility boiler, Conesville station	400-MW tangentially fired; new NSPS design aimed at meeting 301 ng/J NO _X limit	ESP inlet and outlet, one test	ESP inlet and outlet: SASS Method 5 Controlled condensation Gas sample (C1-C6 HC) Continuous NO, NO _X , CO, CO ₂ , O ₂ Coal Bottom ash ESP ash	Exxon Research and Engineering (ER&E) conducting cor- rosion tests		
Nova Scotia Technical College industrial boiler	1.14 kg/s steam (9,000 lb/hr) firetube fired with a mixture of coal-oil-water (COW)	Baseline (COW) Controlled SO ₂ emissions with limestone injection	Boiler outlet: SASS Method 5 Method 8 Controlled condensation Gas sample (C ₁ -C ₆ HC) Continuous O ₂ , CO ₂ , CO, NO _x Fuel	Envirocon per- formed particulate and sulfur emission tests		
Adelphi University industrial boiler	1.89 kg/s steam (15,000 lb/hr) hot water firetube fired with a mixture of coal-oil- water (COW)	Baseline (COW) Controlled SO ₂ emissions with Na ₂ CO ₃ injection	Boiler outlet: SASS Method 5 Method 8 Controlled condensation Gas Sample (C ₁ -C ₆ HC) Continuous O ₂ , CO ₂ , NO _x , CO Fuel	Adelphi University		
Pittsburgh Energy Technology Center (PETC) industrial boiler	3.03 kg/s steam (24,000 lb/hr) watertube fired with a mixture of coal-oil (COM)	Baseline test only with COM	Boiler outlet: SASS Method 5 Controlled condensation Continuous O ₂ , CO ₂ , NO _X , TUHC, CO N ₂ O grab sample Fuel	PETC and General Electric (GE)		

TABLE 1-1. (continued)

Source	Description	Test points unit operation	Sampling protocol	Test collaborator		
TOSCO Refinery vertical crude oil heater	2.54 M1/day Baseline (16,000 bb1/day) natural Staged combustion draft process heater using air injects burning oil/refinery gas lances		Heater outlet: SASS Method 5 Controlled condensation Gas sample (C ₁ -C ₆ HC) Continuous O ₂ , NO _x , CO, CO ₂ , HC N ₂ O, grab sample Fuel oil Refinery gas	KVB coordinated the staged com- bustion operation and continuous emission monitoring		
Mohawk-Getty Oil industrial boiler	8.21 kg/s steam (65,000 lb/hr) watertube burning mixture of refinery gas and residual oil	Baseline Ammonia injection using the noncatalytic thermal deNO _X process	Economizer outlet: SASS Method 5, 17 Controlled condensation Gas Sample (C ₁ -C ₆ HC) Ammonia emissions N ₂ O grab sample Continuous O ₂ , NO _X , CO, CO ₂ Fuels (refinery gas and residual oil)	Mohawk-Getty Oil		
Industria] boiler	2.52 kg/s steam (20,000 lb/hr) watertube burning woodwaste	Baseline (dry wood) Green wood	Boiler outlet: SASS Method 5 Controlled condensation Gas sample (C ₁ -C ₆ HC) Continuous O ₂ , NO _X , CO Fuel Flyash	North Carolina Department of Natural Resources, EPA IERL-RTP		
Industrial boiler	3.16 kg/s steam (29,000 lb/hr) firetube with refractory firebox burning woodwaste	Baseline (dry wood)	Outlet of cyclone particulate collector: SASS Method 5 Controlled condensation Gas sample (C ₁ -C ₆ HC) Continuous O ₂ , NO _X , CO Fuel Bottom ash	North Carolina Department of Natural Resources, EPA IERL-RTP		

TABLE 1-1. (continued)

Source	Description	Test points unit operation	Sampling protocol	Test collaborator
Enhanced oil recovery steam generator	15-MW (50 million Btu/hr) steam generator burning crude oil equipped with MHI low-NO _X burner	Performance mapping Low NO _X operation	Steamer outlet SASS Method 5 Method 8 Gas sample (C ₁ -C ₆ HC) Continuous O ₂ , NO _x , CO, CO ₂ N ₂ O grab sample Fuel	Getty Of 1 Company, CE-Natco
Pittsburgh Energy Technology Center (PETC) industrial boiler	3.03 kg/s steam (24,000 lb/hr) watertube fired with a mixture of coal-water slurry (CWS)	Baseline test only with CWS	Boiler outlet SASS Method 5 Method 8 Gas sample (C ₁ -C ₆ HC) Continuous O ₂ , NO _X , CO, CO ₂ , TUHC N ₂ O grab sample Fuel Bottom ash Collector hopper ash	PETC
Spark-ignited, natural- gas-fueled reciprocating internal combustion engine nonselective NO _X reduction catalyst	610-kW (818-hp) Waukesha rich-burn engine equipped with DuPont NSCR system	Low-NO _X (with catalyst) 15-day emissions monitoring	Catalyst inlet and outlet SASS NH3 HCN N ₂ O grab sample Continuous O ₂ , CO ₂ , NO _X TUHC Lube oil	Southern California Gas Company
Industrial boiler	180 kg/hr steam (400 lb/hr) stoker fired with a mixture of coal and plastic waste	Baseline (coal) Coal and plastic waste	Boiler outlet SASS VOST Method 5 Method 8 HC1 Continuous O ₂ , NO _X , CO, CO ₂ , TUHC N ₂ O grab sample Fuel Bottom ash Cyclone ash	Vermont Agency of Environmental Conservation

TABLE 1-1. (concluded)

Source	Description	Test points unit operation	Sampling protocol	Test collaborator		
Industrial boiler	7.6 kg/s steam (60,000 lb/hr watertube retrofit for coal water slurry firing	Baseline test with CWS 30-day emissions monitoring	Boiler outlet SASS VOST Method 5 Method 8 Grab sample (C ₁ -C ₆ HC) N ₂ O grab sample Continuous NO _x , CO, CO ₂ , O ₂ , TUHC, SO ₂ Fuel	EPRI, DuPont		
Enhanced oil recovery steam generator	15-MW (50 million Btu/hr) steam generator burning crude oil, equipped with the EPA/EER low-NO _X burner	Łow-NO _x burner 30-day emissions monitoring	Steamer outlet SASS VOST Method 5 Method 8 Controller condensation Andersen impactors Grab sample (C ₁ -C ₆ HC) N ₂ O grab sample Continuous NO _x , CO, CO ₂ , O ₂ , SO ₂ Fuel			
Spark-ignited, natural-gas-fueled reciprocating internal combustion engine selective NO _X reduction catalyst	1,500-kW (2,000-hp) Ingersoll-Rand engine equipped with Engelhard SCR system	Low NO _X with catalyst 15-day emissions monitoring	Catalyst inlet and outlet SASS NH3 HCN N ₂ O grab sample Continuous O ₂ , CO ₂ , NO _X , TUHC Lube oil			

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- 1-12. Harris, E. H., "Southern California Gas Company NO_X Emission Control Program 1982 Annual Report," Southern California Gas Company, Los Angeles, California, February 1983.
- 1-13. Castaldini, C. and L. R. Waterland, "Environmental Assessment of a Reciprocating Engine Retrofitted with Nonselective Catalytic Reduction." EPA-600/7-84-073a, NTIS PB 84 224-351, June 1984.

SECTION 2

SOURCE DESCRIPTION AND OPERATION

The tests were performed on a four-stroke turbocharged Ingersoll-Rand 412-KVS, 2,000-hp, gas compressor engine equipped with an Engelhard SCR catalyst system. This engine is located at the SoCal Aliso Canyon compressor station on the Northridge, California underground storage field. Table 2-1 summarizes the engine model specifications. The Engelhard Deoxo catalyst system installed in Spring 1984, is a proprietary metal-oxide-based formulation with operating temperature limits of 288° to 427°C (550° to 800°F). The catalyst, located downstream of the engine silencer, was designed to reduce NO_X emissions by 80 percent or greater, and thereby meet the SCAQMD rule 1110.1. The reducing agent, anhydrous NH3 gas, is injected into the exhaust gas to react with NO_X and O_Z in the presence of this metal catalyst and reduce both NO and NO_Z . The SCR chemical reaction process is typically envisioned to be as follows:

$$4NH_3 + 4NO + O_2 + 4N_2 + 6H_2O$$

$$4NH_3 + 2NO_2 + O_2 + 3N_2 + 6H_2O$$

The SCR process requires fuel-lean engine operation and the addition of the reducing agent NH₃ in the flue gas upstream of the catalyst. An additional requirement is the NH₃ control system whose function is to maintain the appropriate NH₃/NO molar ratio (generally set for 1.0 for \geq 90 percent NO_X

Engine:

Manufacturer Ingersoll-Rand

Mode 1 412DT-KVS

Cycle 4-strokes

Air charging Turbocharged (dual)

Number of cylinders V-12

Bore 0.387m (15.25 in.)

Stroke 0.487m (18.0 in.)

Displacement/cylinder 44.8 1 (2,735 in.³)

Compression ratio 6.5:1

BMEP 1.00 MPa (146 psi)

Bhp/cyl at rpm 125 kW (167 Bhp) at 330 rpm

Compressor:

Manufacturer Ingersoll-Rand

Bore (first stage) 0.235m (9.25 in.)

Stroke (first stage) 0.381m (15.2 in.)

Bore (second stage) 0.159m (6.25 in.)

Stroke (second stage) 0.381m (15.2 in.)

reduction) with varying NO_X concentrations in the exhaust gas and varying engine load. For the Aliso Canyon site, Engelhard installed an ammonia control system which includes a chemiluminescent NO_X analyzer to determine the concentrations upstream and downstream of the catalyst and a microprocessor to compare the values and control the ammonia flowrate. Parametric testing of this catalyst conducted in 1982 on slip stream exhaust indicated 90 percent NO_X reduction capability with 100 ppm NH_3 carryover for NH_3/NO of about 1.0 and a gas temperature in the range of about 400° to 450°C (750° to 850°F) (Reference 2-1).

During the CMEA tests, exhaust emissions (NO_X , O_2 , CO, CO_2), and total unburned hydrocarbon (TUHC) were measured on a continuous basis for a period of 15 days during normal engine operation. In addition, a comprehensive emission test program was performed over a 1-day period during which engine load and NH_3 flowrate were controlled for catalyst NO_X reduction of about 80 percent. Table 2-2 summarizes the engine operation and ambient atmospheric conditions during this 1-day comprehensive testing period.

As noted, engine load was maintained relatively constant throughout the comprehensive test period. Engine power output of 1,270 kW_t (1,700 Bhp) was calculated using compressor performance curves available from the manufacturer. Heat rate based on fuel lower heating value was measured to be about 9,400 kJ/kWh (6,600 Btu/Bhp-hr). Measured turbocharger turbine gas outlet temperature varied from 370° to 390°C (700° to 740°F). These measurements are considered in error (low) though, as suggested by the catalyst inlet temperature measurement which was between 390° to 400°C (740° to 750°F).

TABLE 2-2. ENGINE OPERATION

Parameter	Range	Average			
Ambient					
Dry bulb temperature, °C (°F) Wet bulb temperature, °C (°F) Relative humidity, percent Barometric pressure, kPa (in. Hg)	22 to 33 (72 to 92) 19 to 21 (67 to 70) 45 to 55	29 (84) 20 (68) 50 96.2 (28.5)			
Engine Operation					
Engine load, kWt (Bhp)a Fuel flow, scm/hr (scfh) Heat input, MW (million Btu/hr)b Specific fuel consumption, kJ/kWh (Btu/Bhp-hr)b Air manifold procesure, kPa (neig)	 25 to 28 (3.6 to 4.0)	1,270 (1,700 327 (11,550) 3.29 (11.2) 9,390 (6,610) 26.5 (3.85)			
Air manifold pressure, kPa (psig) Air manifold temperature °C (°F) Speed, rpm	68 to 70 (154 to 158) 320 to 333	69 (156) 325			
Exhaust manifold temperatures, °C (°F) No. 1 cylinder No. 2 cylinder No. 3 cylinder No. 5 cylinder No. 6 cylinder No. 7 cylinder No. 8 cylinder No. 9 cylinder No. 10 cylinder No. 11 cylinder No. 12 cylinder Turbine outlet temperature, °C (°F) L R Catalyst inlet temperature, °C (°F) Catalyst outlet temperature, °C (°F)	380 to 382 (716 to 720) 292 to 360 (560 to 680) 440 to 455 (820 to 850) 430 to 440 (800 to 820) 380 to 390 (720 to 730) 404 to 415 (760 to 780) 290 to 350 (550 to 660) 380 to 390 (710 to 730) 360 to 370 (680 to 700) 380 to 390 (700 to 740) 370 to 393 (700 to 730) 365 to 370 (690 to 700) 396 to 404 (745 to 760) 380 to 390 (720 to 740) 370 to 380 (700 to 740) 370 to 380 (700 to 740) 370 to 380 (700 to 740) 390 to 400 (740 to 750) 344 to 382 (652 to 720)	380 (718) 332 (630) 449 (840) 430 (810) 385 (725) 410 (775) 320 (610) 380 (720) 363 (685) 390 (730) 380 (715) 370 (722) 404 (760) 390 (730) 380 (720) 396 (745) 362 (683)			
Gas Compressor					
Suction pressure, MPa (psig) Interstage pressure, MPa (psig) Discharge pressure, MPa (psig) Suction temperature, "C ("F) Interstage temperature, "C ("F) Discharge temperature, "C ("F) NH ₃ System	 26 to 35 (78 to 95) 88 to 93 (190 to 200) 107 to 118 (225 to 245)	4.02 (583) 7.86 (1,140) 19.97 (2,898) 29 (85) 91 (195) 113 (235)			
NH ₃ flowrate, standard 1/s (scfh)	4.44 to 4.88 (565 to 620)	4.64 (590)			

^aEngine load obtained from engine performance curves.

^bHeat input based on low heating value (LHV) of natural gas from Table 2-3.

Specific fuel consumption based on LHV of fuel.

Ammonia injection rate varied from 4.44 to 4.88 standard 1/s (565 to 620 scfh), corresponding to a NH3/NO molar ratio of about 1.04 to 1.10. Average NH3 injection rate was about 464 standard 1/s (590 scfh) corresponding to a NH3/NO ratio of 1.07.

Table 2-3 summarizes the typical analysis of the natural gas fuel.

This analysis, provided by SoCal, corresponds to a sample obtained prior to the comprehensive test program.

It should be noted that prior to the test period, problems were experienced with the NH $_3$ control system, specifically the NO $_{\rm X}$ analyses and also the NH $_3$ control valve.

TABLE 2-3. NATURAL GAS FUEL ANALYSISa

Component	Percent by volume
CH4 C2H6 C3H8 C4H10 C5H12 C6H14 CO2	89.7 5.75 1.50 0.40 0.128 0.147 0.947 1.30

High heating value^b MJ/m³ (Btu/ft³) 39.8 (1,070)

Low heating value^b 36.2 (973)

Specific gravity 0.622

aTypical fuel analysis bCalculated heating value

REFERENCE FOR SECTION 2

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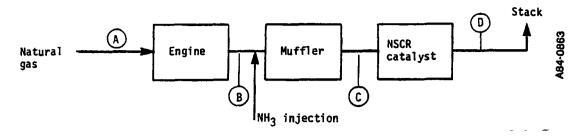
SECTION 3

EMISSION RESULTS

The objectives of this test program were: (1) to measure engine exhaust emissions during a 15-day test period to evaluate the continuous performance of the catalyst, utilizing continuous NO_X and other gas emission analyzers, and (2) to perform comprehensive tests over a 1-day period to measure the effect of the catalyst on organic emissions as well as on NH₃ breakthrough and possible formation of HCN. Emission measurements were performed in cooperation with SoCal, owner and operator of the test site, whose field crew and equipment included an emission monitoring laboratory with operating staff.

3.1 SAMPLING PROTOCOL

Figure 3-1 illustrates a schematic of the test site highlighting the sampling locations, sampling and analytical test matrix, and the test team performing the sampling and evaluation. As indicated, continuous monitoring of flue gas was performed alternatively upstream and downstream of the catalytic reactor utilizing heated sample lines. The catalyst inlet sampling location for the continuous monitors was upstream of the NH3 injection location to avoid any effect of added NH3 on the engine exhaust NO_X measurements. The sampling and gas conditioning system for this test program included continuous monitors for O_2 , CO_2 , CO_3 , CO_4 , CO_5 , CO_6 , C



Sample Location	Type of Sample	<u>Analyses</u> a	Test Number
A Natural gas to engine	Grab sample Fuel	Gas chromatography for composition; heating value, specific gravity	SoCa1
B,D Catalyst inlet, outlet	Extractive Sample Continuous Monitors	0 ₂ , CO ₂ , CO, TUHC, NO, NO _X ,	Acurex SoCalb
	Volatile organic sampling train (VOST)	Volatile organics in accordance with EPA Method 624 (catalyst outlet only)	Acurex
C,D Catalyst inlet, outlet	Sampling train SASS	Particulate by gravimetry, total semivolatile organics by GC/FID, total nonvolatile organics by gravimetry, and semi- and nonvolatile organic compounds in accordance with EPA Method 625	Acurex
	Sampling train Modified Method 6	NH ₃ by selective ion electrode	Acurex
	Sampling train Modified Method 6	HCN by wet chemistry	Acurex
	Grab sample Gas bomb	N ₂ 0 by GC/ECD	Acurex
	Grab sample Method 7 flasks	NO _X by Method 7	Acurex

 $^{^{}a}\mbox{Measurement}$ and analysis techniques used are discussed in detail in Appendix A

Figure 3-1. Sampling sites and analysis test matrix.

bNO_X measurements also provided by SoCal as part of the NH₃ Control System

engine load and NH3 injection rate varied slightly. Certification of the ${\rm NO_X}$ analyzer readings was attempted once during this 15-day test period using standard EPA Method 7 protocol.

The source assessment sampling system (SASS), the NH₃, and the HCN sampling trains were operated during 1 day of tests at both the inlet and outlet of the catalytic converter. Catalyst inlet location for these sampling systems was downstream of the NH₃ injection location. Simultaneous inlet and outlet samples were performed to measure any change in the composition of the exhaust gas across the catalyst. Volatile organics were measured at the catalyst outlet only using the volatile organic sampling train (VOST) per EPA protocol (Reference 3-1). These measurements were performed while engine load was maintained constant and NH₃ injection rate was adjusted for about 80 percent NO_x reduction by the catalyst.

Figure 3-2 illustrates the actual test activity schedule. The following sections summarize the emission results. Sections 3.2 and 3.3 present emission results obtained during the comprehensive tests that took place on August 3, 1984. Section 3.4 summarizes results of continuous emission measurements performed over the 15-day test period. EPA Method 7 certification tests, performed on August 2, 1984, are discussed in Section 4. Details of the sampling and analysis procedures used are discussed in Appendix A.

3.2 CRITERIA POLLUTANT AND OTHER VAPOR SPECIES EMISSIONS

Table 3-1 summarizes gaseous and particulate emissions measured during the 1-day comprehensive tests performed at about the half-way point of the 15-day continuous monitoring period. Exhaust 0_2 was about 11.2 percent at

	July						August								
Test activity	26	27	28	29	30	31	1	2	3	4	5	6	7	8	9
 Continuous monitors / (inlet/outlet) 	7	Δ													(
 Comprehensive tests (inlet/outlet) 															
VOST (outlet only)									Δ						
SASS									Δ						
NH ₃									Δ						
HCN									Δ						
N ₂ 0														Δ	
 Method 7 certification 								Δ							

Figure 3-2. Test activity schedule.

TABLE 3-1. CRITERIA AND OTHER GAS PHASE SPECIES EMISSIONS: COMPREHENSIVE TESTS

Pollutant ^a	Catalyst inlet			Catalyst outlet		
As measured by continuous gas analyzers, range (average):						
O ₂ , percent dry	11.1 to 11.3 (11.2)			10.9 to 11.2 (11.1)		
CO ₂ , percent dry	5.0 to 5.9 (5.5)			5.1 to 6.0 (5.6)		
CO, ppm dry	180 to 310 (245)			170 to 280 (225)		
NO _X , ppm dry	2,200 to 2,600 (2,400)			330 to 560 (445)		
TUHC, ppm dry of CH4 ^f		NA			, NA	
Corrected average gaseous emissions:	ppmp	ng/J ^C	g/Bhp-hrd	ppmb	ng/J ^C	g/Bhp-hrd
CO	150	171	1,19	138	158	1.10
NO _X e	1,470	2,760	19.2	273	513	3.57
TUHCf		NA			NA	
ин3а	1,084	752	5.23	56	39	0.27
Total cyanide ^h	0.004	0.004	3 x 10 ⁻⁵	1.3	1.4	0.010
Solid particulate:						
SASS solids		Negligi	ble	· ==	Negligi	ble

aAppendix A discusses continuous monitor analyses used, sample gas conditioning system, particulate sampling equipment, and other sampling trains and procedures bCorrected to 15 percent 02, dry

COn heat input basis using fuel's lower heating value

dShaft output basis

eAs NO2 (NO and NO2 only)

fTotal hydrocarbon monitor not functioning

gInlet NH3 measured downstream of NH3 injection location. Values report an average of two separate measurements

hAs HCN: value reported is average of two separate measurements

hAs HCN; value reported is average of two separate measurements

both the inlet and outlet location. This indicates an air-fuel ratio of about 35 on a weight basis.

 ${
m NO}_{
m X}$ emissions at the engine outlet varied from 2,200 to 2,600 ppm as measured, with an average of 2,400 ppm, corresponding to about 2.76 mg/J heat input basis (19.2 g/Bhp-hr shaft output). ${
m NO}_{
m X}$ reduction efficiency by the catalyst ranged between 78 to 85 percent with an average for the day of 81 percent. CO emissions were approximately 10 percent lower at the catalyst outlet compared to the emissions measured in the untreated engine exhaust. Unburned hydrocarbon data were not available for the comprehensive test period due to instrument malfunction. However, test data obtained prior to and following these tests showed TUHC concentration in the range of about 1,500 to 1,800 ppm as measured at both inlet and outlet locations.

NH₃ emissions were measured using a wet impinger method and a continuous method using a NO $_{\rm X}$ analyzer. Sampling of NH₃ using the impinger train took place at the inlet to the catalyst, downstream of the NH₃ injection location. Therefore, the measured concentration of NH₃ at this location is the direct result of the NH₃ injected in the engine exhaust for the catalytic reduction of NO $_{\rm X}$. NH₃ concentrations at this location ranged from 1,450 to 2,090 ppm obtained with two separate gas samples. The NH₃ injection rate during this test period was recorded in the range of 4.44 to 4.88 1/s (565 to 620 scfh) which would result in a concentration of 2,422 to 2,700 ppm in the engine exhaust. Therefore, the amount of NH₃ measured at the catalyst inlet by wet chemical analysis accounts for about 60 to 77 percent of the measured NH₃ injection rate.

Table 3-2 summarizes the NH $_3$ gas concentrations recorded using continuous gas monitors. Using two NO $_{\rm x}$ analyzers, the NH $_3$ was measured by

TABLE 3-2. AMMONIA MEASUREMENTS, PPM DRY AS MEASURED

	Emission ^a	Catalyst inlet ^b	Catalyst outlet	Percent change
1.	NO	2,000 to 2,400 (2,200)	300 to 590 (445)	-80
2.	NO + NO ₂	2,000 to 2,600 (2,400)	330 to 560 (445)	-81
3.	$NO + NO_2 + NH_3$	2,200 to 2,600 (2,400)	390 to 622 (505)	- 79
4.	NH ₃ (by difference 3-2)	0	20 to 140 (80)	
5.	${ m NH_3}$ by wet method ${ m C}$	NA	65 to 118 (92)	

aValues for emissions (1 through 4) were recorded using continuous analyzers bMeasurements upstream of NH3 injection location CNH3 measurements by wet method were made downstream of NH3 injection location, therefore a wet method measurement at the catalyst inlet is not available

the difference in readouts between NO + NO₂ and NO + NO₂ + NH₃. Appendix A describes in detail the technique used. Upstream of the NH₃ injection location, the two analyzers showed no difference, indicating no NH₃ present, as expected. At the catalyst outlet location, the two analyzers indicated NH₃ concentration in the range of 20 to 140 ppm as measured. Using two separate wet chemical analysis measurements, NH₃ at this location was recorded at 65 and 118 ppm, respectively. Average values were 80 ppm using continuous monitors and about 90 ppm using wet chemical analysis.

Additional sampling was performed to quantitate cyanide and particulate levels in the exhaust across the catalyst. Total cyanides, as HCN, increased by three orders of magnitude from an average of about 4 pg/J (30 µg/Bhp-hr) to 1.4 ng/J (10 mg/Bhp-hr). Particulate emission levels were negligible at both sample locations (actual particulate matter collected on the filter showed a decrease after corrections for filter tare and blank).

 N_20 emissions were measured by gas chromatography with electron capture detection of exhaust gas grab samples taken at the inlet and outlet of the catalyst. Table 3-3 summarizes results of the N_20 emissions sampled on August 8. Corresponding exhaust NO_X levels are also shown in the table. As indicated, at the time the N_20 samples were taken the SCR system was effecting about 80 percent NO_X reduction. Interestingly, N_20 levels were reduced about 60 percent by the catalyst. The N_20 level was about 4 percent of NO_X level in the exhaust at the catalyst inlet and about 9 percent at the catalyst outlet. These are significantly lower than the fractions measured in tests of external combustion sources, which fall in the 15 to 25 percent range (Reference 3-2). However, the N_20 fractions measured in tests of a rich-running engine were also low (2 to 3 percent of NO_X emission levels) (Reference 3-3).

TABLE 3-3. N20 EMISSIONS: IC ENGINE/SCR TESTSa

	Compound	Catalyst inlet	Catalyst outlet	Percent reduction
NO _X ,	ppm measured ppm at 15% 0 ₂	2,600 1,640	490 300	82
N ₂ 0,	ppm measured ppm at 15% 0 ₂	98 62	43 26	57

^aTests performed on August 8

3.3 ORGANIC SPECIES EMISSIONS

Organic analyses were performed on the exhaust gas samples collected at the catalyst inlet and outlet locations. SASS samples were analyzed for total semivolatile and nonvolatile organics according to the EPA Level 1 protocol (Reference 3-4) as outlined in Appendix A. Semivolatile organic compounds with boiling points in the nominal C_7 to C_{16} range of 100° to 300°C (210° to 570°F) were determined in the laboratory by total chromatographable organic (TCO) analysis of the combined organic module sorbent (XAD-2) and condensate extracts. Nonvolatile organic species having boiling points in the nominal C_{16+} range of >300°C (570°F) were measured by gravimetric (GRAV) analysis of SASS sample extracts.

Infrared spectrometry (IR) was performed on the GRAV residue of SASS train extracts to identify organic functional groups possibly present. Gas chromatography/mass spectrometry (GC/MS) analyses of the XAD-2 extracts were also performed to identify specific polynuclear aromatic hydrocarbons (PAH) and other organic components (the semivolatile organic priority pollutants).

The components sought in the GC/MS analysis and their respective detection limits are listed in Table 3-4.

In addition, emissions of volatile organics were measured at the catalyst outlet using the volatile organic sampling train (VOST) protocol per EPA procedures (Reference 3-1). Analysis of VOST samples was performed also by GC/MS. Volatile organic compounds sought in this analysis are listed in Table 3-5.

3.3.1 TCO, GRAV, GC/MS, and IR Analyses of SASS Sample Extracts

Table 3-6 summarizes the results of the organic analyses of the SASS train XAD-2 sorbent module extract for the catalyst inlet and outlet tests. As noted, total organic emissions decreased about 70 percent across the catalyst from 4.9 to 1.5 mg/dscm. The greatest reduction apparently occurred in the nonvolatile fraction. This fraction accounted for 65 percent of the total organic at the catalyst inlet, but only 40 percent at the catalyst outlet.

Two polynuclear aromatic hydrocarbon (PAH) compounds (naphthalene and phenanthrene) and a nitrophenol were measured in the exhaust at the catalyst inlet. Levels of these were significantly reduced at the catalyst outlet. Concentrations were below 10 μ g/dscm (about 40 μ g/Bhp-hr) for both test locations.

Table 3-7 summarizes the results of the IR analysis of organic module extracts. The data suggest the presence of aliphatic hydrocarbons and possibly some oxygenated hydrocarbons at both the inlet and outlet locations.

TABLE 3-4. COMPOUNDS SOUGHT IN THE GC/MS AND THEIR DETECTION LIMITS (ng/ μ l INJECTED)

Acid	Соп	pounds	
2,4,6-trichlorophenol p-chloro-m-cresol 2-chlorophenol	5 5	2-nitrophenol 4-nitrophenol 2,4-dinitrophenol	5 20 20
2,4-dichlorophenol 2,4-dimethylphenol	5 5 5	4,6-dinitro-o-cresol pentachlorophenol phenol	20 20 5
Base Neut	ral	Compounds	1
1,2,4-trichlorobenzene 1,2-dichlorobenzene	1 1	benzo(c)phenanthrene bis(2-chloroethoxy)methane	40 1
1,2-diphenylhydrazine . (as azobenzene) 1,3-dichlorobenzene	1	<pre>bis(2-chloroethyl)ether bis(2-chloroisopropyl)ether bis(2-ethylhexyl)phthalate</pre>	1 1 1
1,4-dichlorobenzene 2,4-dinitrotoluene	1	butyl benzyl phthalate chrysene	1
2,6-dinitrotoluene 2-chloronaphthalene 3,3'-dichlorobenzidine	1 1 5	<pre>di-n-butyl phthalate di-n-octyl phthalate dibenzo(a,h)anthracene</pre>	1 1 5
3-methyl cholanthrene 4-bromophenyl phenyl ether	40 1	dibenzo(c,g)carbazole diethyl phthalate	40 1
4-chlorophenyl phenyl ether 7,12-dimethyl benz(a)anthracene N-nitrosodi-n-propylamine	1 40 5	dimethyl phthalate fluoranthene fluorene	1 1 1
N-nitrosodimethylamine N-nitrosodiphenylamine	NA 1	hexachlorobenzene hexachlorobutadiene	1 1
acenaphthene acenaththylene anthracene	1 1 1	hexachlorocyclopentadiene hexachloroethane indeno(1,2,3-cd)pyrene	1 1 5
benzo(ghi)perylene benzidine	5 20	isophorone naphthalene	1 1
benzo(b)fluoranthene benzo(k)fluoranthene	. 1	nitrobenzene perylene	1 40 1
benzo(a)anthracene benzo(a)pyrene	1	phenanthrene pyrene	1

Chlorinated Aliphatics

Chlorome thane Dichloromethane Chloroform

Tetrachloromethane

Chloroe thane

1,1-dichloroethane 1,2-dichloroethane 1,1,1-trichloroethane 1,1,2-trichloroethane

1,1,2,2-tetrachloroethane

1,2-dichloropropane **Hexachlorocyclohexane**

Vinyl chloride

1,1-dichloroethylene 1,2-dichloroethylene **Trichloroethylene** Tetrachloroethylene Alkyl chloride 1,3-dichloropropene

Chloroprene

Ethers

Ethylene oxide Propylene oxide

Chlorinated Ethers

Epichlorohydrin 2-chloroethyl vinyl ether

Aldehydes

Ace ta 1 de hyde Acrolein

Amines and Nitriles

Acrylonitrile

Aromatic Hydrocarbons

Benzene Toluene Ethyl benzene o-xylene m-xylene p-xylene

Chlorinated Aromatics

Chlorobenzene

TOTAL ORGANIC AND SEMIVOLATILE ORGANIC PRIORITY POLLUTANT EMISSIONS: IC ENGINE/SCR SYSTEM TESTS, XAD-2 PLUS OMC EXTRACT TABLE 3-6.

	Catalyst inlet		Catalyst	outlet
Component	(mg/train)	(mg/dscm)	(mg/train)	(mg/dscm)
Total semivolatile organics (C, to C ₁₆ by TCO)	44	1.7	22 a	0.9
Total nonvolatile organics (C ₁₆₊ by gravimetry)	83	3.2	16	0.6
Total semi- and nonvolatile organics	127	4.9	38	1.5
Semivolatile organic priority pollutants	(μg/train)	(μg/dscm)	(μg/train)a	(µg/dscm)
Naphthalene	220	8.4	10	0.4
Phenanthrene	10	0.4	<10	<0.4
2-Nitrophenol	140	5.3	<10	<0.4
Di-n-butyl phthalateb	80	3.1	140	5.5
Bis (2-ethylhexyl) phthalateb	50	1.9	25	1.0
Other semivolatile organic priority pollutants	<10	<0.4	<10	<0.4

^aAverage of duplicate injections bSuspected contaminants, commonly found in laboratory blanks

TABLE 3-7. IR SPECTRA SUMMARY

Sample	Wave number (cm ⁻¹)	Intensi ty ^a	Assignment	Possible compound categories present
XAD-2 + OMC extract, catalyst inlet	3350 2955 2920 2850 1570 1460 1340 1260 1055 950 880 770 700 635	W S S S S S W M M W W W W W	OH stretch CH alkyl CH alkyl CH alkyl Not assigned CH bendb CH bendb C-0 stretchb C-0 stretchb C-C stretch CH rock CH rock CH rock CH rock	Aliphatic hydro- carbons possibly with some oxygenates such as aldehydes and alcohols
XAD-2 + OMC extract, catalyst outlet	2955 2920 2850 1710 1450 1410 1255 800	S S S M W S M	CH alkyl CH alkyl CH alkyl C=0 stretch CH bendb CH bendb C-0 stretch CH rock	Aliphatic hydro- carbons possibly with some oxy- genates such as carboxylic acids and ketones

 $^{{}^{}a}S$ = strong, M = moderate, W = weak ${}^{b}T$ entative assignment

3.3.2 Volatile Organic Emissions

Table 3-8 summarizes results of the volatile organic sampling train (VOST) testing of the engine. Only one abbreviated set (two runs) of VOST tests was performed; sampling was at the catalyst outlet. As shown, benzene and several substituted benzenes were emitted at highest concentrations: benzene at 915 μ g/dscm, toluene at 247 μ g/dscm, xylenes at 85 μ g/dscm, chlorobenzene at 61 μ g/dscm, and ethylbenzene at 20 μ g/dscm. Small amounts of chlorinated ethylenes and ethanes were also detected, although these compounds are often Tenax contaminants. The protocol is described in Appendix A.

3.4 EXTENDED CONTINUOUS EMISSION MONITORING

Continuous monitoring for exhaust gas 0_2 , CO_2 , CO_3 , CO_4 , and TUHC was performed over a 15-day period from July 26 to August 9, 1984. Actual emission measurements for SCR performance did not begin until July 27 due to NH $_3$ feed problems and control. The engine was operated under normal conditions with no restrictions on load during this period. NH $_3$ injection rate was controlled by the automatic NO_X feedback system installed on this unit as part of the SCR control package. NH $_3$ feedrate was set to provide 80 percent reduction in NO_X . Figures 3-3 through 3-8 illustrate emission data obtained over this test period. The emission data represent hourly averages of the data taken on 5- to 15-min intervals.

Exhaust 0_2 and $C0_2$, illustrated in Figure 3-3, show that engine operation was fairly steady throughout the 14 days of actual emissions testing. Gaps on the test data indicate engine shutdowns generally due to lubrication system malfunction. This is most evident during the period

TABLE 3-8. VOLATILE ORGANIC SAMPLING TRAIN RESULTS: CATALYST OUTLETA

			Run 1		Run 2				
Compound	Field Method blank blank (µg/trap (µg/trap pair) pair)	(µg/trap pair)			(µg/trap pair)				
		Measured	Correctedb	(µg/dscm) corrected ^b	Measured	Correctedb	(µg/dscm) corrected ^b	Average (µg/dscm)	
Benzene	NDc	13	ND		~-	32,000	32,000	1,830	915
Chlorobenzene	ND	5	1,700	1,700	81	720	715	41	61
1,2-dichloroethane	ND	ND	ND		***	5			
1,1,1-trichloroethane	45	ND	ND			101			
1,1,2,2-tetrachloroethane	ND	9	60	•		11			
Chloroe thane	ND	ND	56	56	2.7	16	16	0.9	1.8
Chloroform	ND	ND	11			10			
1,1-dichloroethene	ND	ND	31	31	1.5	26	26	1.5	1.5
t-1,2-dichloroethene	ND	ND	7			ND			
Ethy Ibenzene	ND	5	700	695	33	127	122	7.0	20
Methylene chloride	1,205	38	1,200			1,700			
Chlorome thane	111	58	155			130			
Bromome thane	5	2	6			5			
Tetrachloroethene	ND	ND	ND			85	85	4.8	2.4
Toluene	ND	31	6,000	5,970	285	3,700	3,670	209	247
Trichloroethene	ND	ND	ND			3			
Vinyl chloride	ND	ND	11			5			
Acetone	5	ND	720	715	34	ND			17
Total xylenes	NĎ	10	ND			3,000	2,990	170	85

^aTraps desorbed and analyzed in pairs (Tenax and Tenax/charcoal)

^bCorrected = measured - maximum of field or method blank. If this not greater than 10 times the blank value and greater than 10 times the method detection limit of 1 ng/trap pair, then assumed not significant, denoted by double dashes.

^cND denotes less than the method detection limit of 1 ng/trap pair

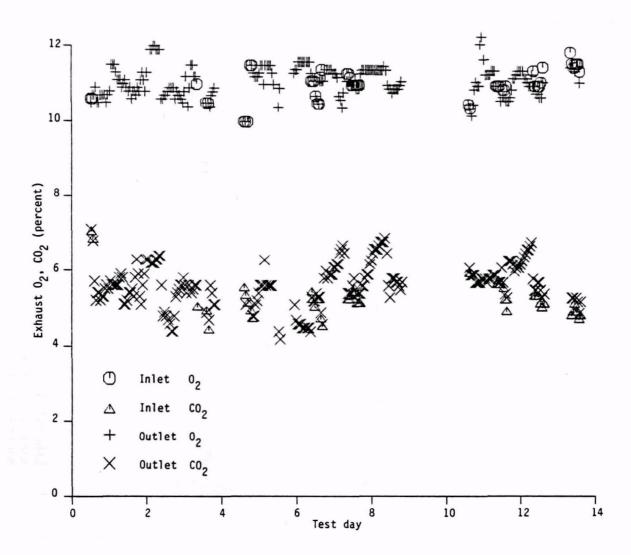


Figure 3-3. Exhaust $\mathbf{0}_2$ and $\mathbf{C0}_2$ for the extended continuous monitoring period.

Figure 3-4. Exhaust $\mathrm{NO}_{\mathbf{X}}$ levels for the extended continuous monitoring period.

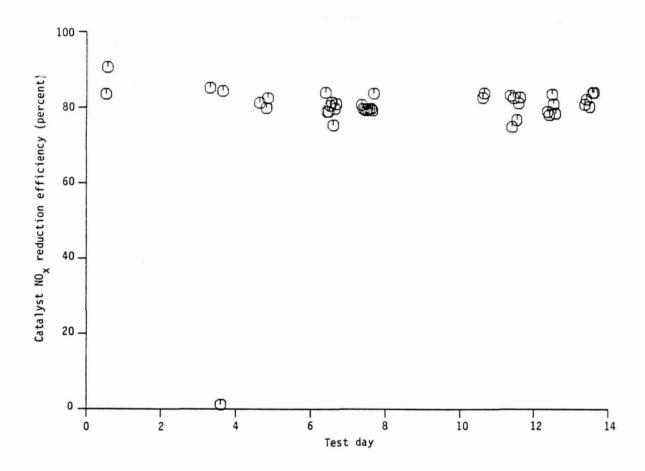
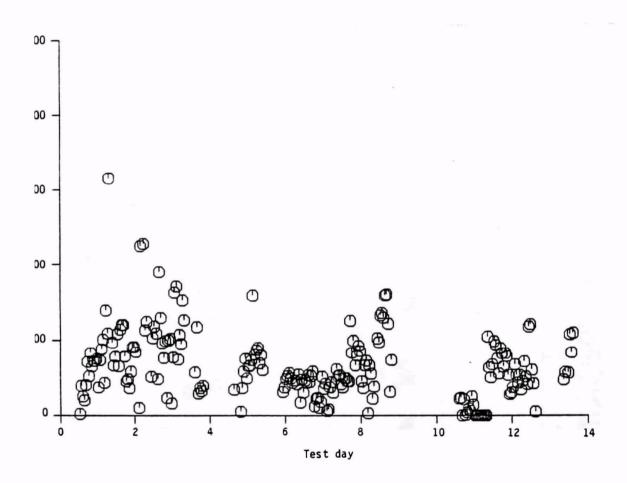


Figure 3-5. Catalyst NO_{X} reduction efficiency for the extended monitoring period.



 $^{\mbox{\scriptsize re}}$ 3-6. Catalyst outlet NH $_{\mbox{\scriptsize 3}}$ emissions for the extended continuous monitoring period.

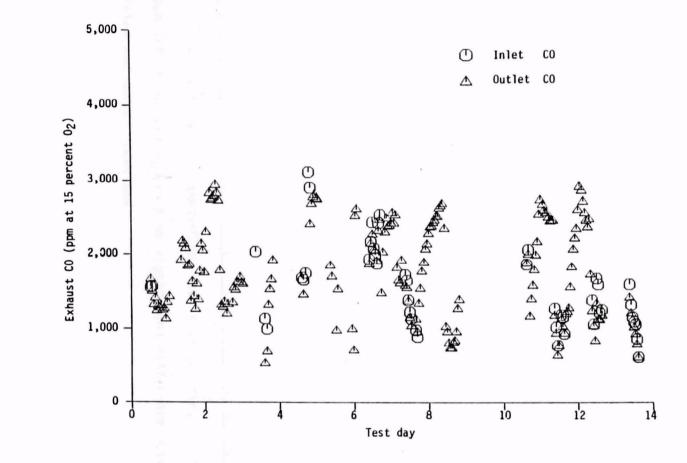


Figure 3-7. Exhaust CO levels for the extended continuous monitoring period.

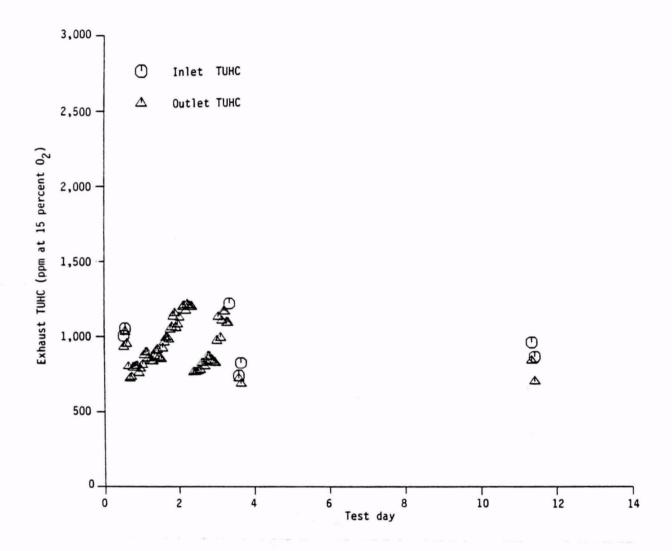


Figure 3-8. Exhaust hydrocarbon levels for the extended continuous monitoring period.

August 5 to 7. Comprehensive tests discussed in the previous sections were performed on August 3.

 NO_X emissions are illustrated in Figure 3-4. Catalyst inlet levels ranged from 1,200 to 1,600 ppm corrected to 15 percent O_2 . Catalyst outlet levels ranged from about 100 to 400 ppm (at 15 percent O_2) with most of the measurements showing NO_X of about 200 ppm. Corresponding NO_X reduction efficiencies are shown in Figure 3-5. Catalyst performance averaged about 80 percent with the exception of a brief period during August when NH₃ flowrate was accidentally interrupted.

Figure 3-6 illustrates the catalyst outlet NH $_3$ recorded using continuous NO $_X$ analyzers as described in Appendix A. For the most part, NH $_3$ emissions throughout the test period were about 55 ppm at 15 percent 0 $_2$ (90 ppm as measured). Figures 3-7 and 3-8 illustrate trends in both CO and TUHC emissions. CO emissions showed a large variation from about 60 to 300 ppm (also corrected to 15 percent 0 $_2$). Changes in CO from average values of about 140 to 150 ppm recorded during the comprehensive tests may be attributed to surges in engine load recorded during some portion of the test period and small variations in air/fuel ratios and ambient temperatures. TUHC data were not obtained for much of the test period due to instrument malfunction. Available data indicate TUHC levels in the range of about 750 to 1,250 ppm (at 15 percent 0 $_2$) with no significant difference between the catalyst inlet and outlet locations.

REFERENCES FOR SECTION 3

- 3-1. "Protocol for the Collection and Analysis of Volatile POHC's Using VOST," EPA-600/8-84-007, NTIS PB84-170042, March 1984.
- 3-2. Waterland, L. R., et al., "Environmental Assessment of Industrial Boilers Firing Coal-Liquid Mixtures and Wood," in Proceedings of the 1982 Joint Symposium of Stationary Combustion NO_X Control, Volume II. EPA 600/9-85-022b, NTIS PB 85-235612, July 1985.
- 3-3. Castaldini, C. and L. R. Waterland, "Environmental Assessment of a Reciprocating Engine Retrofitted with Nonselective Catalytic Reduction," EPA 600/7-84-073a, NTIS PB84-224351, June 1984.
- 3-4. Lentzen, D. E., et al., "IERI-RTP Procedures Manual: Level 1 Environmental Assessement -- Second Edition," EPA-600/7-78-201, NTIS PB 293795, October 1978.

SECTION 4

QUALITY ASSURANCE ACTIVITIES

Specific quality assurance (QA) activities performed to determine the accuracy and precision of the measurements made in this test program included:

- ullet Performing EPA Method 7 certification tests to establish the accuracy of the NO_x continuous analyzers used in the tests
- Spiking a sample of cleaned XAD-2 resin with TCO, GRAV, and semivolatile priority pollutant compounds and analyzing the spiked resin to determine the accuracy (recovery) of the resin extraction and subsequent analyses
- Analyzing a blind spike sample for ammonia to determine the accuracy of the selective ion electrode analysis technique used
- Performing duplicate TCO and GC/MS injections on the SASS train
 XAD-2 extract to determine the precision of these measurements
 The following paragraphs discuss results of these QA activities.

4.1 NO_x CERTIFICATION RESULTS

EPA Method 7 tests were performed once during the 15-day continuous monitoring period, on August 2, 1984. The intent of the tests was to certify the NO_X analyzers by simultaneous measurement of emissions at the catalyst outlet. NO_X emissions by continuous monitors at the catalyst outlet measured between 330 and 550 ppm, dry (445 ppm average) at stack conditions of about

11 percent 02. By contrast, EPA Method 7 results obtained from 27 separate samples indicated NO_v levels between 40 and 370 ppm with an average value of about 132 ppm. During the same test period, visual observation of the SoCal NO_x monitoring instrumentation indicated NO_x in the range of 350 to 600 at the catalyst outlet, reflecting SCR NO_x reduction performance settings of 80 percent. These SoCal NO_x measurements using continuous monitors were generally in good agreement with emissions recorded by the Acurex monitors. Both SoCal and Acurex NO_x instrumentation consisted of Thermo-Electron Model 10 AR monitors equipped with molybdenum and stainless steel converters. The Acurex monitors (two were used as discussed in Appendix A) were calibrated at least twice daily with high (2750 ppm), low (190 ppm), and zero (nitrogen) certified span gases. SoCal and Acurex monitors were also found to be in relatively good agreement for catalyst inlet NO_x concentrations (less than 2 percent). In light of agreement between emissions obtained by SoCal and Acurex using continuous monitors, the EPA Method 7 results are deemed suspect. Therefore, results of the monitor certification tests are considered inconclusive.

4.2 SPIKED XAD-2 RESIN ANALYSES

After extraction of the XAD-2 field blank, the same resin was spiked with 10 mg bis(2-ethylhexyl)phthalate, 40 mg hexadecane, and 400 μ g each of naphthalene, phenanthrene, pyrene, and dodecane. Thus, this resin contained 41 mg TCO compounds (dodecane, hexadecane, and naphthalene), 51 mg GRAV compounds (the phthalate, phenanthrene, pyrene and hexadecane), and 400 μ g each of three polynuclear aromatics for the semivolatile organic priority pollutant analysis (hexadecane will respond in both the TCO and GRAV analyses).

TABLE 4-1. XAD-2 RESIN SPIKE AND RECOVERY RESULTS

Measurement	Spiked amount (mg)	Recovered amount (mg)	Percent recovery	Implied accuracy	Accuracy objective ^a
Total chromatographable organics (TCO)	41.0	29.0	71	-29	±50
Gravimetric organics (GRAV)	51.0	39.0	76	-24	±50
Semivolatile organic priority pollutants: Naphthalene Phenanthrene Pyrene Bis (2-ethylhexyl) phthalate	0.4 0.4 0.4 0.4	0.31 0.34 0.25 0.28	78 85 62	-22 -15 -38	
Average			70	-30	-50 +100

^aReference 4-1.

Results of the analyses of this spiked resin are shown in Table 4-1. As noted, the recovery of the TCO analysis was 71 percent, the GRAV analysis was 76 percent, and averaged 74 percent for the GC/MS analyses. If these are interpreted to be the accuracy of these measurements, all fall within the project accuracy objective (Reference 4-1) also noted in Table 4-1.

4.3 AMMONIA SPIKE SAMPLE ANALYSIS

An ammonia audit sample was prepared by adding a known amount of ammonium hydroxide to a volume of 0.1N HCl and submitted as a blind spike for analysis. The analysis result was 0.38 mg NH₃ per ml of solution, versus the spiked amount of 0.48 mg/ml. This implies an analytical accuracy of -21 percent.

4.4 DUPLICATE ORGANIC ANALYSES OF XAD-2 EXTRACT

The XAD-2 extract samples from the catalyst outlet SASS train for this test were analyzed in duplicate for TCO content, and for the semivolatile organic priority pollutants and other major peaks by GC/MS. The two TCO measures were 21 and 24 mg/train, giving a relative standard deviation of 9.4 percent. This is within the precision objective of this measurement of 10 percent (Reference 4-1).

Results of the duplicate GC/MS injections are summarized in Table 4-2. The relative standard deviations for all compounds quantitated were well within the project precision objective of 50 percent for this measurement.

TABLE 4-2. DUPLICATE GC/MS ANALYSIS RESULTS FOR THE CATALYST OUTLET XAD-2 EXTRACT

Compound	Run 1 (µg/train)	Run 2 (µg/train)	Relative standard deviation (percent)
Naphthalene Di-n-butyl phthalate Bis (2-ethylhexyl) phthalate	10	10	0
	160	120	20.2
	30	20	28.3

REFERENCE FOR SECTION 4

4-1. "Quality Assurance Plan for the Combustion Modification Environmental Assessment," Acurex Corporation under EPA Contract 68-02-2160, September 10, 1982.

SECTION 5

SUMMARY

Field tests were performed in a lean-burn 1,500-kW (2,000-hp) reciprocating internal combustion engine retrofitted with an ammonia-based selective catalytic reduction (SCR) system for NO_X reduction. Two series of tests were performed: a comprehensive test program to characterize catalyst inlet and outlet exhaust gas composition at a catalyst NO_X reduction performance target of 80 percent; and a 15-day exhaust monitoring program to measure the catalyst performance under typical engine operation. Prior to the test period, problems were experienced with the NH3 control system, specifically, the NO_X analyzer and also the NH3 control valve.

 ${
m NO}_{
m X}$ emission reduction during the 1-day comprehensive tests was maintained relatively constant at about 80 percent using an NH3/NO molar ratio of about 1.0. Catalyst inlet ${
m NO}_{
m X}$ levels from the four-stroke turbocharged engine ranged between 2,200 and 2,600 ppm as measured at about 11 percent excess ${
m O}_{
m Z}$. At the catalyst outlet, ${
m NO}_{
m X}$ ranged from 330 to 560 ppm. NH3 carryover measured at the catalyst outlet ranged between 65 and 120 ppm (about 80 ppm average) using an extractive sampling system. Continuous monitoring techniques suggested NH3 carryover levels in the range of 20 to 140 ppm (about 80 ppm average). Other emission measurements suggest relatively minor effects of the catalyst on CO and particulate emissions. Total cyanides increased from about 7 ${
m \mu g/dscm}$ to 2.4 ${
m mg/dscm}$ across the

catalyst. Total organics (C_{7+}) decreased about 70 percent from 4.9 mg/dscm to 1.5 mg/dscm. Analyses for volatile organics showed benzene and toluene as the major compounds with catalyst outlet gas concentrations of about 920 and 250 μ g/dscm, respectively. Semivolatile organic analyses showed a general decrease of PAH compounds (naphthalene and phenanthrene) across the catalyst. Outlet concentrations of these and other organics were generally below 0.4 μ g/dscm (1.6 μ g/Bhp-hr).

During the extended 15-day continuous monitoring of criteria gas emissions, catalyst NO_X reduction performance was maintained at about 80 percent. Brief periods of reduced catalytic performance were attributed to engine load surges and an occasional malfunction in the NH3 injection flowrate. NH3 carryover emissions at the catalyst outlet ranged from 0 to about 150 ppm. Overall, the SCR system tested was found capable of maintaining 80 percent NO_X reduction with no significant environmental impact apart from NH3 carryover of generally less than 100 ppm and cyanide formation to 1.3 ppm.

APPENDIX A

SAMPLING AND ANALYSIS METHODS

Emissions test equipment was provided by Acurex Corporation. Onsite equipment included a continuous monitoring system for emissions measurements of gaseous criteria pollutants; the SASS train for particulate mass, semivolatile and nonvolatile organics; a VOST train by volatile organics; two separate sampling trains for NH3 and HCN measurement; gas grab sampling equipment for determining N2O emissions by laboratory gas chromatography, and for validation of NO $_{\rm X}$ measurements with EPA Method 7. The following sections summarize the sampling and analysis equipment and methods used in the field and laboratory.

A.1 CONTINUOUS MONITORING SYSTEM

Acurex provided a continuous monitoring system modified to allow online simultaneous NO, NO $_{\rm X}$, and NH $_{\rm 3}$ sampling capability alternatively at the inlet and outlet of the catalytic reactor. Figure A-1 illustrates a simplified schematic of the gas conditioning and monitoring system. The monitoring capability included O $_{\rm 2}$, CO $_{\rm 2}$, CO (high and low concentrations), NO, NO $_{\rm X}$, NO $_{\rm X}$ + NH $_{\rm 3}$, and TUHC. The heated sample gas was treated for moisture removal using a permeation dryer. Simultaneous sampling of NO, NO $_{\rm X}$, and NH $_{\rm 3}$ was achieved by using two chemiluminescent analyzers. One was equipped with an unheated molybdenum converter to prevent conversion of NH $_{\rm 3}$ to NO in the sample gas and one was equipped with a standard heated stainless-steel converter to convert

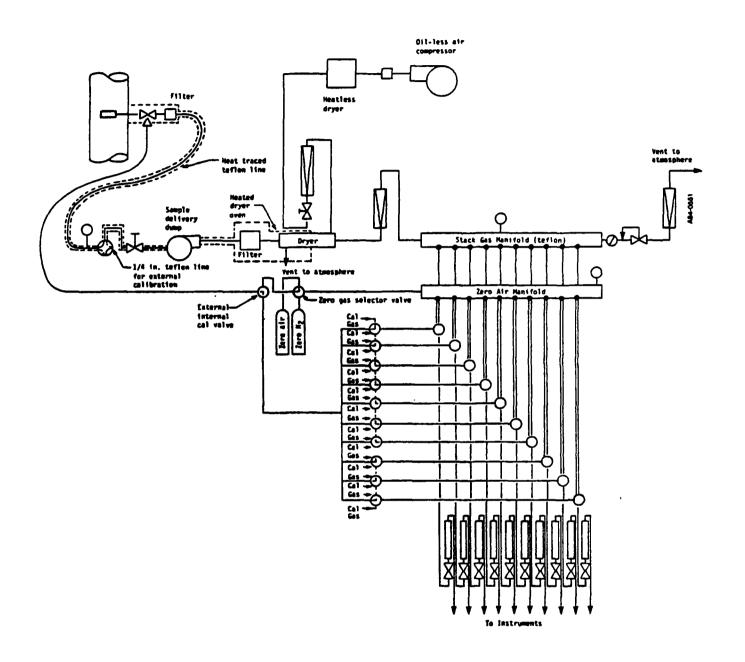


Figure A-1. Schematic for continuous extractive sampling system.

both NO₂ and NH₃ to NO. NH₃ emissions were calculated using the difference in readings between the two analyzers. Table A-1 lists the instrumentation constituting the continuous monitoring and flue gas extractive sampling system. A datalogger was used in addition to strip charts to record data continuously.

A.2 SEMIVOLATILE AND NONVOLATILE ORGANIC EMISSIONS

Emissions of semivolatile and nonvolatile organics were sampled using the source assessment sampling system (SASS). Designed for Level 1 environmental assessment (Reference A-1), the SASS collects large quantities of gas and solid samples required for subsequent analyses of inorganic and organic emissions.

The SASS, illustrated in Figure A-2, is generally similar to the system utilized for total particulate mass emission tests (a high volume Method 5 train) with the exception of:

- The addition of a gas cooler and organic sampling module
- The addition of necessary vacuum pumps to allow a sampling rate of
 2 1/s (4 cfm)

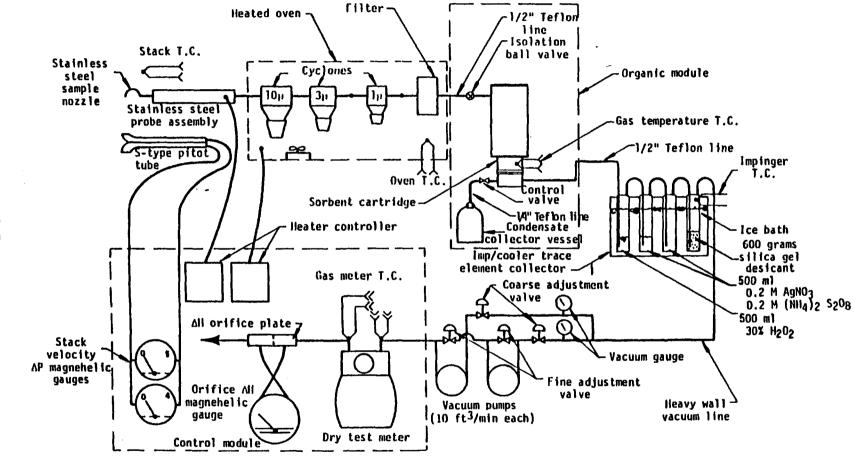
Particulate cyclones shown in Figure A-2 were not used for these tests because of low particulate loading in the flue gas.

Schematics outlining the standard sampling and analytical procedures using the SASS equipment are presented in Figures A-3 and A-4. The following paragraphs briefly describe analytical procedures used in measuring organic emissions.

Quantitative information on total organic emissions was obtained by gas chromatography/flame ionization detector for total chromatographable organics (TCO) and by gravimetry (GRAV) of sample extracts. Infrared spectroscopy

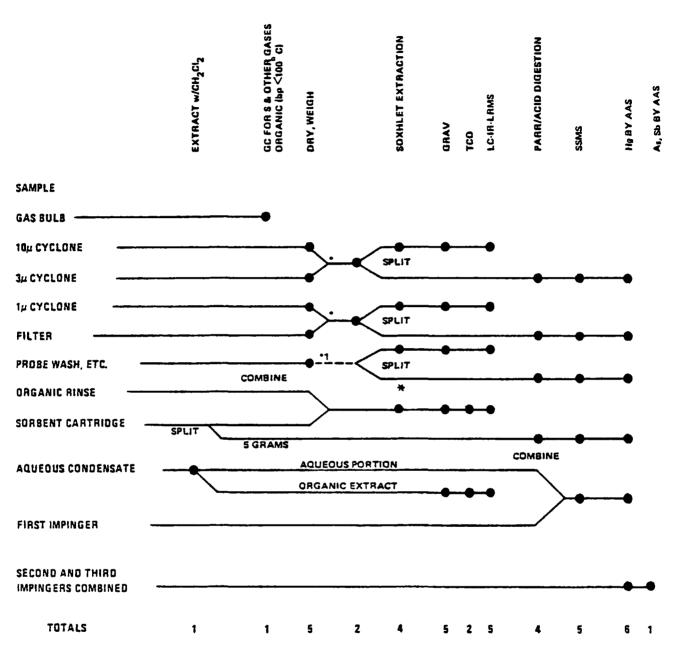
TABLE A-1. CONTINUOUS MONITORING EQUIPMENT IN THE MOBILE LABORATORY

Instrument	Principle of Operation	Manufacturer	Instrument Model	Range
NO NO _X	Chemiluminescence	Thermo Electron	10 AR	0 to 2.5 ppm 0 to 10 ppm 0 to 25 ppm 0 to 100 ppm 0 to 250 ppm 0 to 1,000 ppm 0 to 2,500 ppm 0 to 10,000 ppm
CO (1)	Nondispersive infrared (NDIR)	ANARAD	500R	0 to 1,000 ppm
CO (2)	Nondispersive infrared (NDIR)	ANARAD	500R	0 to 1.0 percent (10,000 ppm)
co ₂	Nondispersive infrared (NDIR)	ANARAD	AR500	O to 20 percent
S0 ₂	Pulsed Fluorescence	Thermo Electron	40	0 to 100 ppm 0 to 1,000 ppm 0 to 5,000 ppm 0 to 10,000 ppm
02	Fuel cell	Teledyne		0 to 5 percent 0 to 10 percent 0 to 25 percent
тинс	Flame ionization detection (FID)	Beckman	400	0 to 500 ppm
Datalogger	Electronic	Acurex/ Autodata	10	99 channels
Sample gas conditioner	Permeation dryer	Permapure	E-4G-SS	10 scfm
Strip chart recorders	Dual pen analog	Linear	400	0 to 10 mV 0 to 100 mV 0 to 1V 0 to 10V



Note: T.C. = Thermocouple

Figure 'A-2. Source assessment sampling train schematic.



^{*} If required, sample should be set aside for biological analysis at this point.

Figure A-3. Flue gas analysis protocol for SASS samples.

This step is required to define the total mass of particulate catch. If the sample exceeds 10% of the total cyclone and filter sample weight proceed to analysis. If the sample is less than 10% of the catch, hold in reserve,

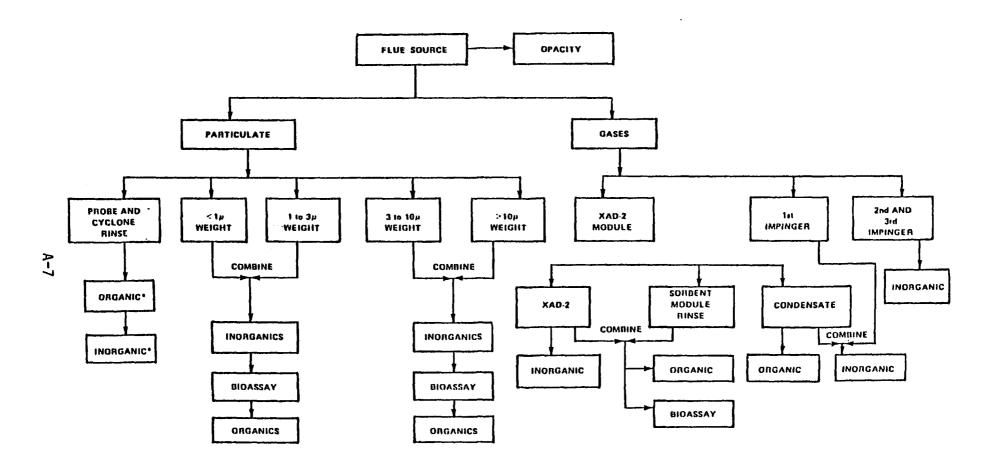


Figure A-4. Flue gas sample analysis protocol.

(IR) and gas chromatography/mass spectroscopy (GC/MS) were used for identification of organic functional groups and for determining polycyclic organic matter (POM) and other organic species concentrations (the semivolatile organic priority pollutants) in extract samples. Figure A-5 illustrates the organic analysis methodology used.

Passivation of the SASS train with 15 percent by volume HNO₃ solution was performed prior to equipment preparation and sampling to produce biologically inert surfaces. Detailed descriptions of equipment preparation, sampling procedures, and sample recovery are discussed in Reference A-1 and will not be repeated here.

A.3 VOLATILE ORGANIC EMISSIONS

A volatile organic sampling train (VOST), shown schematically in Figure A-6, was used to measure the low molecular weight volatile organic compounds (boiling points $\leq 110^{\circ}\text{C}$) in the flue gas according to the EPA protocol (Reference A-2). The train consists of two organic sorbent traps connected in series. The first trap contained $\sim 1.6g$ of the porous polymer Tenax-GC; 35/60 mesh. The second trap consisted of $\sim 1.0g$ each of Tenax-GC and petroleum-based charcoal. Prior to their use in the field, each trap was conditioned to remove organic compounds. Conditioning consisted of baking each trap at 190°C with a N_2 purge for an 8-hr period. The traps were then desorbed at 190°C directly into a GC/FID. If a trap showed no contaminant peaks greater than 20 ng as benzene or toluene, it was considered ready for sampling. The trap was then sealed at each end with compression fittings, placed in clean, muffled culture tubes, and sealed in a metal can for shipping.

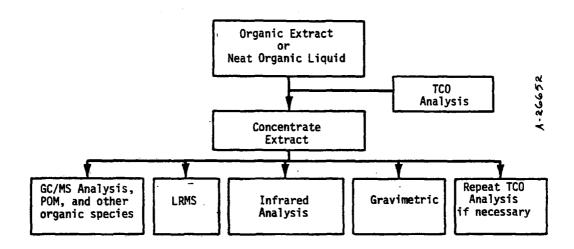


Figure A-5. Organic analysis methodology.

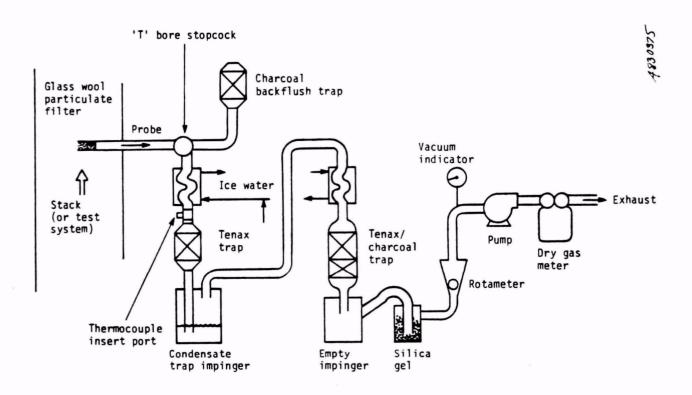


Figure A-6. Schematic of volatile organic sampling train (VOST).

Before the field testing, the entire system was leak-checked at ~15 to 20-in. of vacuum. A leakage rate of 0.05 liter/min was considered acceptable. Ambient air was drawn through a charcoal-filled tube to prevent organic contamination while bringing the system back to ambient pressure.

One set of samples and a field blank were obtained for the test program. The gas sample was obtained at the catalyst outlet (stock) location. A total sample volume of 20 1 was taken over a 40-min period (0.5 1/min). Upon completion of the test, the sample traps were removed from the train, sealed, returned to their original culture tubes, and stored in a metal can on ice. The VOST samples were analyzed by GC/MS according to the EPA VOST protocol. Each pair of traps used was thermally desorbed and analyzed for the EPA Method 624 (volatile) priority pollutants.

A.4 NH3 AND HCN SAMPLING AND ANALYSIS

NH₃ and HCN were measured at the inlet and outlet locations of the catalytic converter utilizing two separate sampling trains. Both trains were similar to an EPA Method 6 train except that impinger solutions for NH₃ absorption were acid based (0.1N HCl) and for HCN were caustic based (0.1N NaOH) Concentrations of NH₃ and HCN in solutions were determined in the laboratory using approved wet chemical methods (HCN) of by specific ion electrode (NH₃) (Reference A-2).

A.5 N₂O SAMPLING AND ANALYSIS

The stack gas grab samples were extracted into stainless-steel cylinders for laboratory analysis for N₂O using a sampling train illustrated in Figure A-7. For analysis each sample cylinder was externally heated to 120°C (250°F), then a 1-ml sample was withdrawn with a gas-tight syringe for injection into the gas chromatograph (GC) equipped with an electron capture

Figure A-7. N₂0 sampling system.

detector (ECD). The GC column used was a 10 ft x 1/8 in. stainless-steel column packed with 80/100 mesh chromosorb 101. The flow of nitrogen was 20 ml/min with the column kept at 45°C. Elution time for N_20 was approximately 5 min.

A.6 NO_X MONITOR CERTIFICATION SAMPLING AND ANALYSIS

Certification of the continuous ${\rm NO}_{\rm X}$ monitor was performed using the standard EPA Method 7 equipment and protocols.

REFERENCES FOR APPENDIX A

- A-1. Lentzen, D. E., et al., "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201, NTIS PB293795, October 1978.
- A-2. "Protocol for the Collection and Analysis of Volatile POHC's Using VOST," EPA-600/8-84-007, NTIS PB84-170042 March 1984.
- A-3. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, NTIS PB 297 686, March 1979.

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15-day continuous emission monitoring for a 1,500 kW (2000 hp) gas-fired, four-stroke turbocharged reciprocating engine equipped with an ammonia-based selective catalytic reduction system for NOx control. Emission reductions were held at about 80% using an ammonia/NO ratio of about 1.0. NOx levels at the catalyst inlet ranged from 2,200 to 2,600 ppm at an exhaust gas oxygen level of about 11%. NOx levels at the catalyst outlet ranged from 65 to 120 ppm. The catalyst had relatively minor effect on CO and particulate emissions, but increased total cyanides by 3 orders of magnitude (from 7 micrograms/dscm to 2.4 mg/dscm) across the catalyst. Total organics decreased about 70%, from 4.9 to 1.5 mg/dscm. Analyses showed benzene and toluene as the major organic constituents in the catalyst exhaust. Polycyclic aromatics also decreased across the catalyst. The 15-day continuous monitoring tests showed that the catalyst was generally able to maintain NOx reductions at about 80%. Departures from these levels occurred only during brief load surges and ammonia flowrate spikes.

7. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS		b.IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group		
Pollution	Ammonia	Pollution Control	13B		
Assessments Nitrogen Oxides		Stationary Sources	14B		
Reciprocating Engi	nes	Environmental Assess-	21G		
Gas Engines		ment			
Catalysis		Selective Catalytic Re-	07D		
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