

# Environmental Technology Verification Report

BACHARACH  
MODEL ECA 450  
PORTABLE EMISSION ANALYZER

Prepared by



Battelle

Under a cooperative agreement with



ETV ✓ ETV ✓ ETV ✓

September 2000

# **Environmental Technology Verification Report**

ETV Advanced Monitoring Systems Center

## **Bacharach Model ECA 450 Portable Emission Analyzer**

By

Thomas Kelly  
Ying-Liang Chou  
Charles Lawrie  
James J. Reuther  
Karen Riggs

Battelle  
Columbus, Ohio 43201

## **Notice**

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency and recommended for public release. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

## Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development (ORD) provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA, to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permittees, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification Organizations oversee and report verification activities based on testing and Quality Assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. At present, there are twelve environmental technology areas covered by ETV. Information about each of the environmental technology areas covered by ETV can be found on the Internet at <http://www.epa.gov/etv.htm>.

Effective verifications of monitoring technologies are needed to assess environmental quality, and to supply cost and performance data to select the most appropriate technology for that assessment. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support to plan, coordinate, and conduct such verification tests, for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at [http://www.epa.gov/etv/07/07\\_main.htm](http://www.epa.gov/etv/07/07_main.htm).

## **Acknowledgments**

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. In particular we recognize Brian Canterbury, Paul Webb, Darrell Joseph, and Jan Satola of Battelle, and David D'Amico and Edward Kosol of Bacharach, Inc.

## Contents

Notice .....	ii
Foreword .....	iii
Acknowledgments .....	iv
List of Abbreviations .....	x
1. Background .....	1
2. Technology Description .....	2
3. Test Design and Procedures .....	3
3.1 Introduction .....	3
3.2 Laboratory Tests .....	4
3.2.1 Linearity .....	6
3.2.2 Detection Limit .....	7
3.2.3 Response Time .....	7
3.2.4 Interrupted Sampling .....	7
3.2.5 Interferences .....	7
3.2.6 Pressure Sensitivity .....	8
3.2.7 Ambient Temperature .....	9
3.3 Combustion Source Tests .....	10
3.3.1 Combustion Sources .....	10
3.3.2 Test Procedures .....	11
4. Quality Assurance/Quality Control .....	15
4.1 Data Review and Validation .....	15
4.2 Deviations from the Test/QA Plan .....	15
4.3 Calibration of Laboratory Equipment .....	17
4.4 Standard Certifications .....	17
4.5 Performance System Audits .....	18
4.5.1 Technical Systems Audit .....	18
4.5.2 Performance Evaluation Audit .....	18
4.5.3 Audit of Data Quality .....	19

5. Statistical Methods .....	21
5.1 Laboratory Tests .....	21
5.1.1 Linearity .....	21
5.1.2 Detection Limit .....	22
5.1.3 Response Time .....	23
5.1.4 Interrupted Sampling .....	23
5.1.5 Interferences .....	23
5.1.6 Pressure Sensitivity .....	24
5.1.7 Ambient Temperature .....	24
5.2 Combustion Source Tests .....	25
5.2.1 Accuracy .....	25
5.2.2 Zero/Span Drift .....	25
5.2.3 Measurement Stability .....	25
5.2.4 Inter-Unit Repeatability .....	26
5.2.5 Data Completeness .....	26
6. Test Results .....	27
6.1 Laboratory Tests .....	27
6.1.1 Linearity .....	27
6.1.2 Detection Limit .....	30
6.1.3 Response Time .....	30
6.1.4 Interrupted Sampling .....	31
6.1.5 Interferences .....	32
6.1.6 Pressure Sensitivity .....	33
6.1.7 Ambient Temperature .....	35
6.1.8 Zero/Span Drift .....	37
6.2 Combustion Source Tests .....	38
6.2.1 Relative Accuracy .....	38
6.2.2 Zero/Span Drift .....	41
6.2.3 Measurement Stability .....	43
6.2.4 Inter-Unit Repeatability .....	43
6.3 Other Factors .....	47
6.3.1 Cost .....	47
6.3.2 Data Completeness .....	47
6.3.3 Maintenance/Operational Factors .....	47

7. Performance Summary .....	48
8. References .....	50

### Figures

2-1. Bacharach ECA 450 .....	2
3-1. Manifold Test Setup .....	6
6-1. Plot of NO Linearity Data .....	29

### Tables

3-1. Identity and Schedule of Tests Conducted on Bacharach Model ECA 450 Analyzers ...	3
3-2. Summary of Interference Tests Performed .....	8
3-3. Span Concentrations Provided Before and After Each Combustion Source .....	13
4-1. Results of QC Procedures for Reference Analyzers for Testing Bacharach Model ECA 450 Analyzers .....	16
4-2. Equipment Type and Calibration Date .....	17
4-3. Performance Evaluation Results on NO/NO <sub>2</sub> Standards .....	20
4-4. Performance Evaluation Results on O <sub>2</sub> and Temperature Measuring Equipment .....	20
6-1a. Data from NO Linearity Test of Bacharach Model ECA 450 Analyzers .....	27
6-1b. Data from NO <sub>2</sub> Linearity Test of Bacharach Model ECA 450 Analyzers .....	28
6-2. Statistical Results for Test of Linearity .....	28
6-3. Estimated Detection Limits for Bacharach Model ECA 450 Analyzers .....	30
6-4. Response Time Data for Bacharach Model ECA 450 Analyzers .....	31
6-5. Response Time Results for Bacharach Model ECA 450 Analyzers .....	31
6-6. Data from Interrupted Sampling Test with Bacharach Model ECA 450 Analyzers ....	32



6-7.	Pre- to Post-Test Differences as a Result of Interruption of Operation of Bacharach Model ECA 450 Analyzers .....	32
6-8.	Data from Interference Tests on Bacharach Model ECA 450 Analyzers .....	33
6-9.	Results of Interference Tests of Bacharach Model ECA 450 Analyzers .....	33
6-10.	Data from Pressure Sensitivity Test for Bacharach Model ECA 450 Analyzers .....	34
6-11.	Pressure Sensitivity Results for Bacharach Model ECA 450 Analyzers .....	35
6-12.	Data from Ambient Temperature Test of Bacharach Model ECA 450 Analyzers .....	36
6-13.	Ambient Temperature Effects on Bacharach Model ECA 450 Analyzers .....	36
6-14.	Data from Linearity and Ambient Temperature Tests Used to Assess Zero and Span Drift of the Bacharach Model ECA 450 Analyzers .....	37
6-15.	Zero and Span Drift Results for the Bacharach Model ECA 450 Analyzers .....	37
6-16a.	Data from Gas Rangetop in Verification Testing of Bacharach Model ECA 450 Analyzers .....	39
6-16b.	Data from Gas Water Heater in Verification Testing of Bacharach Model ECA 450 Analyzers .....	39
6-16c.	Data from Diesel Generator at High RPM in Verification Testing of Bacharach Model ECA 450 Analyzers .....	40
6-16d.	Data from Diesel Generator at Idle in Verification Testing of Bacharach Model ECA 450 Analyzers .....	40
6-17.	Relative Accuracy of Bacharach Model ECA 450 Analyzers .....	41
6-18.	Data Used to Assess Zero and Span Drift for Bacharach Model ECA 450 Analyzers on Combustion Sources .....	42
6-19.	Results of Zero and Span Drift Evaluation for Bacharach Model ECA 450 Analyzers .....	43
6-20.	Data from Extended Sampling Test with Diesel Generator at Idle, Using Bacharach Model ECA 450 Analyzers .....	44

6-21. Results of Evaluation of Measurement Stability for Bacharach Model ECA 450 Analyzer .....	46
6-22. Summary of Repeatability .....	46

## List of Abbreviations

AMS	Advanced Monitoring Systems
ANSI	American National Standards Institute
Btu/hr	British thermal unit per hour
ccm	cubic centimeter per minute
CEM	continuous emission monitoring
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FID	flame ionization detector
gpm	gallons per minute
kW	kilowatt
LOD	limit of detection
lpm	liters per minute
m <sup>3</sup>	cubic meters
NH <sub>3</sub>	anhydrous ammonia
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO <sub>x</sub>	nitrogen oxides
NO <sub>2</sub>	nitrogen dioxide
O <sub>2</sub>	oxygen
PE	performance evaluation
ppm	parts per million, volume
ppmC	parts per million carbon
QA	quality assurance
QC	quality control
QMP	Quality Management Plan
RPM	revolutions per minute
SAS	Statistical Analysis System
SO <sub>2</sub>	sulfur dioxide
UHP	ultra-high purity

---

## **Chapter 1 Background**

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high quality, peer reviewed data on technology performance to those involved in the design, distribution, permitting, purchase and use of environmental technologies.

ETV works in partnership with recognized testing organizations, stakeholder groups consisting of regulators, buyers and vendor organizations, and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center has recently evaluated the performance of portable nitrogen oxides monitors used to determine emissions from combustion sources. This verification statement provides a summary of the test results for the Bacharach Model ECA 450 portable emission analyzer.

---

## Chapter 2 Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water and soil. This verification report provides results for the verification testing of the Bacharach Model ECA 450 portable electrochemical emission analyzer. The following description of the Bacharach ECA 450 analyzer is based on information provided by the vendor.

The ECA 450 is a portable, microprocessor-controlled emission analyzer using electrochemical sensors. The ECA 450 can be fitted with up to seven separate gas sensors to measure oxygen, carbon monoxide (2 ranges), oxides of nitrogen (NO and NO<sub>2</sub>), sulfur dioxide, and hydrocarbons. Only NO and NO<sub>2</sub> measurements were verified in the test reported here.

The ECA 450 measures 18" x 14.5" x 10" and weighs 25 pounds. An on-board printer permits printing hard copy of gas parameters; up to 1,000 data points can be stored internally. An RS232 interface provides the option to send the data to a computer. An optional sample conditioning system that includes a probe with a heated sample line and a Peltier cooler/moisture removal system is available and was used in these verification tests. The conditioning system is recommended for sampling NO, NO<sub>2</sub> and SO<sub>2</sub>. A large vacuum fluorescent display screen displays the gas parameters being measured in real time.



**Figure 2-1. Bacharach ECA 450 Analyzer**

---

## Chapter 3 Test Design and Procedures

### 3.1 Introduction

The verification test described in this report was conducted in April and May, 2000. The test was conducted at Battelle in Columbus, Ohio, according to procedures specified in the *Test/QA Plan for Verification of Portable NO/NO<sub>2</sub> Emission Analyzers*.<sup>(1)</sup> Verification testing of the analyzers involved the following tests:

1. A series of laboratory tests in which certified NO and NO<sub>2</sub> standards were used to challenge the analyzers over a wide concentration range under a variety of conditions.
2. Tests using three realistic combustion sources, in which data from the analyzers undergoing testing were compared to chemiluminescent NO and NO<sub>x</sub> measurements made following the guidelines of EPA Method 7E.<sup>(2)</sup>

The schedule of tests conducted on the Bacharach ECA 450 analyzers is shown in Table 3-1.

**Table 3-1. Identity and Schedule of Tests Conducted on Bacharach Model ECA 450 Analyzers**

<b>Test Activity</b>	<b>Date Conducted</b>
Laboratory Tests	
Linearity	April 17, a.m., and 19, a.m., 2000
Interrupted Sampling	April 17, p.m. – April 18, a.m.
Interferences	April 18, a.m.
Pressure Sensitivity	April 18, a.m.
Ambient Temperature	April 18, p.m.
Combustion Source Tests	
Gas Rangetop	May 1, a.m.
Gas Water Heater	May 2, a.m.
Diesel Generator–High RPM	May 2, a.m.
Diesel Generator–Idle	May 2, p.m.

---

To assess inter-unit variability, two identical Bacharach Model ECA 450 analyzers were tested simultaneously. These two analyzers were designated as Unit A and Unit B throughout all testing. The commercial analyzers were operated at all times by a representative of Bacharach so that each analyzer's performance could be assessed without concern about the familiarity of Battelle staff with the analyzers. At all times, however, the Bacharach representative was supervised by Battelle staff. Displayed NO and NO<sub>2</sub> readings from the analyzers (in ppm) were manually entered onto data sheets prepared before the test by Battelle. Battelle staff filled out corresponding data sheets, recording, for example, the challenge concentrations or reference analyzer readings, at the same time that the analyzer operator recorded data. This approach was taken because visual display of measured NO and NO<sub>2</sub> (or NO<sub>x</sub>) concentrations was the "least common denominator" of data transfer among several NO/NO<sub>2</sub> analyzers tested.

Verification testing began with Bacharach staff setting up and checking out their two analyzers in the laboratory at Battelle. Once vendor staff were satisfied with the operation of the analyzers, the laboratory tests were begun. These tests were carried out in the order specified in the test/QA plan.<sup>(1)</sup> However, the NO linearity test was redone after other laboratory tests were completed, because of concern about flow rates used in the initial test. The start of source testing was delayed due to failure of a reference analyzer. That testing took place in a nearby building where the combustion sources described below were set up, along with two chemiluminescent nitrogen oxides monitors which served as the reference analyzers. The combustion source tests were conducted indoors, with the gas combustion source exhausts vented through the roof of the test facility. The diesel engine was located immediately outside the wall of the test facility; sampling probes ran from the analyzers located indoors through the wall to the diesel exhaust duct. This arrangement assured that testing was not interrupted and that no bias in testing was introduced as a result of the weather. Sampling of source emissions began with the combustion source emitting the lowest NO<sub>x</sub> concentration and proceeded to sources emitting progressively more NO<sub>x</sub>. In all source sampling, the analyzers being tested sampled the same exhaust gas as did the reference analyzers. This was accomplished by inserting the Bacharach analyzers' gas sampling probes into the same location in the exhaust duct as the reference analyzers' probe.

### **3.2 Laboratory Tests**

The laboratory tests were designed to challenge the analyzers over their full nominal response ranges, which for the Bacharach Model ECA 450 analyzers were 0 to 3,000 ppm for NO and 0 to 500 ppm for NO<sub>2</sub>. These nominal ranges greatly exceed the actual NO or NO<sub>2</sub> concentrations likely to be emitted from most combustion sources. Nevertheless, the laboratory tests were aimed at quantifying the full range of performance of the analyzers.

Laboratory tests were conducted using certified standard gases for NO and NO<sub>2</sub>, and a gas dilution system with flow calibrations traceable to the National Institute of Standards and Technology (NIST). The NO and NO<sub>2</sub> standards were diluted in high purity gases to produce a range of accurately known concentrations. The NO and NO<sub>2</sub> standards were EPA Protocol 1 gases, obtained from Scott Specialty Gases, of Troy, Michigan. As required by the EPA Protocol<sup>(3)</sup> the concentration of these gas standards was established by the manufacturer within 1% accuracy using two independent analytical methods. The concentration of the NO standard

---

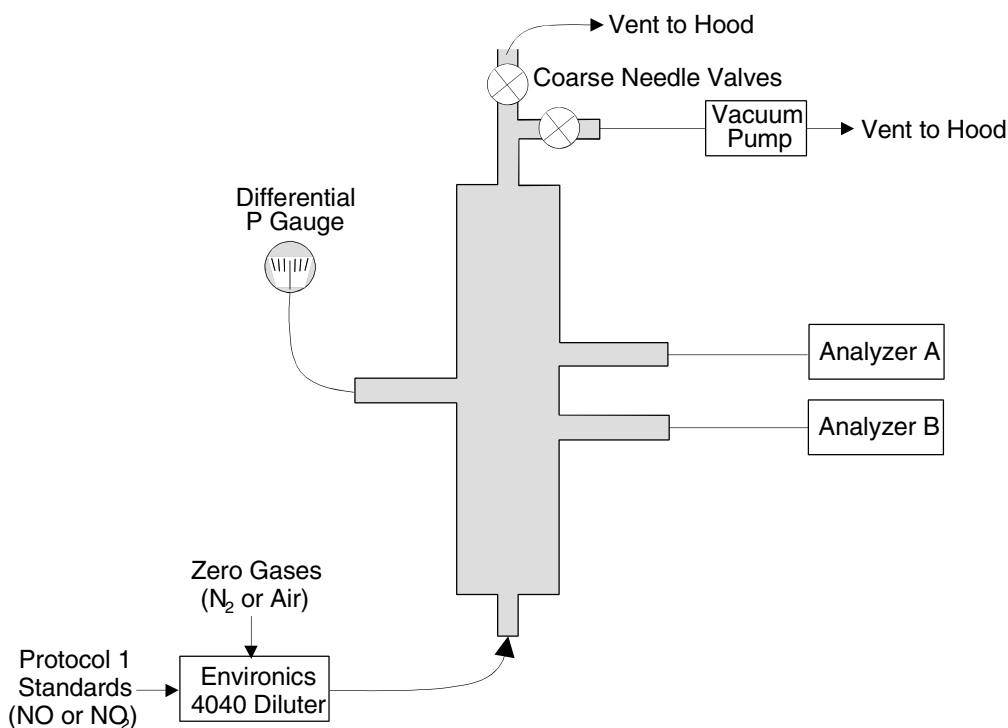
(Scott Cylinder Number ALM 057210) was 3,925 ppm, and that of the NO<sub>2</sub> standard (Scott Cylinder Number ALM 031907) was 512 ppm. These standards were identical to NO and NO<sub>2</sub> standard cylinders used in the combustion source tests, which were confirmed near the end of the verification test by comparison with independent standards obtained from other suppliers.

The gas dilution system used was an Environics Model 4040 mass flow controlled diluter (Serial Number 2469). This diluter incorporated four separate mass flow controllers, having ranges of 10, 10, 1, and 0.1 lpm, respectively. This set of flow controllers allowed accurate dilution of gas standards over a very wide range of dilution ratios, by selection of the appropriate flow controllers. The mass flow calibrations of the controllers were checked against a NIST standard by the manufacturer prior to the verification test, and were programmed into the memory of the diluter. In verification testing, the Protocol Gas concentration, inlet port, desired output concentration, and desired output flow rate were entered by means of the keypad of the personal computer used to operate the 4040 diluter, and the diluter then set the required standard and diluent flow rates to produce the desired mixture. The 4040 diluter indicated on the computer display the actual concentration being produced, which in some cases differed very slightly from the nominal concentration requested. In all cases the actual concentration produced was recorded as the concentration provided to the analyzers undergoing testing. The 4040 diluter also provided warnings if a flow controller was being operated at less than 10% of its working range, i.e., in a flow region where flow control errors might be enhanced. Switching to another flow controller then minimized the uncertainties in the preparation of the standard dilutions.

Dilution gases used in the laboratory tests were Acid Rain CEM Zero Air and Zero Nitrogen from Scott Specialty Gases. These gases were certified to be of 99.9995% purity, and to have the following maximum content of specific impurities: SO<sub>2</sub> < 0.1 ppm, NO<sub>x</sub> < 0.1 ppm, CO < 0.5 ppm, CO<sub>2</sub> < 1 ppm, total hydrocarbons < 0.1 ppm, and water < 5 ppm. In addition the nitrogen was certified to contain less than 0.5 ppm of oxygen, while the air was certified to contain 20 to 21% oxygen.

Laboratory testing was conducted primarily by supplying known gas mixtures to the analyzers from the Environics 4040 diluter, using a simple manifold that allowed the two analyzers to sample the same gas. The experimental setup is shown schematically in Figure 3-1. The manifold itself consisted of a 9.5-inch length of thin-walled 1-inch diameter 316 stainless steel tubing, with 1/4-inch tubing connections on each end. The manifold had three 1/4-inch diameter tubing side arms extending from it: two closely spaced tubes are the sampling points from which sample gas was withdrawn by the two analyzers, and the third provided a connection for a Magnehelic differential pressure gauge ( $\pm 15$  inches of water range) that indicated the manifold pressure relative to the atmospheric pressure in the laboratory. Gas supplied to the manifold from the Environics 4040 diluter always exceeded by at least 0.5 lpm the total sample flow withdrawn by the two analyzers. The excess vented through a "T" connection on the exit of the manifold, and two coarse needle valves were connected to this "T," as shown in Figure 3-1. One valve controlled the flow of gas out the normal exit of the manifold, and the other was connected to a small vacuum pump. Closing the former valve elevated the pressure in the manifold, and opening the latter valve reduced the pressure in the manifold. Adjustment of these two valves allowed close





**Figure 3-1. Manifold Test Setup**

control of the manifold pressure within a target range of  $\pm 10$  inches of water, while maintaining excess flow of the gas mixtures to the manifold. The arrangement shown in Figure 3-1 was used in all laboratory tests, with the exception of interference testing. For most interference testing, gas standards of the appropriate concentrations were supplied directly to the manifold, without use of the EnviroNics 4040 diluter.

Laboratory testing consisted of a series of separate tests evaluating different aspects of analyzer behavior. The procedures for those tests are described below, in the order in which the tests were actually conducted. The statistical procedures that were applied to the data from each test are presented in Chapter 5 of this report. Before starting the series of laboratory tests, the ECA 450 analyzers were calibrated with 500 ppm NO and with 150 ppm NO<sub>2</sub>, prepared by diluting the EPA Protocol Gases using the EnviroNics 4040 diluter.

### 3.2.1 Linearity

Linearity testing consisted of a wide-range 21-point response check for NO and for NO<sub>2</sub>. At the start of this check, the ECA 450 analyzers sampled the appropriate zero gas and then an NO or NO<sub>2</sub> concentration near the respective nominal full scale of the analyzers (i.e., near 3,000 ppm NO or 500 ppm NO<sub>2</sub>). The actual concentrations were 3,000 ppm NO and 450 ppm NO<sub>2</sub>. The 21-point check then proceeded without any adjustments to the analyzers. The 21 points consisted of three replicates each at 10, 20, 40, 70, and 100% of the nominal range, in randomized order, and interspersed with six replicates of zero gas.<sup>(1)</sup> Following completion of all 21 points, the zero

---

and 100% spans were repeated, also without adjustment of the analyzers. This entire procedure was performed for NO and then for NO<sub>2</sub>. Throughout the linearity test, the analyzer indications of both NO and NO<sub>2</sub> concentrations were recorded, even though only NO or NO<sub>2</sub> was supplied to the analyzers. This procedure provided data to assess the cross-sensitivity to NO and NO<sub>2</sub>.

### ***3.2.2 Detection Limit***

Data from zero gas and from 10% of full-scale points in the linearity test were used to establish the NO and NO<sub>2</sub> detection limits of the analyzers, using a statistical procedure defined in the test/QA plan.<sup>(1)</sup>

### ***3.2.3 Response Time***

During the NO and NO<sub>2</sub> linearity tests, upon switching from zero gas to an NO or NO<sub>2</sub> concentration of 70 to 80% of the respective full scale (i.e., about 2,400 ppm NO or 350 ppm NO<sub>2</sub>), the analyzers' responses were recorded at 10-second intervals until fully stabilized. These data were used to determine the response times for NO and for NO<sub>2</sub>, defined as the time to reach 95% of final response after switching from zero gas to the calibration gas.

### ***3.2.4 Interrupted Sampling***

After the zero and span checks that completed the linearity test, the ECA 450 analyzers were shut down (i.e., their electrical power was turned off overnight), ending the first day of laboratory testing. The next morning the analyzers were powered up, and the same zero gas and span concentrations were run without adjustment of the analyzers. Comparison of the NO and NO<sub>2</sub> zero and span values before and after shutdown indicated the extent of zero and span drift resulting from the shutdown. Near full-scale NO and NO<sub>2</sub> levels (i.e., 3,000 ppm NO and 450 ppm NO<sub>2</sub>) were used as the span values in this test.

### ***3.2.5 Interferences***

Following analyzer startup and completion of the interrupted sampling test, the second day of laboratory testing continued with interference testing. This test evaluated the response of the ECA 450 analyzers to species other than NO and NO<sub>2</sub>. The potential interferants listed in Table 3-2 were supplied to the analyzers one at a time, and the NO and NO<sub>2</sub> readings of the analyzers were recorded. The potential interferants were used one at a time, except for a mixture of SO<sub>2</sub> and NO, which was intended to assess whether SO<sub>2</sub> in combination with NO produced a bias in NO response.

The CO, CO<sub>2</sub>, SO<sub>2</sub>, and NH<sub>3</sub> used in the interference test were all obtained as Certified Master Class Calibration Standards from Scott Technical Gases, at the concentrations indicated in Table 3-2. The indicated concentrations were certified by the manufacturer to be accurate within  $\pm 2\%$ , based on analysis. The CO, CO<sub>2</sub>, and NH<sub>3</sub> were all in ultra-high purity (UHP) air, and the SO<sub>2</sub> was in UHP nitrogen. The SO<sub>2</sub>/NO mixture listed in Table 3-2 was prepared by diluting the NO Protocol Gas with the SO<sub>2</sub> standard using the Environics 4040 diluter.

**Table 3-2. Summary of Interference Tests Performed**

<b>Interferant</b>	<b>Interferant Concentration</b>
CO	496 ppm
CO <sub>2</sub>	5.03%
SO <sub>2</sub>	501 ppm
NH <sub>3</sub>	494 ppm
Hydrocarbon Mixture <sup>a</sup>	465 ppm C <sub>1</sub> , 94 ppm C <sub>2</sub> , 46 ppm C <sub>3</sub> + C <sub>4</sub>
SO <sub>2</sub> and NO	451 ppm SO <sub>2</sub> + 393 ppm NO

<sup>a</sup> C<sub>1</sub> = methane; C<sub>2</sub> = ethane; and C<sub>3</sub> + C<sub>4</sub> = 23 ppm propane + 23 ppm n-butane.

The hydrocarbon interferant listed in Table 3-2 was prepared at Battelle in UHP hydrocarbon-free air, starting from the pure compounds. Small quantities of methane, ethane, propane, and n-butane were injected into a cylinder that was then pressurized with UHP air. The required hydrocarbon concentrations were approximated by the preparation process, and then quantified by comparison with a NIST-traceable standard containing 1,020 ppm carbon (ppmC) in the form of propane. Using a gas chromatograph with a flame ionization detector (FID) the NIST-traceable standard was analyzed. The resulting FID response factor (2,438 area units/ppmC) was then used to determine the concentrations of the components of the prepared hydrocarbon mixture. Two analyses of that mixture gave results of 463 and 467 ppm methane; the corresponding results for ethane were 93 and 95 ppm; for propane 22 and 23 ppm; and for n-butane 23 and 23 ppm.

In the interference test, each interferant in Table 3-2 was provided individually to the sampling manifold shown in Figure 3-2, at a flow in excess of that required by the two analyzers. Each period of sampling an interferant was preceded by a period of sampling the appropriate zero gas.

### **3.2.6 Pressure Sensitivity**

The pressure sensitivity test was designed to quantify the dependence of analyzer response on the pressure in the sample gas source. By means of two valves at the downstream end of the sample manifold (Figure 3-1), the pressure in the manifold could be adjusted above or below the ambient room pressure, while supplying the manifold with a constant ppm level of NO or NO<sub>2</sub> from the Environics 4040 diluter. This capability was used to determine the effect of the sample gas pressure on the sample gas flow rate drawn by the analyzers, and on the NO and NO<sub>2</sub> response.

The dependence of sample flow rate on pressure was determined using an electronically timed bubble flow meter (Buck Primary Flow Calibrator, Model M-5, Serial No. 051238). This flow meter was connected in line (i.e., inserted) into the sample flow path from the manifold to one of

---

the commercial analyzers. Zero gas was supplied to the manifold at ambient pressure, and the analyzer's sample flow rate was measured with the bubble meter. The manifold pressure was then adjusted to -8.5 inches of water relative to the room, and the analyzer's flow rate was measured again. The manifold pressure was adjusted to +8.5 inches of water relative to the room, and the flow rate was measured again. The bubble meter was then moved to the sample inlet of the other commercial analyzer, and the flow measurements were repeated.

The dependence of NO and NO<sub>2</sub> response on pressure was determined by sampling the appropriate zero gas, and an NO or NO<sub>2</sub> span gas approximating the respective full scale, at each of the same manifold pressures (room pressure, -8.5 inches, and +8.5 inches). This procedure was conducted simultaneously on both analyzers, first for NO at all three pressures, and then for NO<sub>2</sub> at all three pressures. The data at different pressures were used to assess zero and span drift resulting from the sample pressure differences.

### ***3.2.7 Ambient Temperature***

The purpose of the ambient temperature test was to quantify zero and span drift that may occur as the analyzers are subjected to different temperatures during operation. This test involved providing both analyzers with zero and span gases for NO and NO<sub>2</sub> (at the same nominal range values used in the pressure sensitivity test) at room, elevated, and reduced temperatures. A temperature range of about 7 to 40°C (45 to 105°F) was targeted in this test. The elevated temperature condition was achieved using a 1.43 m<sup>3</sup> steel and glass laboratory chamber heated using external heat lamps. The reduced temperature condition was achieved using a commercial laboratory refrigerated cabinet (Lab Research Products, Inc.).

The general procedure was to provide zero and span gas for NO, and then for NO<sub>2</sub>, to both analyzers at room temperature, and then to place both analyzers and the sampling manifold into the heated chamber. Electrical and tubing connections were made through a small port in the lower wall of the chamber. A thermocouple readout was used to monitor the chamber temperature and room temperature, and the internal temperature indications of the analyzers themselves were monitored, when available. After 1 hour or more of stabilization in the heated chamber, the zero and span tests were repeated. The analyzers, manifold, and other connections were then transferred to the refrigerator. After a stabilization period of 1 hour or more, the zero and span checks were repeated at the reduced temperature. The analyzers were returned to the laboratory bench; and, after a 1-hour stabilization period, the zero and span checks were repeated a final time.

---

### 3.3 Combustion Source Tests

#### 3.3.1 Combustion Sources

Three combustion sources (a gas rangetop, a gas residential water heater, and a diesel engine) were used to generate NO<sub>x</sub> emissions from less than 10 ppm to over 300 ppm. Emissions databases for two of these sources (rangetop and water heater) exist as a result of prior measurements, both of which have been published.<sup>(4,5)</sup>

##### 3.3.1.1 Rangetop

The low-NO<sub>x</sub> source was a residential natural gas fired rangetop (KitchenAid Model 1340), equipped with four cast-iron burners, each with its own onboard natural gas and combustion air control systems. The burner used (front-left) had a fixed maximum firing rate of about 8 KBtu/hr.

The rangetop generated NO in the range of about 5 to 8 ppm, and NO<sub>2</sub> in the range of about 1 to 3 ppm. The database on this particular appliance was generated in an international study in which 15 different laboratories, including Battelle, measured its NO and NO<sub>2</sub> emissions.<sup>(4)</sup>

Rangetop NO<sub>x</sub> emissions were diluted prior to measurement using a stainless-steel collection dome, fabricated according to specifications of the American National Standards Institute (ANSI Z21.1).<sup>(6)</sup> For all tests, this dome was elevated to a fixed position 2 inches above the rangetop surface. Moreover, for each test, a standard “load” (pot) was positioned on the grate of the rangetop burner. This load was also designed according to ANSI Z21.1 specifications regarding size and material of construction (stainless steel). For each test, the load contained 5 pounds of room-temperature water.

The exit of the ANSI collection dome was modified to include seven horizontal sample-probe couplers. One of these couplers was 1/4-inch in size, three were 3/8-inch in size, and three were 1/2-inch in size. These were available to accommodate various sizes of vendor probes, and one reference probe, simultaneously during combustion-source sampling.

This low-NO<sub>x</sub> combustion source was fired using “standard” natural gas, obtained from Praxair, Inc., which was certified to contain 90% methane, 3% ethane, and the balance nitrogen. This gaseous fuel contained no sulfur.

##### 3.3.1.2 Water Heater

The medium-NO<sub>x</sub> source was a residential natural gas-fired water heater (Ruud Model P40-7) of 40-gallon capacity. This water heater was equipped with one stamped-aluminum burner with its own onboard natural gas and combustion air control systems, which were operated according to manufacturer’s specifications. The burner had a fixed maximum firing rate of about 40 KBtu/hr. Gas flow to the water heater was monitored using a calibrated dry-gas meter.

The water heater generated NO emissions in the range of 50 to 80 ppm, and NO<sub>2</sub> in the range of 4 to 8 ppm. NO<sub>x</sub> emissions dropped as the water temperature rose after ignition, stabilizing at the

---

levels noted above. To assure constant operation of the water heater, a continuous draw of 3 gpm was maintained during all verification testing. The database on this particular appliance was generated in a national study in which six different laboratories measured its emissions, including Battelle.<sup>(5)</sup>

Water heater NO<sub>x</sub> emissions were not diluted prior to measurement. The draft hood, integral to the appliance, was replaced with a 3-inch diameter, 7-inch long stainless-steel collar. The exit of this collar was modified to include five horizontal sample-probe couplers. One coupler was 1/4-inch in size, whereas the two other pairs were either 3/8- or 1/2-inch in size. Their purpose was to hold two vendor probes and one reference probe simultaneously during sampling.

This medium-NO<sub>x</sub> combustion source was fired on house natural gas, which contained odorant-level sulfur (approximately 4 ppm mercaptan). The composition of this natural gas is essentially constant, as monitored by a dedicated gas chromatograph in Battelle's laboratories.

### 3.3.1.3 Diesel Engine

The high-NO<sub>x</sub> source was an industrial diesel 8 kW electric generator (Miller Bobcat 225D Plus), which had a Deutz Type ND-151 two-cylinder engine generating 41 KBtu/hr (16 horsepower). This device generates NO<sub>x</sub> emissions over a range of about 200 to 330 ppm, depending on the load on the super-charged engine. High load (3,500 RPM) resulted in the lowest NO<sub>x</sub>; idle (2000 RPM) resulted in the highest NO<sub>x</sub>. At both conditions, about one-third of the NO<sub>x</sub> was NO<sub>2</sub>. Data on diesel generator emissions were generated in tests conducted in the two weeks prior to the start of the verification test.

NO<sub>x</sub> emissions from this engine were not diluted prior to measurement. The 1-inch exhaust outlet of the engine, which is normally merely vented to the atmosphere, was fitted with a stack designed to meet the requirements of the EPA Method 5.<sup>(9)</sup> The outlet was first expanded to 2 inches of 1.5-inch diameter copper tubing, then to 15 inches of 2-inch diameter copper tubing, and finally to 2 inches of 3-inch diameter copper tubing. The 3-inch diameter tubing was modified to include five horizontal sample-probe couplers. One of these couplers was 1/4-inch in size, two were 3/8-inch in size, and two were 1/2-inch in size. These couplers held the sample probes in place. The 3-inch tube was connected to a 3-inch stack extending through the roof of the test laboratory. This high-NO<sub>x</sub> combustion source was fired on commercial diesel fuel, which, by specification, contains only 0.03 to 0.05 weight% sulfur.

### 3.3.2 Test Procedures

The procedures followed during combustion source testing consisted of those involved with the sampling systems, reference method, calibration gas supply, and the sources, as follows.

---

### 3.3.2.1 Sampling Systems

Prior to sampling, the Bacharach representative inserted two of his product's probes into the exhaust duct of the rangetop, water heater, or diesel engine. The Bacharach probes were fitted close to each other, sampling from a point within about 1/4 inch of the inlet of the reference analyzers' probe.

The reference analyzer probe consisted of an 18-inch long, 1/4-inch diameter stainless-steel tube, the upstream 2 inches of which were bent at a right angle for connection to a stainless steel bulkhead union in the wall of the exhaust duct. The inner end of the bulkhead union connected to a short length of 1/4-inch diameter stainless steel tube that extended into the center of the source exhaust duct. The Bacharach Model ECA 450 analyzers were each operated with their own sample probe and sample transfer lines and with the optional sample conditioners to dry and filter the sample. Based on the results of trial runs conducted before the verification test, neither the reference sampling probe nor the reference sample-transfer lines were heated. Visible condensation of combustion-generated water did not occur. The reference analyzer moisture-removal system consisted of a simple condenser in an ice bath connected to the stainless steel probe by a 2-foot length of 1/4-inch diameter Teflon® tubing. The downstream end of the condenser was connected by a 3-foot length of 1/4-inch Teflon tubing to an inlet "tee" connected to both reference analyzers. The reference particulate-removal system consisted of a 47-millimeter in-line quartz fiber filter, which was used only in sampling the diesel emissions.

### 3.3.2.2 Reference Method

The reference method against which the vendor analyzers were compared was the ozone chemiluminescence method for NO that forms the basis of EPA Method 7E.<sup>(2)</sup> The reference measurements were made using two Model 42-C source-level NO<sub>x</sub> monitors (from Thermo Environmental Instruments), located on a wheeled cart positioned near the combustion sources. These monitors sampled from a common intake line, as described above. Both instruments use stainless steel converters maintained at 650°C (1,202°F) for reduction of NO<sub>2</sub> to NO for detection. The two reference analyzers were designated as Unit No. 100643 and 100647, respectively.

The reference analyzers were calibrated before and after combustion source tests using an EnviroNics Series 2020 diluter (Serial No. 2108) and EPA Protocol 1 gases for NO and NO<sub>2</sub> (3,925 ppm, Cylinder No. ALM 15489, and 511.5 ppm, Cylinder No. AAL 5289, respectively; Scott Specialty Gases). The calibration procedure was specified in the test/QA plan, and required calibration at zero, 30%, 60%, and 100% of the applicable range value (i.e., 50, 100, or 1,000 ppm, depending on the emission source). Calibration results closest in time to the combustion source test were used to establish scale factors applicable to the source test data. The conversion efficiency of the stainless steel converters was determined by calibrating with both NO and NO<sub>2</sub> on the applicable ranges, using the EPA Protocol 1 gases. The ratio of the linear regression slope of the NO<sub>2</sub> calibration to that of the NO calibration determined the NO<sub>2</sub> conversion efficiency. For the Bacharach source tests, which took place on May 1 and 2, 2000, calibration data from

---

May 1 were applied. Conversion efficiency values of 91.8 and 99.3% were found for the two reference analyzers, and all reference data were corrected for those conversion efficiencies.

### 3.3.2.3 Calibration Gas Supply

Prior to the start of the combustion source tests, the ECA 450 analyzers were calibrated with NO and NO<sub>2</sub> concentrations of 500 ppm and 150 ppm, respectively. In addition, before and after sampling of each combustion source, both the analyzers undergoing testing and the reference analyzers were supplied with zero gas and with standard NO and NO<sub>2</sub> mixtures at levels comparable to those expected from the source. To prepare these mixtures, Protocol 1 gases identical to those used in the laboratory testing were diluted using an Environics Series 2020 Multi-Gas Calibrator (Serial Number 2108). The same Acid Rain CEM zero gases were used for dilution and zeroing as were used in the laboratory tests. The pre- and post-test span values used with each combustion source are given in Table 3-3.

**Table 3-3. Span Concentrations Provided Before and After Each Combustion Source**

Source	NO Span Level (ppm)	NO <sub>2</sub> Span Level (ppm)
Gas Rangetop	20	10
Gas Water Heater	100	15
Diesel–High RPM	200	50
Diesel–Idle	400	100

The pre- and post-test zero and span values were used to assess the drift in zero and span response of the tested analyzers caused by exposure to source emissions.

### 3.3.2.4 Operation of Sources

Verification testing was conducted with the combustion sources at or near steady-state in terms of NO<sub>x</sub> emission. For the rangetop, steady-state was achieved after about 15 minutes, when the water began to boil. For the water heater, steady-state was achieved in about 15 minutes, when its water was fully heated. Because the water heater tank had a thermostat, cycling would have occurred had about 3 gpm of hot water not been continuously drained out of the tank.

For the diesel engine, steady-state was achieved in about 10 minutes of operation. The diesel engine was operated first at full speed (3,500 RPM) to achieve its lowest NO<sub>x</sub> emissions. Prior to sampling the NO<sub>x</sub> emissions at idle, the diesel engine was operated at idle for about 20 minutes to effectively “detune” its performance.

The order of operation of the combustion sources was (1) rangetop, (2) water heater, (3) diesel engine (high RPM), and (4) diesel engine (idle). This allowed the analyzers to be exposed to



---

continuously increasing NO and NO<sub>2</sub> levels, and avoided interference in low level measurements that might have resulted from prior exposure to high levels.

Sampling of each combustion source consisted of obtaining nine separate measurements of the source emissions. After sampling of pre-test zero and span gases provided from the calibration source, and with both the reference and vendor analyzers sampling the source emissions, the Bacharach operator indicated when he was ready to take the first set of readings (a set of readings consisting of the NO and NO<sub>2</sub> response on both Units A and B). At that time the Battelle operator of the reference analyzers also took corresponding readings. The analyzers undergoing testing were then disconnected from the source, and allowed to sample room air until readings dropped well below the source emissions levels. The analyzers were then reconnected to the source, and after stabilizing another set of readings was taken. There was no requirement that analyzer readings drop fully to zero between source measurements. This process was repeated until a total of nine readings had been obtained with both the vendor and reference analyzers. The same zero and span gases were then sampled again before moving to the next combustion source.

The last operation in the combustion source testing involved continuous sampling of the diesel engine emissions for a full hour with no intervals of room air sampling. Data were recorded for both reference and vendor analyzers at 1-minute intervals throughout that hour of measurement. This extended sampling was conducted only after nine sequential sets of readings had been obtained from all the combustion sources by the procedure described above. Results from this extended sampling were used to determine the measurement stability of the ECA 450 analyzer.

---

## **Chapter 4**

### **Quality Assurance/Quality Control**

Quality control (QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS Center<sup>(7)</sup> and the test/QA plan<sup>(1)</sup> for this verification test.

#### **4.1 Data Review and Validation**

Test data were reviewed and approved according to the AMS Center QMP, the test/QA plan, and Battelle's one-over-one approval policy. The Verification Testing Leader reviewed the raw data and data sheets that were generated each day. Laboratory record notebooks were also signed and dated by testing staff and reviewed by the Verification Testing Leader.

Other data review focused upon the compliance of the reference analyzer data with the quality requirements of Method 7E. The purpose of validating reference data was to ensure usability for the purposes of comparison with the demonstration technologies. The results of the review of the reference analyzer data quality are shown in Table 4-1. The data generated by the reference analyzers were used as a baseline to assess the performance of the technologies for NO/NO<sub>2</sub> analysis.

#### **4.2 Deviations from the Test/QA Plan**

During the physical set up of the verification test, deviations from the test/QA plan were made to better accommodate differences in vendor equipment, and other changes or improvements. Any deviation required the approval signature of Battelle's Verification Testing Leader and Center Manager. A planned deviation form was used for documentation and approval of the following changes:

1. The order of testing was changed in the pressure sensitivity test to require fewer plumbing changes in conducting the test.
2. The order of the ambient temperature test was changed to maximize the detection of any temperature effect.
3. The concentrations used in the mixture of SO<sub>2</sub> and NO for the interference test were changed slightly.
4. For better accuracy, the oxygen sensor used during combustion source tests was checked by comparison to an independent paramagnetic O<sub>2</sub> sensor, rather than to a wet chemical measurement.
5. Single points (rather than triplicate points) were run at each calibration level in calibrating the reference analyzers, in accord with Method 7E.

**Table 4-1. Results of QC Procedures for Reference Analyzers for Testing of Bacharach Model ECA 450 Analyzers**

NO <sub>2</sub> conversion efficiency (Unit 100643)	91.8%					
NO <sub>2</sub> conversion efficiency (Unit 100647)	99.3%					
Calibration of reference method using four points at 0, 30, 60, 100% for NO	Meets criteria (r <sup>2</sup> = 0.9999)					
Calibration of reference method using four points at 0, 30, 60, 100% for NO <sub>2</sub>	Meets criteria (r <sup>2</sup> = 0.9999)					
Calibrations (100 ppm range)	Meet ± 2% requirement (relative to span)	Unit 100643		Unit 100647		
		NO		NO		
		Error, % of Span	at % of Scale	Error, % of Span	at % of Scale	
		0.5	30	0.5	30	
		0.8	60	0.5	60	
		NO <sub>2</sub>		NO <sub>2</sub>		
		Error, % of Span	at % of Scale	Error, % of Span	at % of Scale	
		0.4	30	0.3	30	
		0.7	60	0.8	60	
Zero drift	Meets ± 3% requirement (relative to span) on all combustion sources					
Span drift	Meets ± 3% requirement (relative to span) on all combustion sources					
Interference check	< ± 2% (no interference response observed)					

- A short, unheated sample inlet was used with the reference analyzers, based on pre-test trial runs, on Battelle's previous experience in sampling the combustion sources used in this test, and on other similar sources.
- No performance evaluation audit was conducted on the natural gas flow rate measurement used with the gas water heater. This measurement was made with a newly calibrated dry gas meter.

---

### 4.3 Calibration of Laboratory Equipment

Equipment used in the verification test required calibration before use, or verification of the manufacturer's calibrations. Some auxiliary devices were obtained with calibration from Battelle's Instrument Laboratory. Equipment types and calibration dates are listed in Table 4-2. For key equipment items, the calibrations listed include performance evaluation audits (see Section 4.5.2). Documentation of calibration of the following equipment was maintained in the test file.

**Table 4-2. Equipment Type and Calibration Date**

<b>Equipment Type</b>	<b>Use</b>	<b>Calibration/PE Date</b>
Gas Dilution System Environics Model 4040 (Serial Number 2469)	Lab tests	3/9/00; 5/9/00
Gas Dilution System Environics Model 2020 (Serial Number 2108)	Source tests	3/20/00; 5/9/00
Fluke Digital Thermometer (LN-570068)	Ambient temperature test	10/15/99; 5/26/00
Servomex 570A Analyzer (X-44058)	Flue gas O <sub>2</sub>	11/22/99; 5/18/00
Dwyer Magnahelic Pressure Gauge	Pressure sensitivity test	4/7/00
Doric Trendicator 410A Thermocouple Temperature Sensor (Serial Number 331513)	Flue gas temperature	8/5/99; 5/26/00
American Meter DTM 115 Dry Gas Meter (Serial Number 89P124205)	Gas flow measurement	4/17/00

### 4.4 Standard Certifications

Standard or certified gases were used in all verification tests, and certifications or analytical data were kept on file to document the traceability of the following standards:

- EPA Protocol Gas Nitrogen Dioxide
- EPA Protocol Gas Nitric Oxide
- Certified Master Class Calibration Standard Sulfur Dioxide
- Certified Master Class Calibration Standard Carbon Dioxide
- Certified Master Class Calibration Standard Ammonia
- Certified Master Class Calibration Standard Carbon Monoxide
- Nitrogen Acid Rain CEM Zero

- 
- Acid Rain CEM Zero Air
  - Battelle-Prepared Organics Mixture.

All other QC documentation and raw data for the verification test are located in the test file at Battelle, to be retained for 7 years and made available for review if requested.

#### **4.5 Performance System Audits**

Three internal performance system audits were conducted during verification testing. A technical systems audit was conducted to assess the physical setup of the test, a performance evaluation audit was conducted to evaluate the accuracy of the measurement system, and an audit of data quality was conducted on 10% of all data generated during the verification test. A summary of the results of these audits is provided below.

##### ***4.5.1 Technical Systems Audit***

A technical systems audit (TSA) was conducted on April 18, 2000, (laboratory testing) and May 17 and 18, 2000, (source testing) for the NO/NO<sub>2</sub> verification tests conducted in early 2000. The TSA was performed by the Battelle's Quality Manager as specified in the AMS Center Quality Management Plan (QMP). The TSA ensures that the verification tests are conducted according to the test/QA plan<sup>(1)</sup> and all activities associated with the tests are in compliance with the AMS Center QMP<sup>(7)</sup>. All findings noted during the TSA on the above dates were documented and submitted to the Verification Testing Leader for correction. The corrections were documented by the Verification Testing Leader and reviewed by Battelle's Quality Manager and Center Manager. None of the findings adversely affected the quality or outcome of this verification test and all were resolved to the satisfaction of the Battelle Quality Manager. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

##### ***4.5.2 Performance Evaluation Audit***

The performance evaluation audit was a quantitative audit in which measurement standards were independently obtained and compared with those used in the verification test to evaluate the accuracy of the measurement system. That assessment was conducted by Battelle testing staff on May 23 and 26, 2000, and the results were reviewed by independent QA personnel.

The most important performance evaluation (PE) audit was of the standards used for the reference measurements in source testing. The PE standards were NO and NO<sub>2</sub> calibration gases independent of the test calibration standards that contained certified concentrations of NO and NO<sub>2</sub>. Accuracy of the reference analyzers was determined by comparing the measured NO/NO<sub>2</sub> concentrations using the verification test standards with those obtained using the certified PE standards. Percent difference was used to quantify the accuracy of the results. The PE sample for NO was an EPA Protocol Gas having a concentration (3,988 ppm) nearly the same as the NO standard used in verification testing, but purchased from a different commercial supplier (Matheson Gas Products). The PE standard for NO<sub>2</sub> was a similar commercial standard of 463 ppm NO<sub>2</sub> in air, also from Matheson. Table 4-3 summarizes the NO/NO<sub>2</sub> standard method

---

performance evaluation results. Included in this table are the performance acceptance ranges and the certified gas concentration values. The acceptance ranges are guidelines established by the provider of the PE materials to gauge acceptable analytical results.

Table 4-3 shows that the PE audit confirmed the concentration of the Scott 3,925 ppm NO test standard almost exactly: the apparent test standard concentration was within 0.2% of the test standard's nominal value. On the other hand, the PE audit results for the Scott 511.5 ppm NO<sub>2</sub> standard were not as close. The comparison to the Matheson PE standard indicated that the 511.5 ppm NO<sub>2</sub> Scott standard was only about 480 ppm, a difference of about 7% from its nominal value. This result suggests an error in the Scott test standard for NO<sub>2</sub>. However, a separate line of evidence indicates that the Matheson PE standard is likely in error. Specifically, conversion efficiency checks on the reference analyzers (performed by comparing their responses to the Scott NO and NO<sub>2</sub> standards) consistently showed the efficiency of the converter in 42-C Unit 100647 to be very close to 100%. This finding could not occur if the concentration of the NO<sub>2</sub> standard were low. That is, a conversion efficiency of 100% indicates agreement between the NO standard and the NO<sub>2</sub> standard; and, as shown in Table 4-3, the NO standard is confirmed by the PE comparison. Thus, the likelihood is that the Matheson PE standard was in fact somewhat higher in concentration than its nominal 463 ppm value.

PE audits were also done on the O<sub>2</sub> sensor used for flue gas measurements, and on the temperature indicators used for ambient and flue gas measurements. The PE standard for O<sub>2</sub> was an independent paramagnetic sensor, and for temperature was a certified mercury-in-glass thermometer. The O<sub>2</sub> comparison was conducted during sampling of diesel exhaust; the temperature comparisons were conducted at room temperature. The results of those audits are shown in Table 4-4, and indicate close agreement of the test equipment with the PE standards.

### ***4.5.3 Audit of Data Quality***

The audit of data quality is a qualitative and quantitative audit in which data and data handling are reviewed and data quality and data usability are assessed. Audits of data quality are used to validate data at the frequency of 10% and are documented in the data audit report. The goal of an audit of data quality is to determine the usability of test results for reporting technology performance, as defined during the design process. Validated data are reported in the ETV verification reports and ETV verification statement along with any limitations on the data and recommendations for limitations on data usability.

The Battelle Quality manager audited 10% of the raw data. Test data sheets and laboratory record books were reviewed, and statistical calculations and other algorithms were verified. Calculations that were used to assess the four-point calibration of the reference method were also verified to be correct. In addition, data presented in the verification report and statement are audited to ensure accurate transcription.

**Table 4-3. Performance Evaluation Results on NO/NO<sub>2</sub> Standards**

Reference Analyzer/Standard	Reading on Diluted Standard	Apparent Concentration <sup>a</sup>	Percent Difference <sup>b</sup>	Acceptance Limits
NO in N <sub>2</sub>				
Unit 100643 (ppm)				
Test Std	3,925	98.8 ppm	0.2%	±2%
PE Std	3,988	100.6 ppm		
NO in N <sub>2</sub>				
Unit 100647 (ppm)				
Test Std	3,925	99.6 ppm	0.2%	±2%
PE Std	3,988	101.4 ppm		
NO <sub>2</sub> in Air				
Unit 100643 (ppm)				
Test Std	511.5	44.2 ppm	5.8%	±5%
PE Std	463	42.5 ppm		
NO <sub>2</sub> in Air				
Unit 100647 (ppm)				
Test Std	511.5	49.6 ppm		
PE Std	463	48.8 ppm	7.9%	±5%

<sup>a</sup> Concentration of Test Standard indicated by comparison to the Performance Evaluation Standard; i.e., Apparent Concentration = (Test Std. Reading/PE Std. Reading) × PE Std. Conc.; e.g., Apparent Concentration = 98.8/100.6 × 3,988 ppm = 3,917 ppm.

<sup>b</sup> Percent difference of Apparent Concentration relative to Test Standard concentration; e.g., percent difference =  $\frac{3,925 \text{ ppm} - 3,917 \text{ ppm}}{3,925 \text{ ppm}} \times 100 = 0.2\%$ .

**Table 4-4. Performance Evaluation Results in O<sub>2</sub> and Temperature Measuring Equipment**

Analyzer	Reading	Difference	Acceptance Limits
Servomex 570A O <sub>2</sub>	18.9% O <sub>2</sub>	0% O <sub>2</sub>	–
PE Standard <sup>a</sup>	18.9% O <sub>2</sub>		
Fluke Digital Thermometer	22.1 °C	0.1 °C	2% absolute T
PE Standard <sup>b</sup>	22 °C		
Doric 410A Temp. Sensor	24.8 °C	0.2 °C	2% absolute T
PE Standard <sup>b</sup>	25.0 °C	0.2 °C	

<sup>a</sup> Independent paramagnetic O<sub>2</sub> analyzer.

<sup>b</sup> Certified mercury-in-glass thermometer.

---

## Chapter 5 Statistical Methods

### 5.1 Laboratory Tests

The analyzer performance characteristics were quantified on the basis of statistical comparisons of the test data. This process began by converting the spreadsheet files that resulted from the data acquisition process into data files suitable for evaluation with Statistical Analysis System (SAS) software. The following statistical procedures were used to make those comparisons.

#### 5.1.1 Linearity

Linearity was assessed by linear regression with the calibration concentration as the independent variable and the analyzer response as the dependent variable. Separate assessments were carried out for each EAC 450 analyzer. The calibration model used was

$$Y_c = h(c) + error_c$$

where  $Y_c$  is the analyzer's response to a challenge concentration  $c$ ,  $h(c)$  is a linear calibration curve, and the error term was assumed to be normally distributed. (If the variability is not constant throughout the range of concentrations then weighting in the linear regression is appropriate. It is often the case that the variability increases as the true concentration increases.) The variability ( $\sigma_c$ ) of the measured concentration values ( $c$ ) was modeled by the following relationship,

$$\sigma_c^2 = \alpha + kc^\beta$$

where  $\alpha$ ,  $k$ , and  $\beta$  are constants to be estimated from the data. After determining the relationship between the mean and variability, appropriate weighting was determined as the reciprocal of the variance.

$$weight = w_c = \frac{1}{\sigma_c^2}$$



The form of the linear regression model fitted was  $h(c) = \alpha_o + \alpha_1 c$ . In the concentration sub-region where the linear calibration model provides a valid representation of the concentration-response relation, concentration values were calculated from the estimated calibration curve using the relation

$$\hat{c} = \hat{h}^{-1}(Y_c) = \frac{Y_c - \hat{\alpha}_o}{\hat{\alpha}_1}$$

A test for departure from linearity was carried out by comparing the residual mean square

$$\frac{1}{4} \sum_{i=1}^6 (\bar{Y}_{c_i} - \alpha_o - \alpha_1 c_i)^2 n_{c_i} w_{c_i}$$

to an F-distribution with  $6 - 2 = 4$  numerator degrees of freedom.

$\bar{Y}_{c_i}$  is the average of the  $n_{c_i}$  analyzer responses at the  $i^{\text{th}}$  calibration concentration,  $c_i$ . The regression relation was fitted to the individual responses; however, only the deviation about the sample mean analyzer responses at each calibration concentration provide information about goodness-of-fit.

$$\sum_{i=1}^n \sum_{j=1}^{n_{c_i}} (Y_{cij} - \alpha_o - \alpha_1 c_i)^2 w_{c_i} = \sum_{i=1}^n \sum_{j=1}^{n_{c_i}} (Y_{cij} - \bar{Y}_{c_i})^2 w_{c_i} + \sum_{i=1}^n (\bar{Y}_{c_i} - \alpha_o - \alpha_1 c_i)^2 n_{c_i} w_{c_i}$$

The first summation on the right side of the equation provides information only about response variability. The second summation provides all the information about goodness-of-fit to the straight-line calibration model. This is the statistic that is used for the goodness-of-fit test.

### 5.1.2 Detection Limit

Limit of detection (LOD) is defined as the smallest true concentration at which an analyzer's expected response exceeds the calibration curve at zero concentration by three times the standard deviation of the analyzer's zero reading, i.e.,  $\alpha_o + 3\sigma_o$ , if the linear relation is valid down to zero. The LOD may then be determined by

$$LOD = \frac{[(\alpha_o + 3\sigma_o) - \alpha_o]}{\alpha_1} = \frac{3\sigma_o}{\alpha_1}$$

where  $\sigma_o$  is the estimated standard deviation at zero concentration. The LOD is estimated as  $LOD = 3\hat{\sigma}_o / \hat{\alpha}_1$ . The standard error of the estimated detection limit is approximately

---


$$\hat{SE}(\hat{LOD}) \cong \hat{LOD} \sqrt{\frac{1}{2(n-1)} + \left(\frac{SE(\hat{a}_1)}{\hat{a}_1}\right)^2}$$

Note that the validity of the detection limit estimate and its standard error depends on the validity of the assumption that the fitted linear calibration model accurately represents the response down to zero concentration.

### 5.1.3 Response Time

The response time of the ECA 450 analyzers to a step change in analyte concentration was calculated by determining the total change in response due to the step change in concentration, and then determining the point in time when 95% of that change was achieved. Using data taken every 10 seconds, the following calculation was carried out:

$$\text{Total Response} = R_c - R_z$$

where  $R_c$  is the final response of the analyzer to the calibration gas and  $R_z$  is the final response of the analyzer to the zero gas. The analyzer response that indicates the response time then is:

$$\text{Response}_{95\%} = 0.95(\text{Total Response}) + R_z.$$

The point in time at which this response occurs was determined by inspecting the response/time data, linearly interpolating between two observed time points, as necessary. The response time was calculated as:

$$\text{RT} = \text{Time}_{95\%} - \text{Time}_1,$$

where  $\text{Time}_{95\%}$  is the time at which  $\text{Response}_{95\%}$  occurred and  $\text{Time}_1$  is the time at which the span gas was substituted for the zero gas. Since only one measurement was made, the precision of the response time was not determined.

### 5.1.4 Interrupted Sampling

The effect of interrupted sampling is the arithmetic difference between the zero data and between the span data obtained before and after the test. Differences are stated as ppm. No estimate was made of the precision of the observed differences.

### 5.1.5 Interferences

Interference is reported as both the absolute response (in ppm) to an interferant level, and as the sensitivity of the analyzer to the interferant species, relative to its sensitivity to NO or NO<sub>2</sub>. The relative sensitivity is defined as the ratio of the observed NO/NO<sub>2</sub>/NO<sub>x</sub> response of the analyzer to the actual concentration of the interferant. For example, an analyzer that measures NO is

---

challenged with 500 ppm of CO, resulting in an absolute difference in reading of 1 ppm (as NO). The relative sensitivity of the analyzer is thus 1 ppm/500 ppm = 0.2%. The precision of the interference results was not estimated from the data obtained, since only one measurement was made for each interferant.

### ***5.1.6 Pressure Sensitivity***

At each of ambient pressure, reduced pressure (-10 inches of water), and increased pressure (+10 inches of water), the analyzer flow rate, the response on zero gas, and the response on span gas were measured for each analyzer. Variability in zero and span responses for reduced and increased pressures was assumed to be the same as the variability at ambient pressure. The variability determined in the linearity test was used for this analysis. The duct pressure effects on analyzer flow rates and response were assessed by separate linear regression trend analyses for flow rate and for response. The precision of the pressure effects on zero concentration response and on span gas response was estimated based on the variability observed in the linearity test. Statistical significance of the trends across duct pressures was determined by comparing the estimated trends to their estimated standard errors, based on two-tailed t-tests:

$$t = \hat{\beta} / (0.040825 \hat{\sigma}(c)) \text{ for the zero concentration test}$$

$$t = \hat{\beta} / (0.07071 \hat{\sigma}(c)) \text{ for the span concentration test}$$

### ***5.1.7 Ambient Temperature***

The statistical analysis for evaluation of ambient temperature effects was similar to that used for assessing the pressure sensitivity. At room temperature, low temperature, and high temperature for each analyzer the response on zero gas and the response on span gas were observed. Variability for low and for high temperatures was assumed to be the same as variability at room temperature. The ambient temperature effects on zero and span readings were assessed by trend analysis for response with temperature, using separate linear regression analyses for the zero and for the span data. Precision of the ambient temperature effect was estimated based on the variability observed in the linearity test. Statistical significance of the trends across temperatures was determined by comparing the estimated trends to their estimated standard errors, based on two-tailed t-tests:

$$t = \hat{\beta} / (0.01723 \hat{\sigma}(c)) \text{ for the zero concentration test}$$

$$t = \hat{\beta} / (0.024363 \hat{\sigma}(c)) \text{ for the span concentration test}$$

---

## 5.2 Combustion Source Tests

### 5.2.1 Accuracy

The relative accuracy (RA) of the ECA 450 analyzers with respect to the reference method is expressed as:

$$RA = \frac{|\bar{d}| + t_{n-1}^{\alpha} \frac{S_d}{\sqrt{n}}}{\bar{x}} \times 100\%$$

where  $d$  refers to the difference between the average of the two reference analyzers and one of the tested units and  $x$  corresponds to the average of the two reference analyzers values.  $S_d$  denotes the sample standard deviation of the differences, based on  $n = 9$  samples, while  $t_{n-1}^{\alpha}$  is the  $t$  value for the  $100(1 - \alpha)$ th percentile of the distribution with  $n - 1$  degrees of freedom. For this case,  $t$  is 2.306. The relative accuracy was determined for an  $\alpha$  value of 0.025 (i.e., 97.5% confidence level, one-tailed). The RA calculated in this way can be determined as an upper confidence bound for the relative bias of the analyzer  $|\bar{d}|/\bar{x}$ , where the bar indicates the average value of the differences or of the reference values.

Assuming that the reference method variation is due only to the variation in the output source and the true bias between the test and reference methods is close to zero, an approximate standard error for RA is

$$\hat{SE} \cong \frac{S_d}{\sqrt{n}x} \sqrt{0.3634 + (t_{n-1}^{\alpha})^2 \frac{1}{2(n-1)}} \times 100\%$$

### 5.2.2 Zero/Span Drift

Statistical procedures for assessing zero and span drift were similar to those used to assess interrupted sampling. Zero (span) drift was calculated as the arithmetic difference between zero (span) values obtained before and after sampling of each combustion source. The same calculation was also made using zero and span values obtained before and after the linearity and ambient temperature tests. No estimate was made of the precision of the zero and span drift values.

### 5.2.3 Measurement Stability

The temporal stability of analyzer response in extended sampling from a combustion source was assessed by means of a trend analysis on 60 minutes of data obtained continuously using the diesel generator as the source. The existence of a difference in trend between the test unit and the average of the reference units was assessed by fitting a linear regression line with the difference between the measured concentration for a test unit and the average of the reference units as the

---

dependent variable, and time as the independent variable. Subtracting the average reference unit values adjusts for variation in the source output. The slope and the standard error of the slope are reported. The null hypothesis that the slope of the trend line on the difference is zero was tested using a one-sample two-tailed t-test with  $n - 2 = 58$  degrees of freedom.

#### ***5.2.4 Inter-Unit Repeatability***

The purpose of this comparison was to determine if any significant differences in performance exist between two identical analyzers operating side by side. In tests in which analyzer performance was verified by comparison with data from the reference method, the two identical units of each type of analyzer were compared to one another using matched pairs t-test comparisons. In tests in which no reference method data were obtained (e.g., linearity test), the two ECA 450 analyzer units were compared using statistical tests of difference. For example, the slopes of the calibration lines determined in the linearity test, and the detection limits determined from those test data, were compared. Inter-unit repeatability was assessed for the linearity, detection limit, accuracy, and measurement stability tests.

For the linearity test, the intercepts and slopes of the two units were compared to one another by two-sample t-tests using the pooled standard error, with combined degrees of freedom the sum of the individual degrees of freedom.

For the detection limit test, the detection limits of the two units were compared to one another by two-sample t-tests using the pooled standard error with 10 degrees of freedom (the sum of the individual degrees of freedom).

For the relative accuracy test, repeatability was assessed with a matched-pairs two-tailed t-test with  $n - 1 = 8$  degrees of freedom.

For the measurement stability test, the existence of differences in trends between the two units was assessed by fitting a linear regression to the paired differences between the units. The null hypothesis that the slope of the trend line on the paired differences is zero was tested using a matched-pairs t-test with  $n - 2 = 58$  degrees of freedom.

#### ***5.2.5 Data Completeness***

Data completeness was calculated as the percentage of possible data recovered from an analyzer in a test; the ratio of the actual to the possible number of data points, converted to a percentage, i.e.,

$$\text{Data Completeness} = (N_a)/(N_p) \times 100\%,$$

where  $N_a$  is the number of actual and  $N_p$  the number of planned data points.

## Chapter 6 Test Results

### 6.1 Laboratory Tests

#### 6.1.1 Linearity

Tables 6-1a and b list the data obtained in the linearity tests for NO and NO<sub>2</sub>, respectively. The response of both the NO and NO<sub>2</sub> sensors in each analyzer is shown in those tables.

Table 6-2 shows the results of the linear calibration curve fits for each unit and each analyte, based on the data shown in Tables 6-1a and b.

**Table 6-1a. Data from NO Linearity Test of Bacharach Model ECA 450 Analyzers**

Reading	Actual NO (ppm)	Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)
1	0	2	0	1	0
2	3000	3160	20	3167	17
3	360	359	3	357	2
4	1450	1495	7	1494	5
5	0	4	1	3	0
6	2470	2589	11	2592	10
7	710	726	4	722	2
8	360	363	3	360	2
9	0	7	2	5	1
10	710	721	3	719	2
11	1450	1498	5	1498	4
12	2470	2597	10	2600	9
13	0	8	2	6	1
14	3000	3181	15	3179	13
15	2470	2604	12	2600	10
16	1450	1511	8	1505	5
17	0	13	3	9	1
18	710	728	4	724	2
19	360	366	3	362	2
20	3000	3190	13	3189	12
21	0	9	2	6	1

**Table 6-1b. Data from NO<sub>2</sub> Linearity Test of Bacharach Model ECA 450 Analyzers**

Number	Actual NO <sub>2</sub> (ppm)	Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)
1	0	0	0	0	0
2	450	4	453	4	453
3	45	0	49	0	50
4	210	1	213	1	214
5	0	0	1	0	2
6	350	3	354	3	354
7	100	0	103	0	104
8	45	0	47	0	48
9	0	0	1	0	1
10	100	0	102	0	103
11	210	1	213	1	214
12	350	3	358	0	359
13	0	0	2	0	3
14	450	4	457	4	456
15	350	3	358	0	360
16	210	2	216	2	219
17	0	0	3	0	4
18	100	0	103	0	105
19	45	0	47	0	48
20	450	5	457	5	458
21	0	0	2	0	3

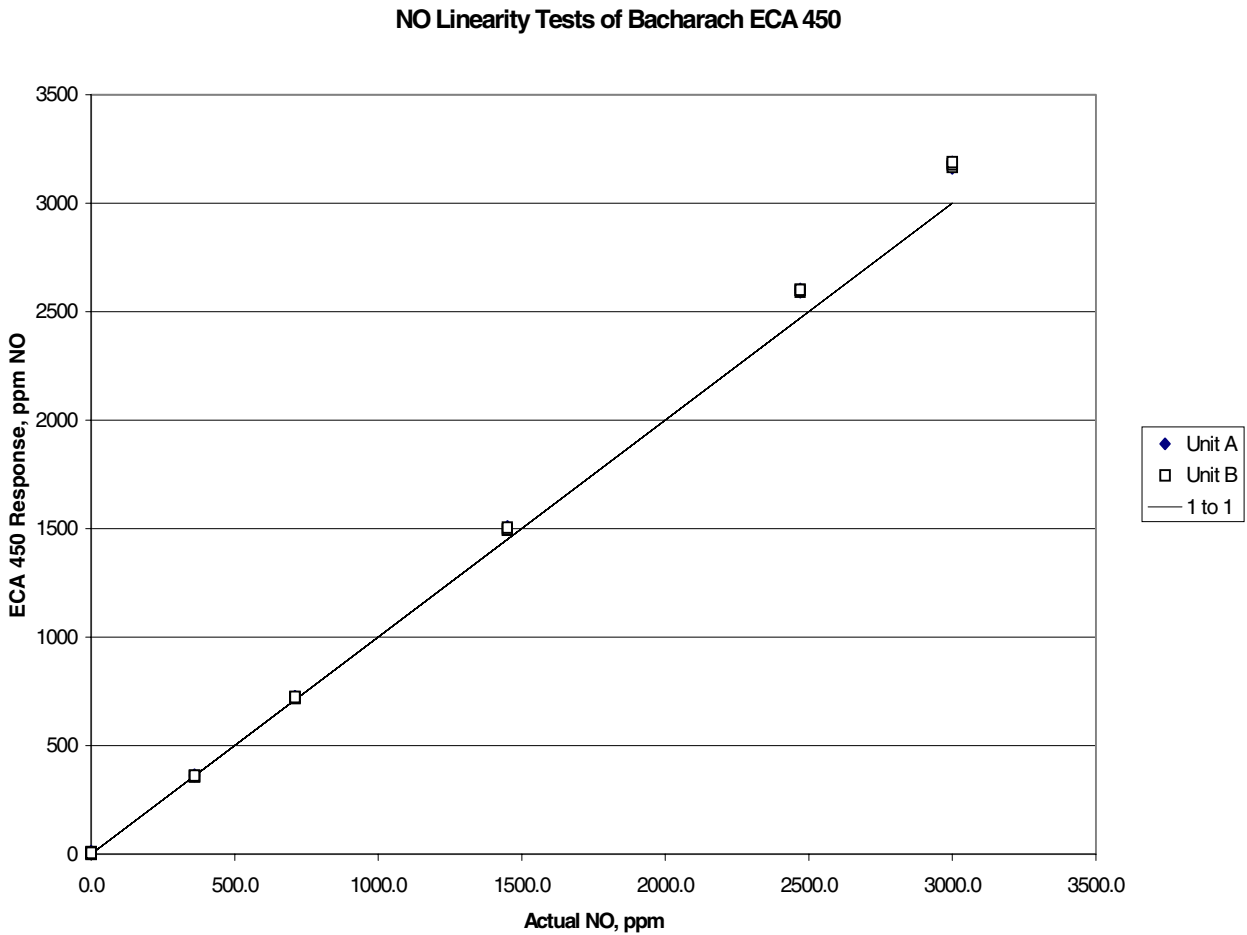
**Table 6-2. Statistical Results for Test of Linearity**

Linear Regression	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Intercept (ppm) (Std Err)	-0.913 (3.680)	1.669 (0.319)	-4.610 (3.950)	3.860 (1.274)
Slope (Std Err)	1.048 (0.004)	1.011 (0.002)	1.049 (0.004)	1.007 (0.004)
r <sup>2</sup>	0.9997	0.9999	0.9997	0.9998

The results in Table 6-2 show that the NO<sub>2</sub> response of the ECA 450 analyzers was linear over the entire range tested of up to 450 ppm. The NO<sub>2</sub> slopes are both approximately 1.01, and the r<sup>2</sup> values are 0.9998 or higher.

The NO linearity results in Table 6-2 show that, over the tested range of up to 3,000 ppm NO, the ECA 450 analyzers gave negative intercept values and slopes of about 1.05, significantly exceeding the upper limit of 1.02 generally expected of these analyzers.<sup>(8)</sup> Inspection of the NO linearity data, plotted in Figure 6-1, shows that the NO response of the ECA 450 analyzers is linear at lower concentrations, but exhibits an upward curvature at higher concentrations,

resulting in the overall regression results shown in Table 6-2. For example, the regression slopes for the two ECA 450 units are 1.007 and 1.009 when the lowest 12 calibration points in Table 6-1a (i.e., up to 710 ppm) are included, but increase to about 1.03 when the lowest 15 data points (i.e., up to 1,450 ppm) are included. These results suggest that the linear range of NO response for the ECA 450 analyzers is about 1,000 ppm, with increasing upward curvature of response above that level.



**Figure 6-1. Plot of NO Linearity Data**

The data in Tables 6-1a and 6-1b also indicate the extent of cross-sensitivity of the Bacharach NO and NO<sub>2</sub> sensors. Regression of the ECA 450 NO<sub>2</sub> responses in the NO linearity test (Table 6-1a) gives the regression results:

$$\text{Unit A NO}_2 = 0.0044 \times (\text{NO, ppm}) + 1.17 \text{ ppm, with } r^2 = 0.904, \text{ and}$$

$$\text{Unit B NO}_2 = 0.0042 \times (\text{NO, ppm}) + 0.05 \text{ ppm, with } r^2 = 0.926.$$

These results indicate a very slight response of the Bacharach NO<sub>2</sub> sensors to NO, amounting to about 0.4% of the NO level present.



Similarly, regression of the ECA 450 NO responses in the NO<sub>2</sub> linearity test (Table 6-1b) gives the regression results:

$$\begin{aligned} \text{Unit A NO} &= 0.0097 \times (\text{NO}_2, \text{ ppm}) - 0.36 \text{ ppm, with } r^2 = 0.932, \text{ and} \\ \text{Unit B NO} &= 0.0078 \times (\text{NO}_2, \text{ ppm}) - 0.33 \text{ ppm, with } r^2 = 0.651. \end{aligned}$$

These results also indicate a very small response of the Bacharach NO sensors to NO<sub>2</sub>, amounting to less than 1% of the NO<sub>2</sub> level present.

### 6.1.2 Detection Limit

Table 6-3 shows the estimated detection limits for each test unit and each analyte, determined from the data obtained in the linearity test. These detection limits apply to the calibrations conducted over a 0 to 3,000 ppm range for NO (Table 6-1a) and a 0 to 450 ppm range for NO<sub>2</sub> (Table 6-1b).

**Table 6-3. Estimated Detection Limits for Bacharach Model ECA 450 Analyzers<sup>a</sup>**

	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Estimated Detection Limit (ppm)	11.1	3.1	7.9	4.4
(Standard Error) (ppm)	(3.5)	(1.0)	(2.5)	(1.4)

<sup>a</sup> Results are based on calibrations over 0-3,000 ppm range for NO and 0-450 ppm range for NO<sub>2</sub>.

Table 6-3 displays the estimated detection limits, and their standard errors for NO and NO<sub>2</sub>, separately for each ECA 450 analyzer. NO detection limits of 8 to 11 ppm, and NO<sub>2</sub> detection limits of 3 to 4 ppm, are indicated. It must be stressed that these detection limits are based on the zero gas responses interspersed with sampling of high levels of NO and NO<sub>2</sub> in the linearity tests. As shown in Tables 6-1a and 6-1b, the zero gas responses tended to increase steadily throughout the linearity tests as a result of the exposures to high concentrations. Substantially lower detection limits are suggested by the results of the source testing (see Section 6.2), which show that, in the absence of this memory effect (due to high concentration exposures), detection limits for both NO and NO<sub>2</sub> appear to be comparable to the 1 ppm resolution of the analyzer.

### 6.1.3 Response Time

Table 6-4 lists the data obtained in the response time test of the ECA 450 analyzers. Table 6-5 shows the response times of the analyzers to a step change in analyte concentration, based on the data shown in Table 6-4. Table 6-5 shows that the response times of the two ECA 450 analyzers were consistent, i.e., 28 to 29 seconds for NO, and 54 to 57 seconds for NO<sub>2</sub>. These response times are more than sufficient for source emission measurements and are well within the 4-minute response criteria required of portable NO/NO<sub>x</sub> analyzers.<sup>(8)</sup>

**Table 6-4. Response Time Data for Bacharach Model ECA 450 Analyzers**

Time (sec)	Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)
0	4	1	2	2
10	601	55	709	28
20	2294	225	2267	199
30	2537	288	2546	273
40	2600	319	2597	311
50	2614	333	2610	329
60	2620	342	2614	340
70	2624	346	2617	344
80	2626	349	2619	347
90	2628	350	2621	349
100	2629	351	2622	351
110	2630	352	2623	352
120	2632	353	2624	353
130	2633	354	2625	354
140	2633	354	2626	354
150	2634	354	2627	354
160	2635		2627	
170	2636		2628	

**Table 6-5. Response Time Results for Bacharach Model ECA 450 Analyzers**

	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Response Time (sec) <sup>a</sup>	29	54	28	57

<sup>a</sup> The analyzer's responses were recorded at 10-second intervals; therefore the point in time when the 95% response was achieved was determined by interpolating between recorded times to the nearest second.

#### **6.1.4 Interrupted Sampling**

Table 6-6 shows the zero and span data resulting from the interrupted sampling test, and Table 6-7 shows the differences (pre- minus post-) of the zero and span values. Span concentrations of 3,000 ppm NO and 450 ppm NO<sub>2</sub> were used for this test.

The change in zero levels observed as a result of the shutdown period are larger for NO than for NO<sub>2</sub>. This difference, and the changes in zero values themselves, probably results from the exposure to elevated NO and NO<sub>2</sub> levels in the linearity tests that immediately preceded the shutdown. That is, the small changes in zero readings are probably the result of the analyzers returning to baseline readings after the linearity tests.

The ECA 450 analyzers showed essentially no change in the NO<sub>2</sub> span response as a result of the shutdown (Table 6-7). The changes observed in the NO span response are much larger (168 and 208 ppm), and amount to 5.6 and 6.9% of the 3,000 ppm NO span value.

**Table 6-6. Data from Interrupted Sampling Test with Bacharach Model ECA 450 Analyzers**

	Unit A NO	Unit A NO <sub>2</sub>	Unit B NO	Unit B NO <sub>2</sub>
<b>Pre-Shutdown Date:</b>	04/17/2000	<b>Time:</b>	15:15	
Pre-Shutdown Zero (ppm):	6	2	3	1
Pre-Shutdown Span (ppm):	3325	457	3264	455
<b>Post-Shutdown Date:</b>	04/18/2000	<b>Time:</b>	8:00	
Post-Shutdown Zero (ppm):	0	0	0	0
Post-Shutdown Span (ppm):	3117	458	3096	457

**Table 6-7. Pre- to Post-Test Differences as a Result of Interruption of Operation of Bacharach Model ECA 450 Analyzers**

Pre-Shutdown—Post-Shutdown	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Zero Difference (ppm)	6	2	3	1
Span Difference (ppm)	208	-1	168	-2

### 6.1.5 Interferences

Table 6-8 lists the data obtained in the interference tests. Table 6-9 summarizes the sensitivity of the analyzers to interferant species, based on the data from Table 6-8. The results in Table 6-8 use the average of the zero readings before and after the interferant exposure to calculate the extent of the interference.

Table 6-9 indicates that no significant interference effects from CO, CO<sub>2</sub>, NH<sub>3</sub>, HCs, and SO<sub>2</sub> were found. However, the response to 393 ppm NO was considerably reduced by the presence of 451 ppm SO<sub>2</sub>, indicating a relative sensitivity to SO<sub>2</sub> of about -9 to -10%. It should be noted that the vendor was not able to reproduce this effect in his own laboratories, using up to 500 ppm each of NO and SO<sub>2</sub>, and has observed no significant interference from SO<sub>2</sub> in the presence of NO with the ECA 450 analyzer.

**Table 6-8. Data from Interference Tests on Bacharach Model ECA 450 Analyzers**

Interferant Gas	Interferant, Conc. (ppm)	Response (ppm equivalent)			
		Unit A NO	Unit A NO <sub>2</sub>	Unit B NO	Unit B NO <sub>2</sub>
Zero		0	4	0	3
CO	496	0	3	0	2
Zero		0	2	0	2
CO <sub>2</sub>	5.03%	0	3	0	3
Zero		0	3	0	3
NH <sub>3</sub>	494	0	1	0	1
Zero		0	0	0	0
HCS	605	0	1	0	0
Zero		0	0	0	0
SO <sub>2</sub>	501	0	0	0	0
Zero		0	0	0	0
SO <sub>2</sub> + NO	451 + 393	354	1	347	1

**Table 6-9. Results of Interference Tests of Bacharach Model ECA 450 Analyzers**

Interferant	Unit A Response ppm (relative sensitivity, %)		Unit B Response ppm (relative sensitivity, %)	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
CO (496 ppm)	0	0%	0	0.1%
CO <sub>2</sub> (5.03%)	0	<0.01%	0	<0.01%
NH <sub>3</sub> (494 ppm)	0	-0.2%	0	-0.2%
HCS (605 ppm)	0	<0.2%	0	0
SO <sub>2</sub> (501 ppm)	0	0	0	0
SO <sub>2</sub> (451 ppm) + NO (393 ppm)	-8.6%	0.2%	-10.2%	0.2%

### 6.1.6 Pressure Sensitivity

Table 6-10 lists the data obtained in the pressure sensitivity test. Table 6-11 summarizes the findings from those data in terms of the ppm differences in zero and span readings at the different duct gas pressures, and the ccm differences in analyzer flow rates at the different duct gas pressures.

Tables 6-10 and 6-11 show that only very small changes in ECA 450 zero readings resulted from the changes in duct pressure, for both NO and NO<sub>2</sub>. The changes observed do not indicate any statistically significant effect of pressure on zero readings. In contrast, an effect of pressure was

seen on span responses for both NO and NO<sub>2</sub> with both ECA 450 analyzers. The effect was consistent, in that lower pressure produced lower response, for both species on both ECA 450 analyzers. The total difference in span responses between +8.5 and -8.5 in. H<sub>2</sub>O amounted to about 3.7 to 7.5% of the 3,000 ppm NO span value, and to about 8 to 14% of the 450 ppm NO<sub>2</sub> span value.

Tables 6-10 and 6-11 also show a substantial effect of pressure on the sample flow rates of the ECA 450 analyzers. The reduced pressure condition reduced the sample flow rates by only about 6 to 15% relative to the flows at ambient pressure. However, under the positive pressure condition, the flow rates of both units were more than doubled.

**Table 6-10. Data from Pressure Sensitivity Test for Bacharach Model ECA 450 Analyzers**

Pressure		Unit A NO	Unit A NO <sub>2</sub>	Unit B NO	Unit B NO <sub>2</sub>
Ambient	Flow rate (ccm)	804	804	774	774
	Zero (ppm)	0	0	0	0
	NO span (ppm)	3209	11	3163	10
	Zero (ppm)	0	1	0	1
	NO <sub>2</sub> span (ppm)	0	460	0	467
	Zero (ppm)	0	2	0	1
+8.5 in. H <sub>2</sub> O	Flow rate (ccm)	1766	1766	1696	1696
	Zero (ppm)	0	1	0	0
	NO span (ppm)	3318	11	3224	10
	Zero (ppm)	0	2	0	1
	NO <sub>2</sub> span (ppm)	0	475	0	500
	Zero (ppm)	0	2	0	2
-8.5 in. H <sub>2</sub> O	Flow rate (ccm)	691	691	730	730
	Zero (ppm)	0	2	0	1
	NO span (ppm)	3093	11	3112	11
	Zero (ppm)	0	3	0	1
	NO <sub>2</sub> span (ppm)	0	439	0	438
	Zero (ppm)	0	3	0	4

**Table 6-11. Pressure Sensitivity Results for Bacharach Model ECA 450 Analyzers**

		Unit A		Unit B	
		NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Zero	High–Ambient (ppm diff*)	0	0.667	0	0.333
	Low–Ambient (ppm diff)	0	1.667	0	1.333
	Significant Pressure Effect	N	N	N	N
Span	High–Ambient (ppm diff)	109	15	61	33
	Low–Ambient (ppm diff)	-116	-21	-51	-29
	Significant Pressure Effect	Y	Y	Y	Y
Flow Rate	High–Ambient (ccm diff*)		962		922
	Low–Ambient (ccm diff)		-113		-44

\*ppm or ccm difference between high/low and ambient pressures. The differences were calculated based on the average of the zero values.

### 6.1.7 Ambient Temperature

Table 6-12 lists the data obtained in the ambient temperature test with the Bacharach Model ECA 450 analyzers. Table 6-13 summarizes the sensitivity of the analyzers to changes in ambient temperature. This table is based on the data shown in Table 6-12, where the span values are 3,000 ppm NO and 450 ppm NO<sub>2</sub>.

Tables 6-12 and 6-13 show that the temperature variations in this test had no significant effect on the NO or NO<sub>2</sub> zero readings of either ECA 450 analyzer. The maximum change in any zero reading as a result of a change in temperature environment was 2 ppm. On the other hand, temperature did have a significant effect on the NO and NO<sub>2</sub> span responses of both ECA 450 analyzers. The effect was consistent between the two analyzers for NO<sub>2</sub>, with warmer environments giving higher span values. The total difference in span readings between cool and heated environments was 2 to 5% of the 450 ppm NO<sub>2</sub> span value. However, the effect was not consistent for NO. Unit A showed lower NO span responses in both cooled and heated environments than at room temperature, whereas Unit B showed lower response at higher temperatures and higher response at lower temperatures. These results do not strongly show a consistent temperature effect for NO, since the maximum difference between heated and cooled NO span responses (i.e., 66 ppm) is only about 2% of the 3,000 ppm NO span value.

**Table 6-12. Data from Ambient Temperature Test of Bacharach Model ECA 450 Analyzers**

Condition		Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)
(Room Temp.)					
Temp.	22.6°C (73°F)	0	0	0	1
	Zero	3248	20	3200	16
	NO span	0	2	0	3
	Zero	0	457	0	458
	NO <sub>2</sub> span				
(Heated)					
Temp.	38.9°C (102°F)				
	Zero	0	0	0	0
	NO span	3167	8	3230	8
	Zero	0	4	0	4
	NO <sub>2</sub> span	14	458	5	466
(Cooled)					
Temp.	7.3°C (45°F)				
	Zero	0	0	0	0
	NO span	3233	28	3265	23
	Zero	0	2	0	3
	NO <sub>2</sub> span	0	449	0	445
(Room Temp.)					
Temp.	23.2°C (74°F)				
	Zero	0	0	0	0
	NO span	3318	20	3285	17
	Zero	0	2	0	1
	NO <sub>2</sub> span	0	456	0	457

**Table 6-13. Ambient Temperature Effects on Bacharach Model ECA 450 Analyzers**

		Unit A		Unit B	
		NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Zero <sup>a</sup>	Heat–Room (ppm diff*)	0	1	0	0.75
	Cool–Room (ppm diff)	0	0	0	0.25
	Significant Temp Effect	N	N	N	N
Span <sup>a</sup>	Heat–Room (ppm diff)	-116	1.5	-12.5	8.5
	Cool–Room (ppm diff)	-50	-7.5	22.5	-12.5
	Significant Temp. Effect	Y	Y	Y	Y

<sup>a</sup> ppm difference between heated/cooled and room temperatures. The differences were calculated using the average of two recorded responses at room temperature (Table 6-12).

### 6.1.8 Zero/Span Drift

Zero and span drift were evaluated from data taken at the start and end of the linearity and ambient temperature laboratory tests. Those data are shown in Table 6-14, and the drift values observed are shown as pre- minus post-test differences in ppm in Table 6-15. The NO and NO<sub>2</sub> span values in these tests were 3,000 ppm and 450 ppm, respectively. Table 6-15 shows that zero drifts in these tests were 4 ppm or less for NO<sub>2</sub>, and 7 ppm or less for NO. Zero drifts were minimal in the temperature test, but were larger in the linearity test, probably because of the elevated zero readings caused by the exposures to high NO and NO<sub>2</sub> levels in the linearity test. Span drift was minimal for NO<sub>2</sub>, amounting to 6 ppm or less (about 1% of the 450 ppm span value) in the linearity test, and only 1 ppm in the ambient temperature test. Span drift for NO was also small, amounting to 30 ppm or less (1% of the 3,000 ppm NO span value) in the linearity test, and 70 to 85 ppm (2 to 3% of the span value) in the ambient temperature test.

**Table 6-14. Data from Linearity and Ambient Temperature Tests Used to Assess Zero and Span Drift of the Bacharach Model ECA 450 Analyzers**

Test		Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)
Linearity	Pre-Test Zero	2	0	1	0
	Pre-Test Span	3160	453	3167	453
	Post-Test Zero	9	2	6	4
	Post-Test Span	3190	457	3189	459
Ambient Temperature	Pre-Test Zero	0	2	0	3
	Pre-Test Span	3248	457	3200	458
	Post-Test Zero	0	2	0	1
	Post-Test Span	3318	456	3285	457

**Table 6-15. Zero and Span Drift Results for the Bacharach Model ECA 450 Analyzers**

Pre- and Post-Differences		Unit A		Unit B	
		NO (ppm)	NO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)
Linearity Test	Zero	-7	-2	-5	-4
	Span	-30	-4	-22	-6
Ambient Temperature Test	Zero	0	0	0	1.5
	Span	-70	1	-85	1



---

## 6.2 Combustion Source Tests

### 6.2.1 Relative Accuracy

Tables 6-16a through d list the measured NO, NO<sub>2</sub>, and NO<sub>x</sub> data obtained in sampling the four combustion sources. Note that the ECA 450 analyzers measure NO and NO<sub>2</sub>, and the indicated NO<sub>x</sub> readings are the sum of those data. On the other hand, the reference analyzers measure NO and NO<sub>x</sub>, with NO<sub>2</sub> determined by difference.

Table 6-17 displays the relative accuracy (in percent) for NO, NO<sub>2</sub>, and NO<sub>x</sub> of Units A and B for each of the four sources. Estimated standard errors are shown with the relative accuracy estimates. These standard error estimates were calculated under the assumption of zero true bias between the reference and test methods. If the bias is in fact non-zero, the standard errors underestimate the variability.

At the request of the Bacharach representative, the ECA 450 analyzers were calibrated before the source tests with 500 ppm NO and 150 ppm NO<sub>2</sub>. The analyzers were adjusted to those standards. The span gas concentrations listed in Table 3-3 were then provided to the analyzers before and after sampling of each respective combustion source, but no adjustment of the analyzers was made.

Table 6-17 shows that relative accuracy for NO ranged from 1.1 to 25.9% over both analyzers and all combustion sources, with better relative accuracy at higher concentrations. On the gas rangetop, the ECA 450 analyzers read about 1 to 1.5 ppm higher than the reference analyzers on the low NO levels present (about 6 ppm). Since the resolution of the ECA 450 analyzers is limited to 1 ppm, the degree of agreement at such a low NO level is good. A similar result is seen in Table 6-17 for NO<sub>2</sub>. The relative accuracy numbers range from 11.6 to 73% for NO<sub>2</sub>, with the best accuracy at the highest concentrations. On the gas rangetop and gas water heater, the NO<sub>2</sub> readings were higher than the reference readings, but almost always agreed with the reference data within the 1 ppm resolution of the analyzers. At the low NO<sub>2</sub> levels produced by these gas combustion sources, the relative accuracy calculation expands this small difference into large relative accuracy values. This is especially true for the gas rangetop, where the reference NO<sub>2</sub> values were only about 1.2 ppm.

The relative accuracy for NO<sub>x</sub> with the two ECA 450 analyzers ranged from 4.3 to 8.6% on all sources except the gas rangetop, for which relative accuracy values were 31 and 34%. As noted above, NO and NO<sub>2</sub> readings on this source were almost always within the 1 ppm resolution of the analyzers.

The unit-to-unit agreement of the two ECA 450 analyzers in source sampling was also good. For example, the differences between the average NO<sub>x</sub> values obtained by ECA 450 Units A and B on the four combustion sources ranged from 1.1 to 4.6%, relative to the average NO<sub>x</sub> values. These results were comparable to the unit-to-unit agreement of the reference analyzers, which ranged from 0.6 to 2.7%. With the diesel source, the agreement of the two ECA 450 analyzers was actually better than that of the two reference analyzers. These results indicate a high degree of consistency in the performance of the ECA 450 analyzers on combustion sources.

**Table 6-16a. Data from Gas Rangetop in Verification Testing of Bacharach Model ECA 450 Analyzers**

	Bacharach Analyzer Data						Reference Analyzer Data					
	Unit A			Unit B			Unit 100643			Unit 100647		
	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)
1	7	2	9	6	2	8	5.46	1.17	6.63	5.38	1.22	6.60
2	7	2	9	6	2	8	5.71	1.11	6.81	5.59	1.23	6.82
3	7	2	9	7	2	9	5.74	1.17	6.91	5.69	1.18	6.87
4	7	2	9	7	2	9	5.94	1.13	7.07	5.82	1.18	7.00
5	7	2	9	7	2	9	5.84	1.11	6.94	5.73	1.17	6.90
6	7	2	9	6	2	8	5.44	1.14	6.58	5.34	1.11	6.45
7	7	2	9	7	2	9	5.63	1.08	6.71	5.52	1.22	6.74
8	7	2	9	7	2	9	5.79	1.19	6.98	5.69	1.24	6.93
9	7	2	9	7	2	9	5.86	1.19	7.05	5.72	1.26	6.98

**Table 6-16b. Data from Gas Water Heater in Verification Testing of Bacharach Model ECA 450 Analyzers**

	Bacharach Analyzer Data						Reference Analyzer Data					
	Unit A			Unit B			Unit 100643			Unit 100647		
	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)
1	47	7	54	45	7	52	50.8	5.0	55.8	49.6	5.56	55.2
2	47	7	54	45	7	52	50.8	5.3	56.1	49.9	5.36	55.3
3	47	7	54	45	6	51	50.9	5.5	56.4	49.7	5.56	55.3
4	48	7	55	45	6	51	51.1	5.4	56.5	50.1	5.56	55.7
5	49	6	55	47	5	52	52.0	5.0	57.0	51.2	5.16	56.3
6	49	7	56	48	6	54	53.3	5.8	59.1	52.1	5.26	57.3
7	50	6	56	48	6	54	53.6	5.3	58.8	52.8	4.87	57.6
8	50	5	55	48	5	53	54.0	4.7	58.8	53.3	4.37	57.6
9	50	5	55	48	5	53	53.2	4.8	58.0	52.3	4.47	56.7

**Table 6-16c. Data from Diesel Generator at High RPM in Verification Testing of Bacharach Model ECA 450 Analyzers**

	Bacharach Analyzer Data						Reference Analyzer Data					
	Unit A			Unit B			Unit 100643			Unit 100647		
	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)
1	131	73	204	131	75	206	132.8	58.3	191.1	128.9	57.5	186.4
2	130	72	202	131	74	205	134.7	59.3	194.0	129.5	60.9	190.3
3	134	72	206	135	73	208	136.6	62.0	198.6	130.4	63.7	194.1
4	131	73	204	133	75	208	138.6	64.5	203.0	129.8	67.5	197.4
5	129	72	201	131	75	206	137.6	64.5	202.1	128.9	66.5	195.4
6	130	71	201	132	72	204	134.7	64.5	199.1	126.9	67.1	194.1
7	131	70	201	131	72	203	133.7	66.6	200.3	127.0	65.3	192.4
8	129	70	199	131	72	203	133.7	63.5	197.2	126.7	64.7	191.4
9	129	71	200	133	74	207	133.5	65.9	199.4	127.2	68.0	195.3

**Table 6-16d. Data from Diesel Generator at Idle in Verification Testing of Bacharach Model ECA 450 Analyzers**

	Bacharach Analyzer Data						Reference Analyzer Data					
	Unit A			Unit B			Unit 100643			Unit 100647		
	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)
1	210	113	323	202	113	315	213.2	97.8	310.9	202.5	101.3	303.8
2	224	109	333	219	110	329	214.1	97.8	311.9	206.4	98.3	304.7
3	228	106	334	219	107	326	216.1	96.7	312.8	207.4	98.3	305.7
4	227	108	335	224	109	333	219.0	98.8	317.8	210.3	98.3	308.6
5	227	111	338	223	112	335	217.1	99.9	317.0	210.3	97.3	307.6
6	226	105	331	221	106	327	225.8	98.8	324.6	215.1	99.3	314.4
7	224	107	331	220	107	327	225.8	99.9	325.7	215.1	99.3	314.4
8	230	108	338	231	109	340	224.8	96.7	321.5	216.1	98.3	314.4
9	227	105	332	224	105	329	220.9	97.8	318.7	211.2	99.3	310.6

**Table 6-17. Relative Accuracy of Bacharach Model ECA 450 Analyzers**

Source	Unit A			Unit B		
	NO (%)	NO <sub>2</sub> (%)	NO <sub>x</sub> (%)	NO (%)	NO <sub>2</sub> (%)	NO <sub>x</sub> (%)
Gas Rangetop (6 ppm NO, 1 ppm NO <sub>2</sub> ) <sup>c</sup>	25.928 <sup>a</sup> (0.831) <sup>b</sup>	73.111 (0.832)	33.752 (0.737)	22.966 (1.889)	73.111 (0.832)	31.118 (1.549)
Gas Water Heater (50 ppm NO, 5 ppm NO <sub>2</sub> )	6.682 (0.225)	30.322 (2.810)	4.290 (0.301)	10.519 (0.213)	23.032 (3.284)	8.551 (0.287)
Diesel Generator–High RPM (130 ppm NO, 65 ppm NO <sub>2</sub> )	1.954 (0.351)	16.488 (1.631)	4.944 (0.613)	1.084 (0.321)	19.544 (1.605)	6.427 (0.492)
Diesel Generator–Idle (220 ppm NO, 100 ppm NO <sub>2</sub> )	6.274 (0.635)	11.621 (0.737)	7.493 (0.501)	4.499 (0.741)	12.372 (0.764)	6.509 (0.580)

<sup>a</sup> Relative accuracy, percent relative to mean of two reference analyzers.

<sup>b</sup> Standard error of the relative accuracy value.

<sup>c</sup> Approximate NO and NO<sub>2</sub> levels from each source are shown; see Tables 6-16a through d.

### 6.2.2 Zero/Span Drift

Table 6-18 shows the data used to evaluate zero and span drift of the Bacharach Model ECA 450 analyzers from the combustion source tests.

Table 6-19 summarizes the zero and span drift results, showing that zero and span drift was never more than a few ppm in any of the combustion source tests, for either NO or NO<sub>2</sub>, with either analyzer. The zero drift values exceeded  $\pm 1$  ppm only once, for the NO response of Unit A with the diesel generator. These low drift values are comparable to the 1 ppm resolution of the analyzers. With the gas rangetop, the zero drift values correspond to 5% of the 20 ppm NO span and 10% of the NO<sub>2</sub> span value. With the gas water heater, the NO<sub>2</sub> zero drift is 7% of the 15 ppm NO<sub>2</sub> span value; and, for the diesel source at high RPM, the NO<sub>2</sub> zero drift is 2% of the 50 ppm NO<sub>2</sub> span value. All zero drift values with the diesel source are 1% of the corresponding span values.

The span drift values in Table 6-19 are similarly very small. Relative to the respective span values, the NO span drift was at most 5% of span (relative to the 20 ppm span value used with the rangetop), and the NO<sub>2</sub> span drift was at most 7% (relative to the 15 ppm span value used with the water heater).

**Table 6-18. Data Used to Assess Zero and Span Drift for Bacharach Model ECA 450 Analyzers on Combustion Sources**

Source		Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)
Gas Rangetop	Pre-Test Zero	0	1	0	0
	Pre-Test Span	17	10	17	10
	Post-Test Zero	1	0	0	0
	Post-Test Span	18	10	17	10
Gas Water Heater	Pre-Test Zero	0	1	0	1
	Pre-Test Span	95	17	93	17
	Post-Test Zero	0	0	0	0
	Post-Test Span	96	17	94	16
Diesel–High RPM	Pre-Test Zero	0	0	0	0
	Pre-Test Span	196	52	195	51
	Post-Test Zero	0	1	0	1
	Post-Test Span	196	50	197	49
Diesel–Idle	Pre-Test Zero	0	1	0	1
	Pre-Test Span	404	100	406	99
	Post-Test Zero	4	0	0	0
	Post-Test Span	407	97	406	95

**Table 6-19. Results of Zero and Span Drift Evaluation for Bacharach Model ECA 450 Analyzers**

	Pre-Test— Post-Test	Unit A		Unit B	
		NO (ppm)	NO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)
Gas Rangetop	Zero	-1	1	0	0
	Span	-1	0	0	0
Gas Water Heater	Zero	0	1	0	1
	Span	-1	0	-1	1
Diesel Generator—High RPM	Zero	0	-1	0	-1
	Span	0	2	-2	2
Diesel Generator—Idle	Zero	-4	1	0	1
	Span	-3	3	0	4

### 6.2.3 Measurement Stability

Table 6-20 shows the data obtained in the extended sampling test, in which the Bacharach Model ECA 450 and reference analyzers sampled diesel emissions for a full hour without interruption or sampling of ambient air. Table 6-21 shows the results of this evaluation in terms of the slopes and standard errors of the NO, NO<sub>2</sub>, and NO<sub>x</sub> data with time. Also shown in Table 6-21 is an indication of whether the slopes observed by the ECA 450 analyzers differed from those observed by the reference analyzers.

Table 6-21 shows that both the ECA 450 analyzers and the reference analyzers determined decreasing trends in NO, NO<sub>2</sub>, and NO<sub>x</sub> during the extended sampling of the diesel source. The trends indicated by both ECA 450 analyzers for NO and for NO<sub>x</sub> in the diesel sampling were not significantly different from those indicated by the reference analyzers. The trends determined for NO<sub>2</sub> by the two ECA 450 analyzers were significantly different from those determined by the reference analyzers. However, the difference in the NO<sub>2</sub> trends was very small. The NO<sub>2</sub> slopes determined by ECA 450 Units A and B were -0.211 ppm/min (-12.7 ppm/hr) and -0.193 ppm/min (-11.6 ppm/hr), respectively, compared to the reference analyzer trend of -0.145 ppm/min (-8.7 ppm/hr). Thus, over a one-hour period, the different trends resulted in a 4 ppm or less deviation from the trend of the reference analyzers, or about 4% of the NO<sub>2</sub> level in the diesel exhaust.

### 6.2.4 Inter-Unit Repeatability

The repeatability of test results between the two ECA 450 analyzers was assessed in those cases where the data lent themselves to application of a t-test. The resulting t-statistics and associated p-values are listed in Table 6-22. Highlighted in bold are those p-values less than 0.05, which indicate a statistically significant difference between the two ECA 450 units at

**Table 6-20. Data from Extended Sampling Test with Diesel Generator at Idle, Using Bacharach Model ECA 450 Analyzers**

	Bacharach Analyzer Data						Reference Analyzer Data					
	Unit A		Unit B		Unit 100643		Unit 100647		Unit 100643		Unit 100647	
	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)
1	222	110	332	221	111	332	211.2	96.7	307.9	204.5	99.3	303.8
2	216	108	324	213	109	322	213.2	96.7	309.9	204.5	98.3	302.8
3	213	105	318	212	107	319	208.3	97.8	306.1	201.6	95.3	296.9
4	202	104	306	199	105	304	206.4	97.8	304.2	200.6	94.3	294.9
5	215	108	323	216	109	325	199.6	94.5	294.1	194.8	94.3	289.1
6	203	106	309	203	108	311	207.4	96.7	304.0	200.6	96.3	296.9
7	212	109	321	209	110	319	197.7	94.5	292.2	189.9	98.3	288.2
8	207	106	313	203	107	310	199.6	96.7	296.3	189.9	96.3	286.3
9	198	104	302	194	106	300	198.6	92.4	291.0	188.0	99.3	287.3
10	216	105	321	210	107	317	197.7	98.8	296.5	189.9	99.3	289.2
11	208	104	312	204	106	310	197.7	94.5	292.2	190.9	96.3	287.2
12	219	108	327	216	109	325	207.4	95.6	303.0	198.6	100.3	299.0
13	220	103	323	214	104	318	206.4	101.0	307.4	198.6	98.3	297.0
14	224	105	329	219	105	324	210.3	96.7	307.0	203.5	96.3	299.8
15	221	108	329	215	108	323	211.2	97.8	309.0	203.5	99.3	302.8
16	208	105	313	201	106	307	202.5	96.7	299.2	194.8	97.3	292.1
17	220	107	327	215	103	318	202.5	96.7	299.2	196.7	96.3	293.0
18	205	99	304	205	99	304	203.5	93.5	297.0	194.8	94.3	289.1
19	223	105	328	216	106	322	206.4	94.5	300.9	198.6	96.3	295.0
20	205	105	310	200	106	306	197.7	96.7	294.4	189.9	95.3	285.3
21	216	107	323	211	108	319	194.8	94.5	289.3	187.0	97.3	284.3
22	210	106	316	206	102	308	202.5	95.6	298.1	194.8	97.3	292.1
23	211	105	316	205	107	312	197.7	95.6	293.3	189.0	95.3	284.3
24	202	104	306	199	105	304	198.6	97.8	296.4	19.4	96.3	115.7
25	197	103	300	197	105	302	185.1	92.4	277.5	175.4	98.3	273.7
26	205	107	312	203	108	311	194.8	98.8	293.6	189.0	95.3	284.3
27	208	104	312	201	106	307	192.8	93.5	286.3	184.1	92.4	276.5
28	206	105	311	203	108	311	195.7	91.3	287.1	188.0	95.3	283.3
29	198	105	303	193	106	299	190.9	98.8	289.7	183.1	102.3	285.4
30	194	103	297	191	106	297	187.0	94.5	281.6	179.3	97.3	276.6

**Table 6-20. Data from Extended Sampling Test with Diesel Generator at Idle, Using Bacharach Model ECA 450 Analyzers  
(continued)**

	Bacharach Analyzer Data				Reference Analyzer Data				
	Unit A		Unit B		Unit 100643		Unit 100647		
	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)
31	191	101	292	188	102	290	188.0	94.5	282.5
32	191	100	291	193	103	296	180.2	91.3	271.5
33	194	104	298	198	106	304	187.0	97.8	284.8
34	187	102	289	183	103	286	177.3	95.6	272.9
35	198	104	302	190	106	296	174.4	93.5	267.9
36	190	99	289	185	101	286	175.4	95.6	271.0
37	197	103	300	191	105	296	171.5	93.5	265.0
38	195	104	299	188	104	292	181.2	97.8	279.0
39	189	101	290	187	102	289	164.7	95.6	260.3
40	196	103	299	198	106	304	186.0	95.6	281.7
41	184	99	283	180	99	279	184.1	93.5	277.6
42	192	101	293	193	103	296	182.2	93.5	275.6
43	191	108	299	185	110	295	184.1	96.7	280.8
44	181	97	278	176	99	275	176.4	95.6	272.0
45	184	103	287	180	104	284	171.5	91.3	262.8
46	177	93	270	171	95	266	167.6	90.2	257.9
47	187	100	287	184	102	286	166.7	90.2	256.9
48	185	96	281	177	97	274	176.4	91.3	267.7
49	179	94	273	175	96	271	168.6	87.0	255.6
50	193	97	290	187	99	286	175.4	87.0	262.4
51	178	94	272	176	95	271	172.5	90.2	262.7
52	193	96	289	186	99	285	166.7	87.0	253.7
53	187	96	283	175	97	272	189.9	87.0	276.9
54	182	95	277	173	96	269	164.7	89.2	253.9
55	178	95	273	180	98	278	181.2	79.5	260.7
56	187	95	282	182	96	278	171.5	93.5	265.0
57	188	97	285	182	98	280	173.4	89.2	262.6
58	183	101	284	178	103	281	176.4	91.3	267.7
59	177	95	272	172	97	269	177.3	89.2	266.5
60	173	95	268	176	97	273	167.6	87.0	254.7



**Table 6-21. Results of Evaluation of Measurement Stability for Bacharach Model ECA 450 Analyzer**

	Unit A			Unit B			Reference Units		
	NO	NO <sub>2</sub>	NO <sub>x</sub>	NO	NO <sub>2</sub>	NO <sub>x</sub>	NO	NO <sub>2</sub>	NO <sub>x</sub>
Slope (Std Err)	-0.689 (0.053)	-0.211 (0.020)	-0.900 (0.064)	-0.716 (0.050)	-0.193 (0.021)	-0.909 (0.060)	-0.681 (0.091)	-0.145 (0.019)	-0.825 (0.094)
Difference in Slopes (ppm/min) (Std Err)	-0.008 (0.092)	-0.067 (0.019) <sub>a</sub>	-0.075 (0.097)	-0.035 (0.092)	-0.049 (0.022) <sub>a</sub>	-0.084 (0.098)	---	---	---

<sup>a</sup> Statistically significant difference in slope between test unit and the average of the reference units at the 5% significance level.

**Table 6-22. Summary of Repeatability**

Unit A vs. Unit B			NO	NO <sub>2</sub>	NO <sub>x</sub>
Linear Regression	Intercept	t-statistic	0.685	-1.668	---
		p-value <sup>a</sup>	0.509	0.126	---
	Slope	t-statistic	-0.200	1.003	---
		p-value	0.845	0.339	---
Detection Limit		t-statistic	0.743	-0.750	---
		p-value	0.464	0.459 <sub>b</sub>	---
Relative Accuracy	Gas Rangetop	t-statistic	2.000		2.000
		p-value	0.081	-	0.081
	Gas Water Heater	t-statistic	12.000	2.530	10.094
		p-value	<b>&lt;0.001</b>	<b>0.035</b>	<b>&lt;0.001</b>
	Generator–High RPM	t-statistic	3.776	8.485	6.400
		p-value	<b>0.005</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>
Generator–Idle	t-statistic	4.566	4.000	3.738	
	p-value	<b>0.002</b>	<b>0.004</b>	<b>0.006</b>	
Measurement Stability	Slope	t-statistic	1.170	-1.960	0.330
		p-value	0.248	0.054	0.746

<sup>a</sup> p-value <0.05 indicates that two test units are statistically different at the 5% significance level (in bold text).

<sup>b</sup> Unit A and Unit B indicated exactly the same NO<sub>2</sub> readings on the gas burner emission. No matched-pairs t-statistic was calculated.

---

the 95% confidence level. As Table 6-22 shows, significant differences were found only in relative accuracy.

The differences found indicate the variability that may be expected from one analyzer to the next. Although some statistically significant differences were found, the practical importance of these differences is often small. Considering the relative accuracy results (Table 6-17), it is apparent that statistically significant differences may exist even when the two analyzers are equally applicable to the measurement at hand. For example, the relative accuracy result for NO for Unit A on the diesel at high RPM is 1.95%, whereas that for Unit B is 1.08%. These results may differ significantly in the statistical sense, but either unit would be more than adequate for determining NO emissions from that source. The fine degree of discrimination provided by the statistical tests should not obscure the fact that the two ECA 450 analyzers essentially worked equally well throughout the verification tests.

### **6.3 Other Factors**

In addition to the performance characteristics evaluated in the laboratory and combustion source tests, three additional factors were recorded: analyzer cost, data completeness, and maintenance/operational factors.

#### **6.3.1 Cost**

The ECA 450 analyzers as tested in this verification test included all options and have a list price of \$14,300. An ECA 450 with only NO and NO<sub>2</sub> capabilities and the Peltier cooler moisture removal system has a list price of \$10,250.

#### **6.3.2 Data Completeness**

The data completeness in the verification tests was 100% for both ECA 450 analyzers.

#### **6.3.3 Maintenance/Operational Factors**

The short duration of the verification test prevented assessment of long-term maintenance costs, durability, etc. However, no maintenance of any kind was required on the ECA 450 analyzers in this test. The analyzers appeared to be rugged, and setup time was about 1/2 hour. The rapid response time and stability of the analyzers allowed verification testing to proceed smoothly.

---

## Chapter 7

### Performance Summary

The Bacharach ECA 450 analyzers provided linear response for NO<sub>2</sub> over the tested range of 0 to 450 ppm. Response for NO was linear over the range of 0 to 1,000 ppm, but showed a slight upward curvature in response above that range. Over the full tested range of 0 to 3,000 ppm NO, the regression slope of NO response was approximately 1.05. Detection limits estimated from these wide-range linearity tests were 8 to 11 ppm for NO and 3 to 4 ppm for NO<sub>2</sub>. However, these detection limits probably were influenced by the high levels of NO and NO<sub>2</sub> used in the linearity tests. Combustion source tests indicated detection capabilities comparable to the 1 ppm measurement resolution of the analyzers. Response times were about 28 seconds for NO and about 56 seconds for NO<sub>2</sub>.

Drift in ECA 450 zero readings before and after laboratory and combustion source tests was within  $\pm 2$  ppm in nearly all circumstances. Span drift for NO<sub>2</sub> was always 1% or less, relative to a 450 ppm NO<sub>2</sub> span gas. Span drift for NO was usually less than 1% relative to the 3,000 ppm NO span gas, and exceeded 5% only after an overnight shut down, following exposure to high NO levels in the linearity test. No interference was found from any of the following: 496 ppm CO; 5.03% CO<sub>2</sub>; 494 ppm NH<sub>3</sub>; 605 ppm of total hydrocarbons; and 501 ppm of SO<sub>2</sub>. In the presence of 451 ppm SO<sub>2</sub>, the analyzers' response to 393 ppm NO was reduced to about 350 ppm.

Over the tested range of + 8.5 to - 8.5 in. H<sub>2</sub>O, sample gas pressure had no effect on ECA 450 zero readings, but did have a significant effect on span readings. The total difference in span responses over this pressure range amounted to 3.7 to 7.5% of the 3,000 ppm NO span value and to 8 to 14% of the 450 ppm NO<sub>2</sub> span value, with higher pressures producing higher response. This finding may be related to the effect of pressure on ECA 450 sample flow rates: reduced pressure lowered the sample flow rates by 6 to 15%, relative to those at ambient pressure, but positive pressure nearly doubled the flow rates of both ECA 450 units. Variations in ambient temperature over the range of 45 to 102 °F had no effect on ECA 450 zero readings, and caused differences in span readings of at most a few percent.

In cases where NO or NO<sub>2</sub> were present at levels below 6 ppm, the ECA 450 analyzers were accurate to within about their 1 ppm measurement resolution. For the balance of the measurements, the relative accuracies of the ECA 450 analyzers were 1 to 20% for NO and NO<sub>2</sub> and 4.3 to 8.6% for NO<sub>x</sub>. Unit-to-unit agreement of the two ECA 450 analyzers for NO<sub>x</sub> from combustion sources ranged from 1.1 to 4.6% and was, in some cases, better than that of the two reference analyzers. Comparison of verification results from the two ECA 450 analyzers showed only a

---

slight difference in relative accuracy, and the overall performance of the two analyzers was essentially identical.

---

## Chapter 8

### References

1. *Test/QA Plan for Verification of Portable NO/NO<sub>2</sub> Emission Analyzers*, Version 2.0, Battelle, Columbus, Ohio, August 1999.
2. *U.S. EPA Method 7E Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)* Code of Federal Regulations, 40 CFR, Ch 1, Part 60, Appendix A (1991).
3. *Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors: Protocol Number 1*, Research Triangle Park, NC: U.S. Environmental Protection Agency, Quality Assurance Division, June 1978.
4. *Interlaboratory Program to Validate a Protocol for the Measurement of NO<sub>2</sub> Emissions from Rangetop Burners*, GRI-94/0458, Gas Research Institute, Chicago, Illinois, December 1994.
5. *Interlaboratory Study to Determine the Precision of an Emission Measurement Protocol for Residential Gas Water Heaters*, GRI-96-0021, Gas Research Institute, Chicago, Illinois, March 1996.
6. American National Standards (ANSI Z21.1) "Household Cooking Gas Appliances," American National Standards Institute, 24th Edition, American Gas Association, 1990.
7. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Pilot*, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, September 1998.
8. *Portable NO<sub>x</sub> Analyzer Evaluation for Alternative Nitrogen Oxide Emission Rate Determination at Process Units*, Source Testing and Engineering Branch, South Coast Air Quality Management District, Los Angeles, CA, September 21, 1994.
9. *U.S. EPA Method 5, Determination of Particulate Emissions from Stationary Sources*, Code of Federal Regulations, 40 CFR, Ch. 1, Part 60, Appendix A (1991).

- 
10. *Determination of Nitrogen Oxides, Carbon Monoxide, and Oxygen Emissions from Natural Gas-Fired Engines, Boilers, and Process Heaters Using Portable Analyzers*, Conditional Test Method (CTM)-030, U.S. EPA, Office of Air Quality Planning and Standards, Emission Measurement Center, October 13, 1997.