

US EPA ARCHIVE DOCUMENT

July 1999

# Environmental Technology Verification Report

## ECOM A-PLUS PORTABLE EMISSION ANALYZER

Prepared by



Battelle Memorial Institute

Under a cooperative agreement with



U.S. Environmental Protection Agency

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July 1999

# Environmental Technology Verification Report

Advanced Monitoring Systems

## ECOM A-PLUS Portable Emission Analyzer

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## Notice

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## 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 Memorial Institute 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 Joseph Tabor, Steve Speakman, and Joshua Finegold of Battelle, and Drew Wilson and Brock Pulliam of ECOM America, Ltd.

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## List of Abbreviations

AC	alternating current
AMS	Advanced Monitoring Systems
ANSI	American National Standards Institute
Btu/hr	British thermal unit per hour
ccm	cubic centimeter per minute
CEMS	continuous emission monitoring system
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
DC	direct current
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FID	flame ionization detector
ft <sup>3</sup>	cubic feet
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
rms	root-mean-square
RPM	revolutions per minute
SAS	Statistical Analysis System

SCAQMD	South Coast Air Quality Management District
SCR	selective catalytic reduction
SO <sub>2</sub>	sulfur dioxide
UHP	ultra-high purity

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## 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 Memorial Institute, operate the Advanced Monitoring Systems (AMS) program under ETV. The AMS program 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 ECOM A-PLUS Portable Emission Analyzer.

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## Chapter 2 Technology Description

The objective of the ETV Advanced Monitoring Systems pilot 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 ECOM A-PLUS electrochemical NO and NO<sub>2</sub> analyzer, manufactured by ECOM America, Ltd., Norcross, Georgia. The following is a description of the ECOM A-PLUS analyzers, based on information provided by the vendor.

The ECOM A-PLUS (Figure 2-1) is a portable, microprocessor controlled, electrochemical sensor-based emission analyzer. The ECOM A-PLUS can be fitted with up to five separate gas sensors to measure oxygen, carbon monoxide, oxides of nitrogen (NO and NO<sub>2</sub>), and sulfur dioxide. The A-PLUS measures 21" x 10" x 11.8" and weighs 30 pounds.

The ECOM A-PLUS is designed for a variety of applications: boiler/burner flue gas analysis; engine emissions analysis; pollution source testing; and environmental reporting of stack gas parameters, among others. Measuring ranges are oxygen (O<sub>2</sub>), 0.0 percent to 21.0 percent; carbon monoxide (CO), 0 to 4,000 ppm and/or 0 to 40,000 ppm; nitric oxide (NO), 0 to 4,000 ppm; nitrogen dioxide (NO<sub>2</sub>), 0 to 500 ppm; and sulfur dioxide (SO<sub>2</sub>), 0 to 4,000 ppm. The A-PLUS also measures gas and ambient temperatures and stack draft (pressure) and will perform a standardized smoke test. The calculated parameters include carbon dioxide (CO<sub>2</sub>), combustion efficiency, excess air, and losses. Only the NO and NO<sub>2</sub> measurement capabilities were verified in the tests reported here.



Figure 2-1. ECOM A-PLUS

An on-board printer allows hard copy printing of vital stack parameters, while an RS232 interface provides the option to store the data to a computer. Windows-based data acquisition software is available. The A-PLUS incorporates a sample conditioning system that includes a heated sample line, heated probe head, peltier cooler, and moisture removal assembly. This system cools and dries the gas sample, providing the gas sensors with a stable sample of gas (i.e., temperature/humidity), to aid the long-term stability and reliability of the instrument.

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Designed for semi-continuous operation, the ECOM A-PLUS is not recommended for continuous gas emission measurement.

In all verification testing reported here, two ECOM A-PLUS analyzers, designated as units A and B, were operated simultaneously. The performance of each analyzer was verified independently; however, results from the two analyzers were compared to assess unit-to-unit repeatability.



## Chapter 3 Test Design and Procedures

### 3.1 Introduction

The verification test described in this report was conducted in January and February 1999 on commercial portable nitrogen oxides analyzers. The tests were 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 for the ECOM A-PLUS tests is shown in Table 3-1.

**Table 3-1. Identity and Schedule of Verification Tests Conducted on ECOM A-PLUS Analyzers**

Test Activity	Date Conducted
Laboratory Tests	
Linearity*	January 17, 1999, p.m. and February 19, 1999, a.m.
Interrupted Sampling	January 17, p.m. to January 18, a.m.
Interferences	January 18, a.m.
Pressure Sensitivity	January 18, a.m.
Ambient Temperature*	February 18, p.m.
Source Tests	
Gas Rangetop	February 17, a.m.
Gas Water Heater	February 17, a.m.
Diesel Generator High RPM	February 19, a.m.
Diesel Generator–Idle	February 19, a.m.

\* The ECOM analyzers were damaged due to an overheating of the test chamber during the high temperature test on January 18, 1999; this test and the source tests were completed February 17-19, after repairing the analyzers. A repeat of the linearity test was also conducted at that time over reduced ranges for NO and NO<sub>2</sub>.

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To assess inter-unit variability, two identical ECOM A-PLUS 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 ECOM 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 ECOM 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. Copies of the blank data recording sheets used by Battelle and vendor staff are included as Appendix A of this report.

Verification testing began with ECOM 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> Upon completion of laboratory tests, the analyzers were moved to 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 combustion source exhausts vented through the roof of the test facility. 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 ECOM 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 ECOM A-PLUS analyzers were 0 to 4,000 ppm for NO and 0 to 500 ppm for NO<sub>2</sub>. These nominal ranges exceed the actual NO or NO<sub>2</sub> concentrations likely to be emitted from most combustion sources. Nevertheless, the lab 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 percent 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 019660) was 493.2 ppm. These concentrations were confirmed in a

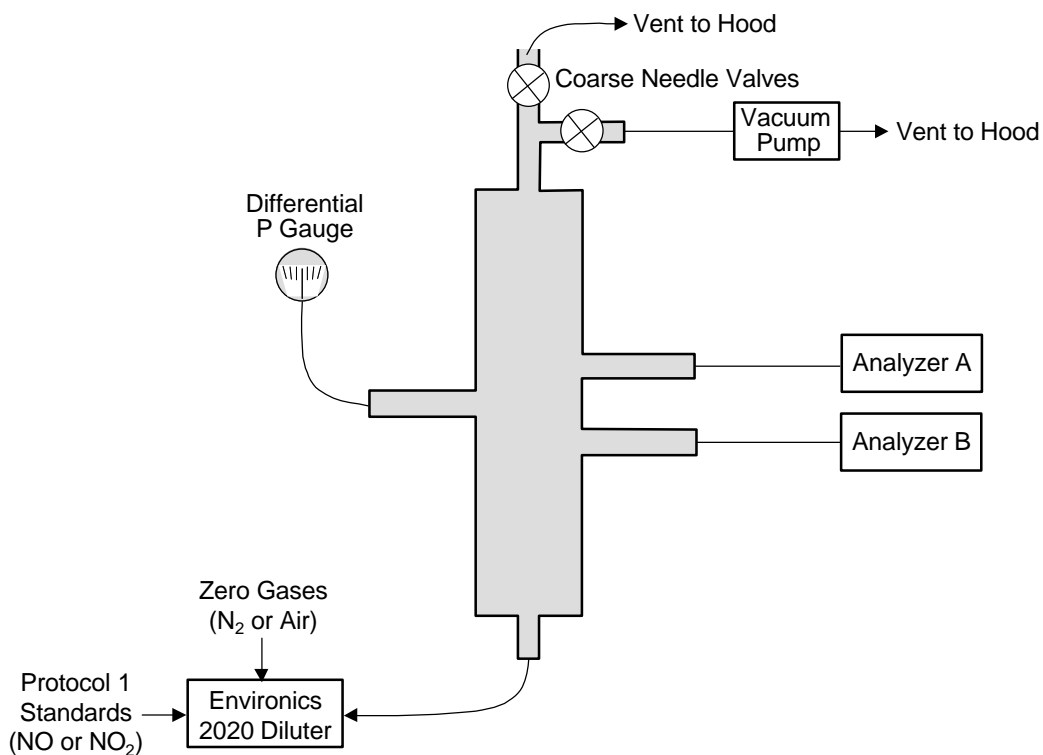
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performance evaluation audit conducted near the end of the verification tests by comparison with independent standards obtained from other suppliers.

The gas dilution system used was an Environics Model 2020 mass flow controlled diluter (Serial Number 2108). 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 front panel keypad of the 2020 diluter, and the diluter then set the required standard and diluent flow rates to produce the desired mixture. The 2020 diluter indicated on its front panel 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 2020 diluter also provided warnings if a flow controller was being operated at less than 10 percent 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 percent purity, and to have the following maximum content of specific impurities:  $\text{SO}_2 < 0.1$  ppm,  $\text{NO}_x < 0.1$  ppm,  $\text{CO} < 0.5$  ppm,  $\text{CO}_2 < 1$  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 percent oxygen.

Laboratory testing was conducted primarily by supplying known gas mixtures to the analyzers from the Environics 2020, 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 2020 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 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,



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

gas standards of the appropriate concentrations were supplied directly to the manifold, without use of the EnviroNics 2020 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.

### 3.2.1 Linearity

The linearity of analyzer response was tested by wide-range multipoint calibrations with NO and NO<sub>2</sub>. Linearity testing consisted of a 21-point response check for NO, and for NO<sub>2</sub>. Prior to this check, the ECOM analyzers were provided with the appropriate zero gas, and then with an NO or NO<sub>2</sub> span gas concentration near the respective nominal full scale of the analyzers (i.e., near 4,000 ppm NO or 500 ppm NO<sub>2</sub>). The actual values of the span gases provided were 3,925 ppm NO and 493.2 ppm NO<sub>2</sub>. After adjustments to the analyzers to accurately match that span value, the 21-point check proceeded without further adjustments. The 21 points consisted of three replicates each at 10, 20, 40, 70, and 100 percent 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 percent 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> were supplied to the analyzers. This procedure provided data to assess the cross-sensitivity to NO and NO<sub>2</sub>.

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When the ECOM analyzers were returned to complete the verification testing, a second linearity test was conducted at the request of ECOM. This second test covered ranges of 1,000 ppm NO and 200 ppm NO<sub>2</sub>, but was otherwise identical to the 21-point procedure described above.

### **3.2.2 Detection Limit**

Data from zero gas and from 10 percent 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 percent of the respective full scale (i.e., about 2,100 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 percent 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 ECOM 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., 3,925 ppm NO and 493.2 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 ECOM 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 single components, 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> mixtures 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  $\pm 2$  percent, based on analysis. The CO, CO<sub>2</sub>, and NH<sub>3</sub> mixtures were all in Ultra-High Purity (UHP) air, and the SO<sub>2</sub> mixture was in UHP nitrogen. The SO<sub>2</sub>/NO mix listed in Table 3-2 was prepared by diluting the SO<sub>2</sub> standard with the NO Protocol Gas using the Environics 2020.

**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*	485 ppm C <sub>1</sub> , 98 ppm C <sub>2</sub> , 48 ppm C <sub>3</sub> + C <sub>4</sub>
SO <sub>2</sub> and NO	451 ppm SO <sub>2</sub> + 388 ppm NO

\* C<sub>1</sub> = methane; C<sub>2</sub> = ethane; and C<sub>3</sub> + C<sub>4</sub> = 24 ppm propane + 24 ppm n-butane.

The hydrocarbon mixture 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 standard containing 8.61 ppm carbon (ppmC) in the form of propane. Using a gas chromatograph with a flame ionization detector (FID) the NIST standard was first analyzed twice, producing peak areas of 18,627 and 18,791 area units per 8.61 ppmC of propane. The average FID response factor (18,709 units ( $\pm$  116 units)/8.61 ppmC) was then used to determine the concentrations of the components of the prepared hydrocarbon mixture. Two analyses of that mixture both gave a result of 485 ppm methane; the corresponding results for ethane were 97 and 98 ppm; for propane 23 and 24 ppm; and for n-butane 24 and 25 ppm.

In the interference test, each interferant in Table 3-2 was provided individually to the sampling manifold shown in Figure 3-1, 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 dilution system. 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 (Ultra Flow Primary Gas Flow Calibrator, Model 709, Serial No. 010928;



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SKC, Inc.). 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 -10 inches of water relative to the room, and the analyzer's flow rate was measured again. The manifold pressure was adjusted to +10 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 equivalent to about 70 percent of the respective full scale, at each of the same manifold pressures (room pressure, -10 inches, and +10 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. The actual NO and NO<sub>2</sub> span concentrations used were 2,600 ppm and 350 ppm, respectively.

### *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 700 ppm and 140 ppm concentrations, respectively) at room, elevated, and reduced temperatures. A temperature range of 7 to 41 °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, thermostated at 105 °F using external heat lamps. The reduced temperature condition was achieved using a conventional domestic refrigerator (Crosley Model CT19A5W) with a refrigerator volume of 13.1 ft<sup>3</sup>.

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 stabilization period, the zero and span checks were repeated a final time.

In conducting the ambient temperature test on the ECOM analyzers, the analyzers were inadvertently damaged due to accidental overheating in the heated chamber. After being repaired at ECOM, the analyzers were returned to Battelle to complete the verification testing, and the ambient temperature test was repeated in its entirety.

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### 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 nearly 500 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 4 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. Their purpose was 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 percent methane, 3 percent 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 70 ppm, and NO<sub>2</sub> in the range of 5 to 10 ppm. NO<sub>x</sub> emissions dropped as the water temperature rose after ignition, stabilizing at the



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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 accommodate various sizes of 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 (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 generated NO<sub>x</sub> emissions over a range of about 150 to 450 ppm, depending on the load on the super-charged engine. High load (3,500 RPM) resulted in the lowest NO<sub>x</sub>; idle (2,000 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>. The database on the diesel generator emissions was generated in tests conducted in the 2 weeks prior to the start of the verification tests.

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 U.S. 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 percent 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.

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### 3.3.2.1 Sampling Systems

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

The reference analyzer probe consisted of a 26-inch long, 1/4-inch diameter stainless-steel tube, the upstream 2 inches of which were bent at a right angle for passage into the center of the source exhaust duct. Each combustion source had a dedicated sampling probe, connected to the reference analyzers with 1/4-inch tubing. The lengths of sample-transfer tubing required to connect vendor instruments to the rangetop, water heater, and diesel engine were about 4 feet, 4 feet, and 8 feet, respectively. The lengths of sample-transfer tubing required to connect reference instruments to the rangetop, water heater, and diesel engine were about 7 feet, 9 feet, and 4 feet, respectively.

The ECOM analyzers were operated during source testing with their integral sample transfer lines and sampling filtering and drying devices. 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 ice bath (0°C, 32°F). The reference particulate-removal system consisted of a 47-millimeter in-line quartz filter.

### 3.3.2.2 Reference Method

The reference method of NO determination 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 a Model 10 and a Model 14A source-level NO<sub>x</sub> monitor (both from Thermo Environmental Instruments), located side-by-side near the combustion sources. These monitors sampled from a common intake line and operated on identical ranges of 100 ppm or 1,000 ppm full scale, depending on the source. Both instruments use stainless steel catalytic converters maintained at 650°C (1,202°F) for reduction of NO<sub>2</sub> to NO for detection. Digital electronic voltmeters were connected directly to the amplifier output of the monitors, to provide direct digital display of the data. The Model 10 and 14A monitors provide sequential, rather than simultaneous, measurement of NO and NO<sub>x</sub>, so display of both readings required manual switching of sampling modes on both instruments. This requirement resulted in the NO and NO<sub>x</sub> readings from the reference analyzers being separated in time by about 15 seconds, due to the stabilization needed after switching. This effect is believed to have negligible impact on the verification results due to the stability of source emissions.

The chemiluminescence analyzers were calibrated using the EnviroNics Series 100 and the EPA Protocol 1 gases. The calibration procedure was specified in the test/QA plan, and required calibration at zero, 30 percent, 60 percent, and 100 percent of the applicable range value (i.e., 100 or 1,000 ppm). Calibration results closest in time to the verification 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 ECOM source tests,

which took place on February 17 and 19, 1999, calibration data from February 16 were applied. Conversion efficiency values of 94.5 percent and 94.1 percent were found for the Model 14A and Model 10 monitors, respectively, and all reference analyzer results were corrected to account for these conversion efficiencies.

### 3.3.2.3 Calibration Gas Supply

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 100 Computerized Multi-Gas Calibrator (Serial Number 2416). The same Acid Rain CEM zero gases were used for dilution and zeroing as were used in the laboratory tests. When low dilution ratios were required for some calibration points, Tylan FC-260 (3 lpm) and FC-280 (5 lpm) mass flow controllers were used instead of the Environics calibrator. The Tylan flow controllers were calibrated using the same SKC electronic bubble flow meter used in the laboratory tests, and were operated with a Tylan four-unit control and readout device. The pre- and post-test span values used with each combustion source are given in Table 3-3.

At the request of the ECOM representative, the ECOM analyzers were calibrated before any source testing using 50 ppm NO and 30 ppm NO<sub>2</sub> standards, prepared as described above. No adjustment was made to the ECOM analyzers when sampling the span gas indicated in Table 3-3 for the two gas combustion sources.

**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 reference and 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

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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 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 ECOM 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.

One addition to this procedure was the extended sampling test, conducted as the last operation in the combustion source testing. This test 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 test was conducted only after nine sequential sets of readings had been obtained from all the combustion sources by the procedure described above.

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## Chapter 4

### Quality Assurance/Quality Control

Quality control (QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS pilot<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 pilot 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 and approved them by adding his signature and date. Laboratory record notebooks were also reviewed, signed, and dated by the Verification Testing Leader.

Other data review focused upon the compliance of the chemiluminescent 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 analyzers undergoing verification. 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, availability of Battelle personnel and equipment, and other changes or improvements. Any deviation required the approval signature of Battelle's Verification Testing Leader and the pilot manager. A planned deviation form was used for documentation and approval of the following changes:

1. Dr. Agnes Kovacs did not participate in the statistical analysis of data from the verification test.
2. The order of testing was changed, and a span value of 70 percent of range (rather than 100 percent) was used in the pressure sensitivity test.
3. The order of the ambient temperature test was changed.
4. The exact concentrations used in the mixture of SO<sub>2</sub> and NO for the interference test were changed.
5. A different diesel generator was used than that originally planned.
6. An oxygen sensor was not used during source tests.

7. Thermo Environmental Models 14A/10 NO/NO<sub>x</sub> analyzers were used for reference method.
8. Triplicate calibration points were not run on reference method analyzers.
9. Unheated sample line and tubing were used, based on Battelle's previous experience in sampling of the combustion sources used in this test and other similar sources.

**Table 4-1. Results of QC Procedures for Reference NO<sub>x</sub> Analyzers for Testing ECOM A-PLUS Analyzers**

NO <sub>2</sub> conversion efficiency	94.5% for Model 14A in 100 ppm and 1,000 ppm ranges						
NO <sub>2</sub> conversion efficiency	94.1% for Model 10 in 100 ppm and 1,000 ppm ranges						
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 10		Unit 14A			
		NO		NO			
		Error, % of Span	% of Scale	Error, % of Span	% of Scale		
		0.3%	30%	0.6%	30%		
		0.1%	60%	<0.1%	60%		
		NO <sub>2</sub>		NO <sub>2</sub>			
		Error, % of Span	% of Scale	Error, % of Span	% of Scale		
		0.3%	30%	0.1%	30%		
		<0.1%	60%	0.2%	60%		
		Zero drift	Meets ± 3% requirement (relative to span)	Rangetop Test	Unit 10	< ± 3%	
Rangetop Test	Unit 14A			< ± 3%			
Water Heater Test	Unit 10			> 3% on NO span (see text)			
Water Heater Test	Unit 14A			< ± 3%			
Diesel Engine Test (High RPM)	Unit 10			< ± 3%			
Diesel Engine Test (High RPM)	Unit 14A			< ± 3%			
Diesel Engine Test (Low RPM)	Unit 10			< ± 3%			
Diesel Engine Test (Low RPM)	Unit 14A			< ± 3%			
Interference check	< ± 7% (No interference response detected)						



There was one undocumented deviation. Due to a delay in the arrival of the protocol gases used in the verification test, Battelle was not able to run one instrument through the entire test sequence prior to verification testing. The impact of this deviation on the final data is described in the Performance System Audits section of this report.

### 4.3 Calibration of Laboratory Equipment

Equipment used in the verification test required calibration before use. Equipment types and calibration dates are listed in Table 4-2. Documentation for calibration of the following equipment was required before use in the verification test, and was maintained in the test file.

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

Equipment Type	Calibration Date/ Temperature Check
Flow Controllers (Gas Dilution System) Environics Series 100	6/11/98
Flow Controllers (Gas Dilution System) Environics Model 2020	12/16/98
Digital Temperature Indicator Model 402A	1/7/99
Dwyer Magnahelic Pressure Gauge	1/11/99
Model R-275 In-line Dry Gas Meter	1/11/99
Doric Trendicator 400A Thermocouple Temperature Sensor	1/18/99
Model DTM-115 Reference Dry Gas Meter	9/22/98

### 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.

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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

Internal and external performance system audits were conducted and the results are summarized in the following sections.

### 4.5.1 Internal Audits

Three internal 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 percent of all data generated during the verification test. A summary of the results of these audits is provided below.

#### 4.5.1.1 Technical Systems Audit

A technical systems audit is a qualitative onsite audit of the physical setup of the test. The auditors determine the compliance of testing personnel with the test/QA plan. A self-assessment is required for each test as outlined in the AMS pilot QMP. The QA/QC Reviewer for the verification test conducted the internal technical systems audit on January 18, 1999, by reviewing data obtained prior to the ECOM tests reported here. Observations and findings from this audit are listed in Table 4-3.

#### 4.5.1.2 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. One such assessment was conducted by Battelle QA staff on February 4, 1999. No independent assessments of this type were conducted by EPA staff.

The performance evaluation (PE) samples were NO and NO<sub>2</sub> calibration gases independent of the test calibration standards containing 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 values. Percent difference was used to quantify the accuracy of the results. The PE sample for NO was an EPA protocol gas having nearly the same concentration as the NO standard used in verification testing, but purchased from a different commercial supplier. The PE standard for NO<sub>2</sub> was a commercial standard of 50.5 ppm NO<sub>2</sub> in air, whose concentration had been confirmed by comparison with a 50 ppm standard reference material of NO in nitrogen, obtained from the National Institute of Standards and Technology. Table 4-4 summarizes the reference 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. As shown in Table 4-4, all of the observed concentrations were well within the acceptance ranges.



**Table 4-3. Observations and Findings From the Internal Technical Systems Audit**

Observation/Finding	Corrective Action/Impact on Final Data
<p>Method 7E calibration was not completed prior to verification testing. Analyzers gave unreliable results during first test, which prompted a calibration on 1/13/99. Full four-point calibration was not performed until 1/15/99 on the 0-100 range and 1/16/99 on the 0-1000 range for both Models 14A and 10. All criteria meet stated objectives in Method 7E for the calibration (linearity, calibration error) performed on the 15<sup>th</sup> and 16<sup>th</sup>.</p>	<p>Vendor source testing that was conducted prior to the first full four-point Method 7E calibration was repeated at a later date. Thus all vendor testing was conducted with fully calibrated reference analyzers. There is no impact on verification data because the first vendor test was repeated after Method 7E calibration was implemented.</p>
<p>From Pressure Sensitivity Test conducted 1/12/99 an explanation is needed of correction factor to be applied to data.</p>	<p>The O<sub>2</sub> sensors of the vendor's analyzers showed the presence of O<sub>2</sub> in the sample gas at a time when only NO in pure N<sub>2</sub> was being provided to the analyzers. This indicated a leakage of air into the sample manifold (which was at reduced pressure relative to the room). The amount of dilution caused by the leakage of air was calculated from the O<sub>2</sub> level observed, and exactly accounted for an apparently low NO response from the vendor's analyzers. That is, the O<sub>2</sub> data were used to correct the observed NO responses to what they would have been with no air leakage. The leak was fixed, and no impact exists in any test data.</p>
<p>Start and stop time for instruments to equilibrate at each temperature is not noted on data sheets.</p>	<p>Added start and stop time to data sheets as a method to document equilibration.</p>
<p>Calibration drift for all data reviewed is less than ± 3% relative to the span except Model 10 span post-test on 1/14/99 for diesel engine test which = 3.6%. Data for test should be flagged at minimum.</p>	<p>All source tests with the ECOM analyzers met a slightly expanded drift requirement (see text). No impact on final data.</p>
<p>Data and calculations for calibration drift test not found on test data sheets. Recommend a better system be implemented for assessing quality of the calibration drift for reference analyzers immediately following collection of test data so decision whether or not to proceed is clear to all participants.</p>	<p>Comparison of drift is easily made visually; written comments will be added if termination of a test is called for.</p>
<p>Zero/span values are documented on diesel engine test data sheets for all tests except on 01-13-98 post-test blank with no explanation.</p>	<p>This test was terminated. Notes were added as suggested and the test was later repeated in its entirety. No impact on ECOM data</p>

**Table 4-4. Performance Evaluation Results**

		Reading (V)	Zero (V)	Zero Corrected	Apparent Concentration*	Percent Difference**	Limits
<b>Unit 14A</b>	NO in N <sub>2</sub> (ppm)						
<b>Test Std</b>	3,925	9.92	0.01	9.91	3905.3	0.5%	± 2%
<b>PE Std</b>	3,988	10.13	0.01	10.12			
<b>Unit 10</b>	NO in N <sub>2</sub> (ppm)						
<b>Test Std</b>	3,925	1.01	-0.01	1.03	3895.7	0.7%	± 2%
<b>PE Std</b>	3,988	1.04	-0.01	1.05			
<b>Unit 14A</b>	NO <sub>2</sub> in Air (ppm)						
<b>Test Std</b>	50.0***	4.40	0.01	4.39	48.7	2.5%	± 5%
<b>PE Std</b>	50.5	4.56	0.02	4.54			
<b>Unit 10</b>	NO <sub>2</sub> in Air (ppm)						
<b>Test Std</b>	50.0***	0.44	-0.01	0.45	50.0	0.1%	± 5%
<b>PE Std</b>	50.5	0.44	-0.01	0.45			

\*Concentration of Test Standard indicated by comparison to the Performance Evaluation Standard

\*\*Percent difference of apparent concentration Relative to Test Standard concentration.

\*\*\*Prepared by dilution of 493.2 ppm NO<sub>2</sub> Protocol Gas.

#### 4.5.1.3 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 percent 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 QA/QC Reviewer for the verification test audited 10 percent of the raw data. Test data sheets and laboratory record books were reviewed, and calculations and other algorithms were verified. Calibration drift test results were calculated and compared to the Method 7E criteria. Calculations that were used to assess the four-point calibration of the reference method were also verified to be correct.

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Review of vendor and reference method data sheets revealed the following discrepancy which may have an impact on data quality for the ECOM tests:

1. Relative accuracy test 2/17/99 using water heater, NO reading on Model 10 pre-test span check = 0.950 V ppm and post-test span check = 1.000 V, implying a drift of 4.4 percent of full scale (after zero correction).

This item is noted in Table 4-1, which summarizes the reference method data quality for the ECOM verification test. The span drift noted in this instance exceeded the Method 7E criterion of  $\pm 3$  percent of scale. However, certain departures from strict Method 7E procedures were required in this verification test, which argue for a slightly wider allowable tolerance on span drift. Those departures are detailed in the QC test file for this verification effort; a brief summary follows.

Method 7E calls for using undiluted gas standards equal to the full- and mid-scale points on the analyzer's measurement range. A drift in span of  $\pm 3$  percent of scale is allowed over the course of a source emission measurement. This  $\pm 3$  percent allowable drift is that attributed to the analyzer itself, since the undiluted standards are assumed not to change over the brief duration of a source measurement. In contrast, in this verification test, gas standards were diluted using precision mass flow controllers to achieve the wide range of span gases required. This dilution process necessarily introduces additional uncertainty of up to about 1.4 percent (i.e., the root-mean-square error resulting from two flow controllers each with 1 percent random error). As a result, we estimate an allowable drift of about 4.4 percent, by adding the additional uncertainty noted above to the 3 percent stated in Method 7E. The drift value noted in Table 4-1 is within this allowable drift criterion, and no adverse impact on the ECOM test data is inferred.

#### **4.5.2 External Audit**

EPA conducted an on-site technical systems audit during the verification testing. This audit was conducted to observe and evaluate whether the verification team followed the test/QA plan. The external technical systems audit report is attached in Appendix B and the assessment is summarized below.

The auditors assessed the verification test procedures and personnel against the *Quality Management Plan for the ETV Advanced Monitoring Systems Pilot*,<sup>(7)</sup> the *Test/QA Plan for Verification of Portable NO/NO<sub>2</sub> Emission Analyzers*,<sup>(1)</sup> and *U.S. EPA Method 7E Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)*.<sup>(2)</sup> The auditors were on site from January 20, 1999, through January 21, 1999. The technical systems audit was performed on the flow rate and ambient temperature laboratory tests and the relative accuracy tests with the gas rangetop, water heater, and a portion of the high RPM emissions of the diesel generator. No performance evaluations were conducted as a part of this audit.

This external technical systems audit showed that the verification test was well managed, particularly considering its complexity. All personnel appeared to be well trained for their particular duties. All involved showed enthusiasm and ingenuity during the verification testing. Personnel were very familiar with the test/QA plan. With one exception, differences for this verification test from the original test/QA plan were well documented by deviation reports on file

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at Battelle. The deviation report format includes a date, cites the deviation, provides an explanation of the deviation, and requires a Battelle approval signature. It was impressive that the deviation reports were present and were completed up front.

Two major findings resulted from this external technical systems audit. First, as a result of a delay in the arrival of the protocol gases used in the verification test, Battelle was not able to run one of the instruments through the test sequence prior to the first test. This undocumented deviation was from Section 5.6 of the test/QA plan, Test Schedule, and stated "To avoid bias in testing of the first analyzers through the sequence, Battelle's personnel will first conduct the entire test sequence using an analyzer already on hand at Battelle. Testing will then continue with analyzers named in Section 2.4." Second, the test/QA plan states that "The chemiluminescent monitors to be used for Method 7E reference measurements will be subjected to a four-point calibration with NO prior to the start of verification testing, on each measurement range to be used for verification." The combustion source tests were started on January 13, 1999. No four-point calibration with NO was recorded in the combustion source testing laboratory notebook prior to January 13. This finding is also a finding in Battelle's internal audit conducted during the first week of the verification test.

The impact of these two findings on the data presented in this report is as follows. Although Battelle did not run an instrument through the entire test sequence prior to initiating testing, each component of the test system was checked independently. Therefore, the absence of this pre-test check will not impact the final data. The lack of initial calibration of the reference analyzers does not affect the ECOM A-PLUS data since the appropriate calibration was performed before combustion source testing with the ECOM analyzers.

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## 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 ECOM analyzer. The calibration model used was

$$Y_c = h(c) + error_c \quad (1)$$

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,

$$\sigma_c^2 = \alpha + kc^\beta \quad (2)$$

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.

$$weight = w_c = \frac{1}{\sigma_c^2} \quad (3)$$

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

$$\hat{c} = \hat{h}^{-1}(Y_c) = \frac{Y_c - \hat{\alpha}_o}{\hat{\alpha}_1} \quad (4)$$

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

$$\frac{1}{4} \sum_{i=1}^6 (\bar{Y}_{c_i} - \alpha_o - \alpha_1 c_i)^2 n_{c_i} w_{c_i} \quad (5)$$

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.

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

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

$$LOD = \frac{[(\alpha_o + 3\sigma_o) - \alpha_o]}{\alpha_1} = \frac{3\sigma_o}{\alpha_1} \quad (6)$$

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 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 percent 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  $\text{Response}_{\text{RT}}$  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



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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 percent. 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:

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

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

### *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:

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

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



## 5.2 Combustion Source Tests

### 5.2.1 Accuracy

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

$$RA = \frac{|\bar{d}| + t_{n-1}^{\alpha} \frac{S_d}{\sqrt{n}}}{\bar{x}} \times 100\% \quad (7)$$

where  $d$  refers to the difference between the average of the two reference units and one of the tested units and  $x$  corresponds to the average of the two reference unit 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. The relative accuracy was determined for an  $\alpha$  value of 0.025 (i.e., 97.5 percent 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

$$\hat{SE} \cong \frac{S_d}{\sqrt{n} \bar{x}} \sqrt{0.3634 + (t_{n-1}^{\alpha})^2 \frac{1}{2(n-1)}} \times 100\% \quad (8)$$

### 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

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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 units of each analyzer 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 possible data points.

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## Chapter 6 Statistical Results

### 6.1 Laboratory Tests

#### 6.1.1 Linearity

Tables 6-1a, b, c, and d list the data obtained in the linearity tests for NO and NO<sub>2</sub>. Tables 6-1a and b list the results of the initial NO and NO<sub>2</sub> linearity tests, respectively. These tests were performed over ranges of 0 to 4,000 ppm NO and 0 to 500 ppm NO<sub>2</sub> on January 17, 1999. Tables 6-1c and d list the corresponding results of the second linearity tests, performed over ranges of 0 to 1,000 ppm NO and 0 to 200 ppm NO<sub>2</sub> on February 19, 1999. The response of both the NO and NO<sub>2</sub> sensors in each analyzer is shown in those tables.

Tables 6-2a and b show the results of the linear calibration curve fits for each unit and each analyte, based on the data shown in Tables 6-1a, b, c, and d. Table 6-2a shows the statistical results obtained from a linear regression to all of the data points obtained in the first linearity test (Tables 6-1a and b). The results shown indicate substantial departure from linearity for both NO and NO<sub>2</sub> with both analyzers. Table 6-2a indicates that all regression slopes are greater than 1.05, well outside the range of 0.98 to 1.02 stated as acceptable in the SCAQMD test protocol.<sup>(8)</sup> In addition, Table 6-2a indicates relatively high intercept values for NO, and R<sup>2</sup> values for both NO and NO<sub>2</sub> that are below the 0.999 value stated in the SCAQMD protocol.

In contrast, Table 6-2b shows good results from the second linearity test of the ECOM analyzers. Intercepts are below 5 ppm for NO, and below 0.6 ppm for NO<sub>2</sub>, on both analyzers, and the slopes range from 0.994 to 1.011. All the slopes are well within the acceptable range of 0.98 to 1.02. The R<sup>2</sup> values in Table 6-2b also all exceed 0.9995.

The results in Tables 6-2a and b give conflicting views of the linearity of the ECOM analyzers. The main difference between these two sets of results is the concentration range over which the analyzers were tested. Table 6-2a reports results from testing over 0 to 4,000 ppm NO and 0 to 500 ppm NO<sub>2</sub>, whereas Table 6-2b reports results from testing over 0 to 1,000 ppm NO and 0 to 200 ppm NO<sub>2</sub>. Investigation of the data has shown that the difference in these two sets of results has to do with these concentration ranges and with the actual linear range of the ECOM analyzers, as discussed below.

**Table 6-1a. Data from NO Linearity Test over 0-4,000 ppm Range for ECOM A-PLUS 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	0.0	5	7	5	8
2	3925.0	3911	24	3906	30
3	397.5	469	13	520	10
4	1499.7	1665	14	1913	16
5	0.0	9	5	8	6
6	2600.7	2849	NR	3271	NR
7	747.3	869	11	978	13
8	397.5	468	9	521	10
9	0.0	10	7	9	7
10	747.3	847	7	965	8
11	1499.7	1668	9	1913	11
12	2601.3	2846	12	3269	14
13	0.0	12	7	11	8
14	3925.0	3912	12	3905	14
15	2601.3	2881	14	3290	15
16	1499.7	1706	12	1936	13
17	0.0	18	8	17	9
18	747.3	854	8	968	9
19	397.5	459	8	512	7
20	3925.0	3911	11	3906	12
21	0.0	16	7	19	8

NR: Not recorded.

**Table 6-1b. Data from NO<sub>2</sub> Linearity Test over 0-500 ppm Range for ECOM A-PLUS 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	0
2	493.2	20	505	14	505
3	49.8	5	61	5	62
4	179.9	9	199	8	199
5	0.0	4	3	3	3
6	350.3	NR	375	NR	374
7	89.7	7	108	7	108
8	49.7	6	62	6	62
9	0.0	4	4	4	5
10	89.7	6	102	6	102
11	179.9	10	199	8	198
12	350.3	17	376	15	376
13	0.0	4	4	4	3
14	493.2	25	522	16	524
15	350.3	19	386	13	388
16	179.9	11	209	9	210
17	0.0	5	7	5	9
18	89.6	7	104	6	104
19	49.7	6	61	6	61
20	493.2	22	519	18	521
21	0.0	5	9	5	11

NR: Not recorded.

**Table 6-1c. Data from NO Linearity Test over 0 - 1,000 ppm Range for ECOM Analyzers**

<b>Number</b>	<b>Actual NO<sub>2</sub> (ppm)</b>	<b>Unit A NO (ppm)</b>	<b>Unit A NO<sub>2</sub> (ppm)</b>	<b>Unit B NO (ppm)</b>	<b>Unit B NO<sub>2</sub> (ppm)</b>
1	0	0	0	0	0
2	997.8	1001	3	1000	3
3	96.6	108	1	106	0
4	400.2	417	1	416	1
5	0	4	0	3	0
6	700.5	718	1	718	1
7	200	214	0	212	0
8	100	109	0	107	0
9	0	4	0	3	0
10	200	209	0	209	0
11	400.2	416	0	415	0
12	700.6	718	1	718	0
13	0	3	0	3	0
14	997.8	1000	1	1001	1
15	700.5	718	1	718	1
16	400.2	422	0	419	0
17	0	4	0	3	0
18	200	210	0	209	0
19	100	109	0	107	0
20	997.8	1000	1	1001	1
21	0	3	0	2	0

**Table 6-1d. Data from NO<sub>2</sub> Linearity Test Over 0-200 ppm Range for ECOM 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	200	7	200	7	200
3	19.7	3	19	3	19
4	79.6	4	79	4	79
5	0	3	1	2	1
6	139.8	6	139	5	139
7	39.7	4	40	3	40
8	19.7	4	20	3	19
9	0	3	1	3	1
10	39.7	4	39	3	39
11	79.7	4	79	4	79
12	139.8	6	140	5	140
13	0	3	1	3	1
14	200	7	199	6	199
15	139.8	7	141	6	141
16	79.7	5	81	4	81
17	0	4	1	3	1
18	39.7	4	39	3	39
19	19.7	4	19	3	19
20	200	8	200	7	199
21	0	4	1	3	1

**Table 6-2a. Statistical Results for First Linearity Test with ECOM Analyzers (1/17/99)**

Linear Regression	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Intercept (ppm) (Std Err)	20.514 (7.161)	6.600 (1.308)	53.186 (33.002)	7.336 (1.447)
Slope (Std Err)	1.080 (0.014)	1.054 (0.009)	1.137 (0.035)	1.053 (0.010)
R <sup>2</sup>	0.997	0.9986	0.9828	0.9984

**Table 6-2b. Statistical Results for Second Linearity Test on ECOM Analyzers (2/18/99)**

Linear Regression	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Intercept (ppm) (Std Err)	4.841(1.182)	0.566 (0.182)	4.326(1.191)	0.585 (0.185)
Slope (Std Err)	1.011 (0.004)	0.995 (0.003)	1.011 (0.004)	0.994 (0.003)
R <sup>2</sup>	0.9997	0.9999	0.9997	0.9999

The results shown in Table 6-2a are from linearity testing over the nominal full-scale ranges of the ECOM analyzers (i.e., the ranges stated in vendor literature). Those tests were conducted by first calibrating the analyzers with NO or NO<sub>2</sub> span gas at concentrations near the nominal full-scale range values. Subsequent data points were then obtained without further adjustment of the analyzers. Inspection of the test data has shown that the results in Table 6-2a are not due to a non-linearity of analyzer response, but rather to a limitation in the extent of the linear range. This is illustrated in Figure 6-1, which shows the linearity test data for the Unit B NO response, taken directly from Table 6-1a. That figure shows that the analyzer response at the full-scale data point (3,925 ppm NO actual concentration) agrees well with the actual value, but for all lower data points, the analyzer response is too high. However, except for the full-scale data point, all the analyzer response data appear to be highly linear. The conclusion drawn from Figure 6-1 is that the linear range of the Unit B NO sensor is not 4,000 ppm, as stated, but approximately 3,000 ppm. The analyzer's response to NO levels above 3,000 ppm flattens out, or saturates. The slopes shown in Table 6-2a are an artifact of this saturation effect, since calibrating with an artificially low response near full scale makes response at all lower concentrations appear erroneously high. Based on those slopes, the effect seems to be larger for the NO sensors than for the NO<sub>2</sub> sensors. Figures similar to Figure 6-1 indicate that the linear ranges of the Unit A NO and NO<sub>2</sub> sensors are actually about 0 to 3,500 ppm and 0 to 450 ppm, respectively. The linear ranges of the Unit B NO and NO<sub>2</sub> sensors are about 0 to 3,000 ppm and 0 to 450 ppm, respectively.

For the purpose of estimating detection limits (see Section 6.1.2), both sets of linearity test data were used. However, before estimating detection limits, the data from the highest concentration point in the first linearity test (Tables 6-1 a and b) were omitted, and the regression was recalculated using the remaining points, to avoid biasing the intercept due to the effect shown in Figure 6-1. In addition, consistently increasing responses on zero gas were observed in the first linearity tests (Tables 6-1a and b). This behavior is apparently due to a "memory" effect, in which the analyzers do not fully return to baseline after exposure to elevated NO or NO<sub>2</sub> levels. This behavior is a transient response, which can be minimized by sufficiently long refresh cycles between measurements.<sup>(10)</sup> However, this behavior might be important in real sampling, as in measuring widely different NO<sub>x</sub> levels upstream and downstream of a selective catalytic reactor (SCR) for NO<sub>x</sub> removal. If a single calibration covering the entire range of concentrations to be encountered were prepared, measurements at the low concentrations (i.e., downstream of the SCR) might be compromised. In that instance it would be preferable to conduct a low-level calibration and low-level measurements (downstream), followed by a high-level calibration and upstream measurements. Alternatively, dilution of the high-level stream, or use of two separate analyzers for the low and high concentration regimes, would be preferable.



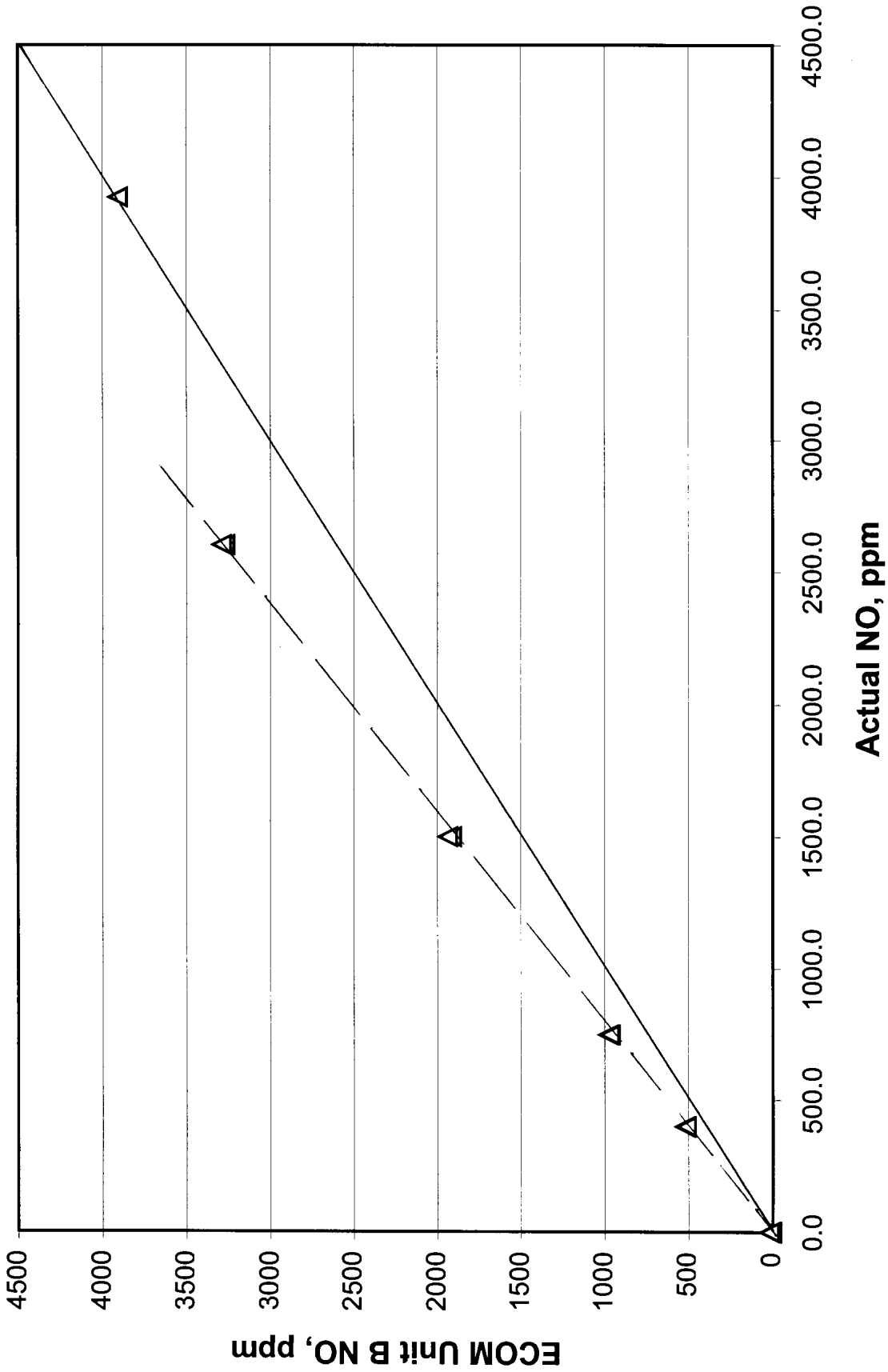


Figure 6-1. Results of First NO Linearity Test on ECOM Unit B

The linearity test data in Tables 6-1a through d also indicate the extent of cross-sensitivity of the ECOM NO and NO<sub>2</sub> sensors. Using the results from the second linearity test (Table 6-1c), linear regression of the NO<sub>2</sub> responses of the analyzers against the NO levels provided gives the following regression equations:

$$\begin{aligned} \text{Unit A NO}_2 \text{ Response} &= 0.00159 (\text{Actual NO}) - 0.07 \text{ ppm} \\ \text{Unit B NO}_2 \text{ Response} &= 0.00154 (\text{Actual NO}) - 0.15 \text{ ppm} \end{aligned}$$

with R<sup>2</sup> values of 0.59 and 0.87, respectively. These results indicate a very slight sensitivity of the NO<sub>2</sub> sensors to NO, amounting to about 0.15 percent of the actual NO level. This degree of cross-sensitivity is negligible in any real-world application.

The corresponding linear regression of NO response to NO<sub>2</sub> levels provided in Table 6-1d gives the following equations:

$$\begin{aligned} \text{Unit A NO Response} &= 0.0224 (\text{Actual NO}_2) + 2.9 \text{ ppm} \\ \text{Unit B NO Response} &= 0.0214 (\text{Actual NO}_2) + 2.3 \text{ ppm} \end{aligned}$$

with R<sup>2</sup> values of 0.78 and 0.84, respectively. These results indicate that the ECOM NO sensors have a cross-sensitivity to NO<sub>2</sub> that amounts to about 2 percent of the actual NO<sub>2</sub> level. This interference is likely to be significant only in a source where NO<sub>2</sub> levels equal or exceed NO levels.

### 6.1.2 Detection Limit

Tables 6-3a and b show the estimated detection limits for each test unit and each analyte, determined from the data obtained in the linearity tests.

**Table 6-3a. Estimated Detection Limits From First Linearity Test (1/17/99) for the ECOM Analyzers**

	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Estimated Detection Limit (ppm)	12.834	8.957	12.896	11.738
(Standard Error) (ppm)	(4.061)	(2.834)	(4.078)	(3.713)

**Table 6-3b. Estimated Detection Limits From Second Linearity Test 2 (2/18/99) for the ECOM Analyzers**

	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Estimated Detection Limit (ppm)	4.595	1.231	3.593	1.232
(Standard Error) (ppm)	(1.453)	(0.389)	(1.136)	(0.390)

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Table 6-3a shows the detection limits calculated based on the data from the first linearity tests of the ECOM analyzers (Tables 6-1 and b), excluding the highest concentration points. Detection limits of about 13 ppm for NO are indicated for both analyzers. Detection limits of about 9 ppm and 12 ppm for NO<sub>2</sub> are indicated for Unit A and Unit B, respectively. These detection limits result in part from elevation of the zero readings of the ECOM analyzers due to the high NO and NO<sub>2</sub> levels used in the first linearity tests. For example, Table 6-1a indicates that the NO readings of the two ECOM analyzers on zero gas increased from 5 ppm to 16 and 19 ppm, respectively, over the course of the NO linearity test. Similarly, Table 6-1b shows that the NO<sub>2</sub> readings of the two analyzers on zero gas increased from zero to 9 and 11 ppm, respectively, over the course of the NO<sub>2</sub> linearity test. These observations indicate a memory effect, in that the analyzers did not return to their previous zero reading after exposure to elevated NO or NO<sub>2</sub> levels, and the zero readings continued to increase with continued exposure through the test. Thus, the detection limits shown in Table 6-3a are biased upward by this effect, but indicate the behavior that may be expected when the analyzers are calibrated over their full-scale ranges.

Table 6-3b shows the detection limits determined from the second set of linearity tests (Tables 6-1c and d). NO detection limits are about 5 ppm and 4 ppm for Unit A and Unit B, respectively, and NO<sub>2</sub> detection limits are 1.2 ppm for both units. The data from the second linearity tests clearly show more stable zero readings as the tests progressed than those observed in the first tests at higher concentrations, indicating that the differences in zero readings are related directly to the exposure to high concentrations. The detection limits shown in Table 6-3b are more representative of those achievable in actual source monitoring, since exposure to NO and NO<sub>2</sub> at levels approaching the maximum full-scale range of the analyzer is not likely to occur. In fact, the relative accuracy obtained with low-NO<sub>x</sub> sources (Section 6.2.1) suggests detection limits for both NO and NO<sub>2</sub> that are comparable to the 1 ppm measurement resolution of the ECOM analyzers.

### **6.1.3 Response Time**

Table 6-4 lists the data recorded by the operator in the response time test of the ECOM A-PLUS analyzers. It is clear from the first line of entries in Table 6-4 that data recording started after the onset of the step change had been missed, and consequently only lower limits to the response times can be determined. Table 6-5 shows the lower limit response times estimated from the data in Table 6-4. For NO<sub>2</sub>, lower limit response times of about 100 seconds are estimated. For NO, the lower limit response times are quite different, 37 seconds for Unit A and 11 seconds for Unit B. This difference is likely a result of the incomplete data recorded and consequent estimation of the response times. However, the data do indicate that the ECOM analyzers respond more rapidly to NO than to NO<sub>2</sub>, and discussion with the vendor indicates that the results in Table 6-5 are typical of the response times of the A-PLUS analyzers.

**Table 6-4. Response Time Data for ECOM A-PLUS 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	1455	118	1503	119
10	2606	251	3170	261
20	2734	295	3229	302
30	2761	331	3234	327
40	2780	339	3239	343
50	2791	346	3244	347
60	2798	351	3246	352
70	2802	355	3248	354
80	2806	358	3250	356
90	2810	360	3251	359
100	2813	361	3252	360
110	2816	362	3253	361
120	2818	364	3254	362
130	2819	365	3255	363
140	2822	366	3256	364
150	2823	367	3257	365
160	2826	368	3258	366
170	2828	369	3258	366
180	2828	370	3259	367
190	2830	370	3260	368
200	2832	370	3261	369
210	2833	371	3261	369
220	2834	371	3262	370
230	2835	371	3262	370
240	2837	372	3263	371
250	2838	372	3264	371
260	2839	373	3265	371
270	2840	373	3266	372
280	2841	373	3266	372
290	2842	374	3267	373
300	2843	374	3267	373

**Table 6-5. Lower Limits of Response Times Estimated for ECOM A-PLUS Analyzers**

Response Time* (sec)	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
	37	102	11	103

\* The analyzer's responses were recorded at 10-second intervals; therefore the point in time when the 95 percent 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 3,925 ppm NO and 493.2 ppm NO<sub>2</sub> were used for this test. As noted above, the pre-shutdown NO and NO<sub>2</sub> zero readings were apparently elevated due to prolonged exposure to high levels in the linearity test. This elevation of zero levels was no longer present after the overnight shutdown. That is, all zero readings dropped to zero as a result of the shutdown period. Units A and B performed similarly in terms of both zero and span response for both NO and NO<sub>2</sub>. The changes in NO span response due to the shutdown are equivalent to less than 0.5 percent of the 3,925 ppm NO span value, and to 1.6 to 1.8 percent of the 493.2 ppm NO<sub>2</sub> span value.

**Table 6-6. Data from Interrupted Sampling Test with ECOM A-PLUS Analyzers**

	Unit A NO	Unit A NO <sub>2</sub>	Unit B NO	Unit B NO <sub>2</sub>
<b>Pre-Shutdown Date:</b>	<b>1/17/99</b>	<b>Time:</b>	<b>17:40</b>	
Pre-Shutdown Zero (ppm):	12	6	11	6
Pre-Shutdown Span (ppm):	3911	516	3906	511
<b>Post-Shutdown Date:</b>	<b>1/18/99</b>	<b>Time:</b>	<b>09:15</b>	
Post-Shutdown Zero (ppm):	0	0	0	0
Post-Shutdown Span (ppm):	3928	507	3915	503

**Table 6-7. Pre- to Post-Test Differences as a Result of Interruption of Operation of ECOM A-PLUS Analyzers**

Pre-Shutdown—Post-Shutdown	Unit A		Unit B	
	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Zero Difference (ppm)	12	6	11	6
Span Difference (ppm)	-17	9	-9	8

### 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. Note that cross-sensitivity to NO and NO<sub>2</sub> has been addressed using the linearity data, in Section 6.1.1.

**Table 6-8. Data from Interference Tests on ECOM A-PLUS Analyzers**

Interferant Gas	Interferant, Conc. (ppm)	Response (ppm)			
		Unit A NO	Unit A NO <sub>2</sub>	Unit B NO	Unit B NO <sub>2</sub>
Zero		3	1	2	1
CO	496 ppm	2	1	3	2
Zero		4	1	3	1
CO <sub>2</sub>	5.03%	2	1	2	1
Zero		3	1	3	1
NH <sub>3</sub>	494 ppm	3	0	2	0
Zero		3	0	2	0
HCS	590 ppm	3	0	2	0
Zero		2	0	2	0
SO <sub>2</sub>	501 ppm	3	0	3	0
Zero		2	0	2	1
SO <sub>2</sub> + NO	451+388 ppm	480	1	540	1

**Table 6-9. Results of Interference Tests of ECOM A-PLUS Analyzers**

Interferent	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)	-1 (-0.2%)	0	1 (0.2%)	1 (0.2%)
CO <sub>2</sub> (5.03%)	-2 (<0.01%)	0	-1 (<0.01%)	0
NH <sub>3</sub> (494 ppm)	0	-1 (-0.2%)	-1 (0.2%)	-1 (-0.2%)
HCS (590 ppm)	0	0	0	0
SO <sub>2</sub> (501 ppm)	1 (0.2%)	0	1 (0.2%)	0
SO <sub>2</sub> (451 ppm) + NO (388 ppm)*	478 (20.0%)*	1 (0.2%)*	538 (33.3%)*	0

\*See text.

Table 6-9 indicates that none of the five individual interferants has a significant effect on the NO or NO<sub>2</sub> sensors of the ECOM analyzers. The maximum difference in reading relative to the zero readings was 2 ppm, and no individual interferant had an apparent relative sensitivity exceeding 0.2 percent of that for NO or NO<sub>2</sub>.

The mixture of SO<sub>2</sub> and NO<sub>2</sub> produced NO readings on Units A and B of 478 ppm and 538 ppm, respectively, after correction for zero gas readings (Table 6-9). If the excess signal above the true NO value of 388 ppm were due to an effect of the SO<sub>2</sub> present, then the effect of the SO<sub>2</sub> would be equivalent to a 20 percent relative sensitivity for Unit A (i.e.,  $(478 - 388)/451 \times 100 =$

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20.0). The corresponding calculation for Unit B gives a 33.3 percent relative sensitivity. However, the elevated response to the SO<sub>2</sub>/NO mixture is more likely related to the “non-linearity” found in the initial linearity tests, discussed in Section 6.1.1. As Table 6-1a shows, when sampling an NO concentration of 397.5 ppm in the first linearity test, Unit A gave readings of 459 to 469 ppm, and Unit B indicated 512 to 521 ppm. This effect has been traced to the actual linear range of the analyzers, as described in Section 6.1.1. Since the interference test described here was done before the findings of Section 6.1.1 were known, and without adjustment or calibration after the linearity test, it is likely that most if not all of the excess NO response shown in Table 6-9 is an artifact of the linear range effect. No interference effect of SO<sub>2</sub> in the presence of NO can be inferred from the results in Table 6-9.

### **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. No significant effect of duct pressure was seen with either ECOM A-PLUS analyzer. Zero readings changed with pressure by 1 ppm or less for both NO and NO<sub>2</sub> on both analyzers. Span readings for NO<sub>2</sub> changed by 4 ppm or less, equivalent to about 1 percent or less of the 350 ppm NO<sub>2</sub> span concentration. Span readings for NO changed by 40 ppm or less, equivalent to about 1.5 percent or less of the 2,600 ppm NO span concentration.

Tables 6-10 and 6-11 also indicate that the sample gas flow rate drawn by the two analyzers is only slightly dependent on the duct pressure. Sample flow rates at +10 inches of water exceeded those at ambient pressure by 0.7 to 1.9 percent; flow rates at -10 inches of water were reduced by 3.1 to 4.3 percent. As noted above, no significant zero or span changes were associated with these small flow differences.

### **6.1.7 Ambient Temperature**

Table 6-12 lists the data obtained in the ambient temperature test with the ECOM A-PLUS 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 700 ppm for NO and 140 ppm for NO<sub>2</sub>.

Table 6-13 indicates that no significant effect of ambient temperature was found with the ECOM analyzers, with the exception of the NO span readings on Unit B. Zero differences over the course of this test were 1.5 ppm or less for both NO and NO<sub>2</sub> on both analyzers. The span differences observed for NO and NO<sub>2</sub> are larger (relative to room temperature results) for the reduced temperature test (i.e., -9 to -21.5 ppm) than for the elevated temperature test (i.e., 0 to 8.5 ppm). For NO<sub>2</sub> the span differences are equivalent at most to 7.5 percent of the 140 ppm span concentration. For NO the span differences are equivalent to 0.6 to 3.1 percent of the 700 ppm span concentration, with only the value for Unit B being statistically significant.

**Table 6-10. Data from Pressure Sensitivity Test for ECOM A-PLUS Analyzers**

Pressure		Unit A NO	Unit A NO <sub>2</sub>	Unit B NO	Unit B NO <sub>2</sub>
Ambient	Flow rate (ccm)	2280	2280	2175	2175
	Zero (ppm)	0	0	0	0
	NO span (ppm)	2975	2	3410	1
	Zero (ppm)	0	0	0	0
	NO <sub>2</sub> span (ppm)	14	378	14	371
	Zero (ppm)	2	1	2	1
+10 in. H <sub>2</sub> O	Flow rate (ccm)	2323	2323	2190	2190
	Zero (ppm)	1	0	1	0
	NO span (ppm)	2990	1	3431	1
	Zero (ppm)	1	0	1	0
	NO <sub>2</sub> span (ppm)	14	382	15	374
	Zero (ppm)	1	1	1	0
-10 in. H <sub>2</sub> O	Flow rate (ccm)	2209	2209	2082	2082
	Zero (ppm)	1	0	2	0
	NO span (ppm)	3008	1	3450	1
	Zero (ppm)	1	0	1	0
	NO <sub>2</sub> span (ppm)	16	377	11	370
	Zero (ppm)	1	1	2	1

**Table 6-11. Pressure Sensitivity Results for ECOM A-PLUS Analyzers**

		Unit A		Unit B	
		NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Zero	High–Ambient (ppm diff*)	0.33	0	0.33	-0.33
	Low–Ambient (ppm diff)	0.33	0	1	0
	Significant Pressure Effect	N	N	N	N
Span	High–Ambient (ppm diff)	15	4	21	3
	Low–Ambient (ppm diff)	33	-1	40	-1
	Significant Pressure Effect	N	N	N	N
Flow Rate	High–Ambient (ccm diff*)		43		15
	Low–Ambient (ccm diff)		-71		-93

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



**Table 6-12. Data from Ambient Temperature Test of ECOM A-PLUS 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.	24.4°C (76°F)				
	Zero	2	0	2	0
	NO span	716	0	717	0
	Zero	2	0	1	0
	NO <sub>2</sub> span	5	137	4	137
(Heated)					
Temp.	40°C (104°F)				
	Zero	1	0	2	0
	NO span	719	3	720	3
	Zero	4	0	3	0
	NO <sub>2</sub> span	6	135	6	135
(Cooled)					
Temp.	8.9°C (48°F)				
	Zero	0	0	0	0
	NO span	704	2	690	2
	Zero	0	1	0	1
	NO <sub>2</sub> span	0	126	0	124
(Room Temp.)					
Temp.	24.4°C (76°F)				
	Zero	1	0	0	0
	NO span	713	3	706	3
	Zero	1	1	1	1
	NO <sub>2</sub> span	3	133	3	132

**Table 6-13. Ambient Temperature Effects on ECOM A-PLUS Analyzers**

		Unit A		Unit B	
		NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
Zero	Heat - room (ppm diff*)	1	-0.25	1.5	-0.25
	Cool - room (ppm diff)	-1.5	0.25	-1	0.25
	Significant Temp Effect	N	N	N	N
Span	Heat - room (ppm diff)	4.5	0	8.5	0.5
	Cool - room (ppm diff)	-10.5	-9	-21.5	-10.5
	Significant Temp Effect	N	N	Y	N

\* ppm difference between heated/cooled and room temperatures. The differences were calculated from the average of the recorded responses at room temperature.

### 6.1.8 Zero and Span Drift

Zero and span drift was evaluated from data taken at the start and end of the linearity and ambient temperature 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. Table 6-15 is of interest because it provides zero and span drift information from three different sets of span concentrations. Zero drift for both NO and NO<sub>2</sub> on both ECOM units was greatest in the first linearity test, in which the highest span concentrations were used. The cause of this drift is discussed in Section 6.1.1. In the other two tests listed in Table 6-15, zero drift never exceeded 3 ppm on either analyzer. Span drift also was greatest as a result of the first linearity test. Span values for NO decreased over the course of that test (i.e., pre- minus post-test differences in Table 6-15 are positive), by amounts equal to less than 0.5 percent of the 3,925 ppm span value. NO<sub>2</sub> span values increased over the course of the first linearity test (differences in Table 6-15 are negative) by amounts equal to 3.6 to 4.6 percent of the 493.2 ppm span concentration. Span differences in the second linearity test were 2 ppm or less (less than 1 percent relative to span). In the ambient temperature test, span drift for NO<sub>2</sub> was equivalent to about 3 to 4 percent of the 140 ppm span concentration and 0.4 to 1.6 percent of the 700 ppm NO span concentration.

**Table 6-14. Data from Linearity and Ambient Temperature Tests Used to Assess Zero and Span Drift of the ECOM A-PLUS Analyzers.**

Test		Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)
First Linearity*	Pre-Test Zero	0	0	0	0
	Pre-Test Span	3925	493.2	3925	493.2
	Post-Test Zero	12	6	11	6
	Post-Test Span	3911	516	3906	511
Second Linearity**	Pre-Test Zero	0	0	0	0
	Pre-Test Span	1000	200	1000	201
	Post-Test Zero	3	0	2	0
	Post-Test Span	1000	200	1001	199
Ambient Temperature***	Pre-Test Zero	2	0	2	0
	Pre-Test Span	716	137	717	137
	Post-Test Zero	1	1	0	1
	Post-Test Span	713	133	706	132

\*NO 0 - 4,000 ppm and NO<sub>2</sub> 0 - 500 ppm.

\*\*NO 0 - 1,000 ppm and NO<sub>2</sub> 0 - 200 ppm.

\*\*\*Span values were 700 ppm NO and 140 ppm NO<sub>2</sub>.

**Table 6-15. Zero and Span Drift Results for the ECOM A-PLUS Analyzers**

		Unit A		Unit B	
		NO (ppm)	NO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)
<b>Pre- and Post-Differences</b>					
First Linearity Test	Zero	-12	-6	-11	-6
	Span	14	-22.8	19	-17.8
Second Linearity Test	Zero	-3	0	-2	0
	Span	0	0	-1	2
Ambient Temperature Test	Zero	0	-1	2	-1
	Span	3	4	11	5

## 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 of the four combustion sources. Note that the ECOM analyzers measure NO and NO<sub>2</sub>, and the indicated NO<sub>x</sub> totals are the sum of those data; in contrast, the reference monitors measure NO and NO<sub>x</sub>, and NO<sub>2</sub> is determined by difference. Tables 6-16a through d show that a wide range of NO and NO<sub>2</sub> concentrations was emitted by the four sources.

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.

Table 6-17 shows that for nearly all source sampling, the ECOM A-PLUS analyzers exhibited relative accuracy of 1.3 to 15 percent for NO, NO<sub>2</sub>, and NO<sub>x</sub>. For all sources tested, the NO<sub>x</sub> relative accuracy was 12.1 percent or better. The only exceptions were those conditions in which NO and/or NO<sub>2</sub> were present at levels of 6 ppm or less. For NO from the rangetop, relative accuracy of about 20 percent was found on Unit B. For NO<sub>2</sub> from the rangetop, relative accuracy values of about 50 percent were found with both analyzers. This relative accuracy at the low levels observed from this source implies that the ECOM and reference results agree within about 1 ppm at these low levels, or within the measurement resolution of the ECOM analyzers (the ECOM analyzers report data in whole ppm units only). Relative accuracy of 50 to 70 percent for NO<sub>2</sub> was observed on the gas water heater (Table 6-17). Although the 1 ppm resolution of the ECOM analyzers certainly contributes to these relative accuracy values, inspection of Table 6-16b shows that variability in the NO<sub>2</sub> data from the two reference analyzers also contributes. Determination of NO<sub>2</sub> by difference using the chemiluminescence method is especially subject to error at high NO/NO<sub>2</sub> ratios, as in the water heater emissions.

Table 6-16a. Data from Gas Rangetop in Verification of ECOM Analyzers

	ECOM Analyzer Data						Reference Analyzer Data					
	Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit A NO <sub>x</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)	Unit B NO <sub>x</sub> (ppm)	14A NO (ppm)	14A NO <sub>2</sub> (ppm)	14A NO <sub>x</sub> (ppm)	10 NO (ppm)	10 NO <sub>2</sub> (ppm)	10 NO <sub>x</sub> (ppm)
1	5	1	6	5	1	6	4.1	1.9	6.1	5.2	1.9	7.1
2	5	1	6	6	1	7	4.8	1.6	6.4	5.7	1.6	7.3
3	6	1	7	6	1	7	4.9	1.8	6.7	5.6	1.8	7.4
4	6	1	7	6	1	7	5.1	1.6	6.7	5.9	1.9	7.8
5	6	1	7	6	1	7	5.1	1.8	6.8	6.0	1.8	7.8
6	6	1	7	7	1	8	5.3	1.6	6.9	6.0	1.9	7.9
7	6	1	7	7	1	8	5.3	2.0	7.3	6.0	2.3	8.2
8	7	1	8	7	1	8	5.5	1.9	7.4	6.4	1.8	8.2
9	7	1	8	7	1	8	5.4	2.0	7.4	6.5	1.8	8.3

Table 6-16b. Data from Gas Water Heater in Verification of ECOM Analyzers

	ECOM Analyzer Data						Reference Analyzer Data					
	Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit A NO <sub>x</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)	Unit B NO <sub>x</sub> (ppm)	14A NO (ppm)	14A NO <sub>2</sub> (ppm)	14A NO <sub>x</sub> (ppm)	10 NO (ppm)	10 NO <sub>2</sub> (ppm)	10 NO <sub>x</sub> (ppm)
1	72	4	76	73	4	77	69.6	8.5	78.1	66.9	4.6	71.5
2	64	3	67	66	3	69	59.8	3.0	62.8	58.3	1.7	60.0
3	63	3	66	65	2	67	57.4	3.9	61.3	56.2	2.6	58.8
4	64	3	67	66	3	69	58.2	3.7	61.9	56.5	3.9	60.4
5	64	3	67	66	2	68	59.0	3.8	62.8	57.4	2.9	60.3
6	64	3	67	65	2	67	59.1	2.8	62.0	57.1	2.1	59.2
7	65	3	68	66	2	68	53.1	9.7	62.8	56.4	3.7	60.1
8	63	3	66	64	2	66	58.5	1.2	59.7	56.9	1.6	58.4
9	61	3	64	62	2	64	54.5	5.6	60.1	55.0	3.9	58.9

Table 6-16c. Data from Diesel Generator at High RPM in Verification of ECOM Analyzers

	ECOM Analyzer Data					Reference Analyzer Data						
	Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit A NO <sub>x</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)	Unit B NO <sub>x</sub> (ppm)	14A NO (ppm)	14A NO <sub>2</sub> (ppm)	14A NO <sub>x</sub> (ppm)	10 NO (ppm)	10 NO <sub>2</sub> (ppm)	10 NO <sub>x</sub> (ppm)
1	118	73	191	117	69	186	115.8	71.2	187.0	113.2	75.5	188.7
2	112	69	181	109	66	175	106.0	68.9	174.9	109.2	62.8	172.0
3	109	67	176	108	64	172	108.0	60.5	168.5	111.2	66.0	177.2
4	110	65	175	108	62	170	102.1	62.6	164.6	106.3	69.1	175.4
5	110	65	175	109	63	172	106.0	58.4	164.4	111.2	66.0	177.2
6	110	64	174	108	62	170	102.1	60.5	162.5	106.3	70.2	176.4
7	109	65	174	107	63	170	101.1	62.6	163.6	106.3	70.2	176.4
8	110	65	175	109	63	172	102.1	63.6	165.7	107.2	71.3	178.5
9	115	65	180	114	62	176	107.0	56.3	163.3	114.2	61.8	176.0

Table 6-16d. Data from Diesel Generator at Idle in Verification of ECOM Analyzers

	ECOM Analyzer Data					Reference Analyzer Data						
	Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit A NO <sub>x</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)	Unit B NO <sub>x</sub> (ppm)	14A NO (ppm)	14A NO <sub>2</sub> (ppm)	14A NO <sub>x</sub> (ppm)	10 NO (ppm)	10 NO <sub>2</sub> (ppm)	10 NO <sub>x</sub> (ppm)
1	328	137	465	326	135	461	326.6	131.9	458.5	325.7	130.2	455.9
2	332	135	467	332	134	466	330.5	134.0	464.6	326.7	134.4	461.1
3	335	136	471	332	135	467	331.5	135.1	466.6	329.7	135.5	465.2
4	335	135	470	333	134	467	332.5	132.0	464.5	330.7	131.3	461.9
5	335	135	470	335	133	468	330.5	129.8	460.4	326.7	131.2	457.9
6	332	137	469	329	135	464	325.6	135.0	460.6	322.7	133.3	456.1
7	332	138	470	330	136	466	332.5	126.7	459.2	324.7	130.2	454.9
8	336	141	477	333	139	472	331.5	136.1	467.7	328.7	132.3	461.0
9	303	157	460	299	154	453	302.1	151.5	453.6	289.0	142.8	431.7

**Table 6-17. Relative Accuracy of ECOM A-PLUS 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 (5.5 ppm NO, 2 ppm NO <sub>2</sub> )***	14.95* (2.04)**	51.50 (2.06)	8.57 (1.45)	20.63 (1.90)	51.50 (2.06)	3.73 (1.34)
Gas Water Heater (60 ppm NO, 4 ppm NO <sub>2</sub> )	12.81 (0.84)	52.60 (12.15)	10.78 (0.77)	15.31 (0.85)	70.72 (12.43)	12.09 (0.79)
Diesel Generator–High RPM (105 ppm NO, 65 ppm NO <sub>2</sub> )	5.24 (0.57)	5.00 (1.24)	3.97 (0.40)	3.62 (0.51)	5.77 (1.18)	1.47 (0.38)
Diesel Generator–Idle (325 ppm NO, 135 ppm NO <sub>2</sub> )	2.00 (0.18)	5.62 (0.70)	2.85 (0.26)	1.33 (0.17)	4.00 (0.60)	1.82 (0.19)

\*Relative accuracy calculated using equation 7.

\*\*Standard error of relative accuracy value, estimated using equation 8.

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

In addition to exhibiting good relative accuracy even at low analyte levels, the ECOM A-PLUS analyzers exhibited excellent unit-to-unit precision in source emission measurements. In all combustion tests, the two ECOM analyzers actually showed better unit-to-unit agreement than did the two reference analyzers. For example, the differences between the average NO<sub>x</sub> values obtained by ECOM Unit A and Unit B on the four combustion sources ranged from 0.8 to 4.2 percent, relative to the mean NO<sub>x</sub> values. This result indicates a high degree of consistency in the performance of the ECOM analyzers on combustion sources.

### 6.2.2 Zero and Span Drift

Table 6-18 shows all the data used to evaluate zero and span drift of the ECOM A-PLUS analyzers from the combustion source tests.

Table 6-19 summarizes the zero and span drift results, and shows that zero and span drift for both NO and NO<sub>2</sub> with both analyzers was within ± 1 ppm in sampling of the two gas combustion sources. Zero and span drift increased in progressing to the diesel source, indicating that exposure to higher NO<sub>x</sub> levels increases both types of drift. With the diesel source, zero and span drift for NO were both larger than the corresponding drift values for NO<sub>2</sub>. The span drift values for NO on the diesel source are equivalent to 1 to 3 percent of the respective NO span concentrations used. The span drift values for NO<sub>2</sub> on the diesel source at idle are equivalent to 4 to 5 percent of the NO<sub>2</sub> span concentration used. This drift is a transient phenomenon that can be minimized by allowing sufficiently long refresh cycles between source measurements.<sup>(10)</sup>

**Table 6-18. Data Used to Assess Zero and Span Drift for ECOM A-PLUS 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	1	0	1	0
	Pre-Test Span	20	11	21	11
	Post-Test Zero	1	0	1	0
	Post-Test Span	20	10	20	10
Gas Water Heater**	Pre-Test Zero	1	0	1	0
	Pre-Test Span	100	16	100	16
	Post-Test Zero	2	0	2	0
	Post-Test Span	100	15	100	15
Diesel-High RPM***	Pre-Test Zero	0	0	0	0
	Pre-Test Span	200	50	200	50
	Post-Test Zero	3	1	3	1
	Post-Test Span	196	50	198	50
Diesel-Idle****	Pre-Test Zero	3	1	3	1
	Pre-Test Span	400	100	400	100
	Post-Test Zero	NR	NR	NR	NR
	Post-Test Span	390	105	388	104

\*Span values 20 ppm NO and 10 ppm NO<sub>2</sub>.

\*\*Span values 100 ppm NO and 15 ppm NO<sub>2</sub>.

\*\*\*Span values 200 ppm NO and 50 ppm NO<sub>2</sub>.

\*\*\*\*Span values 400 ppm NO and 100 ppm NO<sub>2</sub>.

NR: Not recorded.

**Table 6-19. Results of Zero and Span Drift Evaluation for ECOM A-PLUS Analyzers**

Pre-Test— Post-Test		Unit A		Unit B	
		NO (ppm)	NO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)
Gas Burner	Zero	0	0	0	0
	Span	0	1	1	1
Gas Water Heater	Zero	-1	0	-1	0
	Span	0	1	0	1
Diesel Generator-High RPM	Zero	-3	-1	-3	-1
	Span	4	0	2	0
Diesel Generator-Idle	Zero*	—	—	—	—
	Span	10	-5	12	-4

\* Post-test zero readings were not recorded.

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### 6.2.3 Measurement Stability

Table 6-20 shows the data obtained in the extended sampling test, in which the ECOM A-PLUS and reference analyzers sampled diesel emissions at engine idle for a full hour without interruption or sampling of ambient air. The ECOM data were compared to the average of the reference analyzer data to assess whether a different trend in the emission data was observed for the ECOM analyzers relative to the reference analyzers. 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.

Table 6-21 indicates that both the ECOM analyzers and the reference analyzers showed a gradual decrease in NO and an increase in NO<sub>2</sub> during the 1-hour sampling period. The trends shown by ECOM analyzers were not significantly different from those of the reference analyzers. For NO, NO<sub>2</sub>, or NO<sub>x</sub>. This result is consistent with the relative accuracy for all three species achieved by the ECOM analyzers on diesel emissions, as shown in Section 6.2.1.

### 6.2.4 Inter-Unit Repeatability

The repeatability of test results between the two ECOM 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 ECOM A-PLUS units at the 95 percent confidence level. As Table 6-22 shows, significant differences between Units A and B were found only in relative accuracy and in the slopes of the first NO linearity test. The differences found indicate the variability that may be expected from one analyzer to the next. Nevertheless, although some significant differences were found between the two analyzers, the practical importance of those differences is small. Considering the relative accuracy results (Table 6-17), it is apparent that statistically significant differences in relative accuracy may exist even when the two analyzers are equally applicable to the measurement at hand. To show just one example, the relative accuracy results for Unit A on the diesel generator at idle (Table 6-17) are 2.00, 5.62, and 2.85 percent for NO, NO<sub>2</sub>, and NO<sub>x</sub>, respectively. These results may differ significantly from those for Unit B (1.33, 4.00, and 1.82 percent, respectively), but either unit would be more than adequate for determining emissions from that source. The fine degree of discrimination provided by the statistical tests should not obscure the fact that the two ECOM A-PLUS analyzers essentially worked equally well throughout the verification tests.

## 6.3 Other Factors

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



Table 6-20. Data from Extended Sampling Test with Diesel Generator at Idle, Verification of ECOM Analyzers

	ECOM Analyzer Data					Reference Analyzer Data						
	Unit A NO <sub>x</sub> (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit A NO <sub>x</sub> (ppm)	Unit B NO <sub>x</sub> (ppm)	Unit B NO <sub>2</sub> (ppm)	Unit B NO <sub>x</sub> (ppm)	14A NO <sub>x</sub> (ppm)	14A NO <sub>2</sub> (ppm)	14A NO <sub>x</sub> (ppm)	10 NO <sub>x</sub> (ppm)	10 NO <sub>2</sub> (ppm)	10 NO <sub>x</sub> (ppm)
1	333	142	475	330	140	470	330.1	137.2	467.2	327.7	138.7	466.3
2	339	143	482	335	142	477	332.0	137.2	469.2	329.7	138.7	468.3
3	335	144	479	332	142	474	330.1	128.8	458.8	328.7	127.0	455.7
4	333	145	478	329	143	472	331.0	130.9	461.9	329.7	128.1	457.7
5	331	145	476	327	142	469	330.1	130.9	460.9	328.7	129.1	457.8
6	333	146	479	329	144	473	332.0	133.0	465.0	330.7	131.3	461.9
7	328	145	473	324	143	467	320.2	134.9	455.2	320.7	133.3	454.1
8	329	147	476	326	144	470	323.2	135.0	458.2	323.7	133.3	457.1
9	324	146	470	321	144	465	318.3	138.1	456.3	316.8	137.6	454.3
10	327	147	474	324	144	468	324.2	137.1	461.3	320.7	135.5	456.2
11	328	147	475	321	145	466	314.3	147.5	461.8	310.8	147.1	457.9
12	324	148	472	324	146	470	319.2	141.2	460.5	319.7	137.6	457.3
13	330	150	480	327	148	475	324.2	141.3	465.5	321.7	140.7	462.5
14	330	148	478	327	146	473	326.1	134.0	460.1	322.7	133.3	456.1
15	333	149	482	329	147	476	331.0	134.0	465.1	326.7	134.4	461.1
16	332	148	480	327	146	473	326.1	134.0	460.1	322.7	133.3	456.1
17	331	149	480	328	146	474	328.1	134.0	462.1	324.7	132.3	457.0
18	335	149	484	331	147	478	331.0	134.0	465.1	328.7	132.3	461.0
19	334	150	484	332	147	479	326.1	141.3	467.5	325.7	137.6	463.3
20	331	150	481	327	147	474	324.2	140.3	464.4	323.7	134.4	458.1
21	332	150	482	328	148	476	325.1	140.3	465.4	324.7	135.5	460.2
22	332	150	482	328	148	476	324.2	141.3	465.5	323.7	136.5	460.2
23	330	150	480	325	147	472	328.1	131.9	460.0	321.7	132.3	454.0
24	331	150	481	326	148	474	323.2	135.0	458.2	328.7	122.8	451.5
25	327	150	477	324	148	472	324.2	133.9	458.1	329.7	122.8	452.5
26	326	150	476	322	148	470	321.2	138.1	459.3	316.8	135.4	452.2
27	318	150	468	315	148	463	311.4	143.2	454.6	306.8	140.7	447.5
28	320	151	471	317	149	466	319.2	134.9	454.2	313.8	134.4	448.2
29	318	151	469	313	149	462	310.4	145.3	455.7	305.8	141.8	447.6
30	324	151	475	322	149	471	324.2	130.8	454.9	321.7	125.9	447.7

Table 6-20. Data from Extended Sampling Test with Diesel Generator at Idle, Verification of ECOM Analyzers (continued)

	ECOM Analyzer Data						Reference Analyzer Data					
	Unit A NO (ppm)	Unit A NO <sub>2</sub> (ppm)	Unit A NO <sub>x</sub> (ppm)	Unit B NO (ppm)	Unit B NO <sub>2</sub> (ppm)	Unit B NO <sub>x</sub> (ppm)	14A NO (ppm)	14A NO <sub>2</sub> (ppm)	14A NO <sub>x</sub> (ppm)	10 NO (ppm)	10 NO <sub>2</sub> (ppm)	10 NO <sub>x</sub> (ppm)
31	324	151	475	319	149	468	316.3	141.2	457.5	310.8	139.7	450.5
32	320	152	472	315	150	465	311.4	147.5	458.8	304.9	144.9	449.8
33	320	153	473	319	151	470	314.3	145.4	459.7	308.8	140.7	449.5
34	322	152	474	318	150	468	315.3	144.4	459.7	309.8	140.7	450.5
35	325	152	477	325	150	475	316.3	145.4	461.7	313.8	140.7	454.5
36	327	151	478	325	149	474	324.2	135.0	459.2	317.8	131.2	449.0
37	331	151	482	328	149	477	323.2	136.0	459.2	317.8	132.3	450.0
38	329	151	480	325	149	474	321.2	140.2	461.4	317.8	130.2	447.9
39	332	151	483	328	150	478	322.2	143.4	465.6	318.8	130.2	448.9
40	328	151	479	321	149	470	323.2	143.4	466.6	319.7	136.5	456.3
41	324	151	475	320	149	469	323.2	133.9	457.1	315.8	131.2	447.0
42	323	151	474	319	149	468	318.3	134.9	453.2	311.8	128.0	439.8
43	321	150	471	319	149	468	320.2	138.1	458.3	314.8	132.3	447.0
44	319	152	471	313	150	463	315.3	140.1	455.5	305.8	139.6	445.5
45	310	151	461	304	149	453	308.4	137.9	446.4	298.9	133.3	432.2
46	307	153	460	302	151	453	309.4	133.7	443.2	300.9	132.2	433.1
47	305	154	459	302	152	454	311.4	133.8	445.2	301.9	132.2	434.1
48	309	153	462	305	151	456	308.4	142.2	450.6	297.9	139.6	437.5
49	306	154	460	301	152	453	304.5	141.0	445.6	294.9	136.4	431.3
50	306	154	460	302	152	454	303.5	142.1	445.6	296.9	136.4	433.3
51	306	154	460	302	152	454	308.4	141.1	449.5	299.9	146.0	445.9
52	303	154	457	299	152	451	302.5	143.1	445.7	294.9	137.5	432.4
53	301	154	455	297	152	449	296.7	145.1	441.8	289.0	137.5	426.4
54	305	154	459	301	152	453	300.6	143.1	443.7	294.9	135.4	430.3
55	299	154	453	295	152	447	299.6	142.0	441.6	293.9	135.4	429.3
56	302	155	457	298	153	451	301.6	148.4	449.9	294.9	140.7	435.6
57	306	155	461	303	153	456	302.5	148.4	450.9	295.9	140.7	436.6
58	303	156	459	298	154	452	300.6	153.6	454.2	292.9	144.9	437.8
59	302	157	459	298	155	453	303.5	143.1	446.7	294.9	139.6	434.5
60	304	157	461	299	155	454	302.5	145.2	447.8	294.9	140.7	435.6

**Table 6-21. Results of Evaluation of Measurement Stability for ECOM A-PLUS 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)	-0.554 (0.044)	0.178 (0.009)	-0.375 (0.045)	-0.568 (0.045)	0.184 (0.008)	-0.384 (0.047)	-0.545 (0.043)	0.123 (0.034)	-0.423 (0.036)
Difference in Slopes (ppm/min) (Std Err)	-0.009 (0.023)	0.057 (0.033)	0.048 (0.027)	-0.023 (0.023)	0.062 (0.033)	0.039 (0.029)	—	—	—

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

Unit A vs. Unit B			NO	NO <sub>2</sub>	NO <sub>x</sub>
First Linear Regression	Intercept	t-statistic	0.030	-0.378	---
		p-value*	0.977	0.714	---
	Slope	t-statistic	-21.481	0.078	---
		p-value	<b>&lt;0.001</b>	0.939	---
Detection Limit (First Linearity Test)		t-statistic	-0.010	-0.595	---
		p-value	0.992	0.556	---
Second Linear Regression	Intercept	t-statistic	0.307	-0.072	---
		p-value*	0.765	0.944	---
	Slope	t-statistic	0.014	0.267	---
		p-value	0.989	0.795	---
Detection Limit (Second Linearity Test)		t-statistic	0.544	-0.002	---
		p-value	0.591	0.998	---
Relative Accuracy	Gas Rangetop	t-statistic	2.000	**	2.000
		p-value	0.081	**	0.081
	Gas Water Heater	t-statistic	8.222	4.000	2.800
		p-value	<b>&lt;0.001</b>	<b>0.004</b>	<b>0.023</b>
	Generator-High ppm	t-statistic	6.424	11.314	13.034
		p-value	<b>&lt;0.001</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>
Generator-Idle	t-statistic	4.642	8.000	6.614	
	p-value	<b>0.002</b>	<b>&lt;0.001</b>	<b>&lt;0.001</b>	
Measurement Stability	Slope	t-statistic	1.452	-1.954	0.824
		p-value	0.152	0.056	0.413

\* p-value < 0.05 indicates that two test units are statistically different at the 5% significance level.

\*\* Unit A and Unit B had exactly the same NO<sub>2</sub> readings on the gas rangetop emission. The matched-pairs t-statistic could not be calculated.

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### **6.3.1 Cost**

The cost of each analyzer as tested in this verification test was approximately \$12,000. This represents the cost of the analyzers, sampling probe, and sample conditioning system.

### **6.3.2 Data Completeness**

The data completeness in the verification tests was 100 percent for both ECOM analyzers.

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

The verification tests were too short to assess the long-term maintenance costs or reliability of the ECOM analyzers. The analyzers showed no operational difficulties during laboratory or source testing. The interruption in verification testing of the analyzers was caused by a loss of temperature control in the heated chamber during the ambient temperature test, and not by a fault of the analyzers themselves. The ECOM analyzers successfully completed the ambient temperature test and all other tests when testing was resumed.

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## Chapter 7

### Performance Summary

The ECOM A-PLUS analyzers provided linear response, but not quite over their full nominal ranges of 0 to 4,000 ppm for NO and 0 to 500 ppm for NO<sub>2</sub>. The actual linear ranges for the ECOM analyzers were about 0 to 3,500 ppm for NO, and about 0 to 450 ppm for NO<sub>2</sub>. Detection limits estimated from the wide-range linearity test data were 1.2 ppm for NO<sub>2</sub> and about 4 ppm for NO. Subsequent combustion source tests indicated NO and NO<sub>2</sub> detection limits comparable to the 1 ppm measurement resolution of the analyzers. Response times found were 11 to 37 seconds for NO and about 100 seconds for NO<sub>2</sub>. Drift in zero and span readings obtained before and after source combustion and laboratory tests varied with the NO and NO<sub>2</sub> levels to which the analyzers were exposed. In the worst case, drift in span gas readings amounted to about 5 percent of the span value. Shutting the analyzer off completely overnight had no significant additional effect on the drift observed. No interference was found from any of the following: 496 ppm CO; 5.03 percent CO<sub>2</sub>; 494 ppm NH<sub>3</sub>; 590 ppm of total hydrocarbons; 501 ppm of SO<sub>2</sub>; and 451 ppm of SO<sub>2</sub> in the presence of 388 ppm NO.

Over the tested range of -10 to +10 inches of water (relative to ambient pressure), the sample gas pressure had no significant effect on the zero or span readings of the ECOM analyzers. Ambient temperature over the range of 7 to 41 °C (45 to 105 °F) also had little impact on zero and span readings of the ECOM analyzers. For example, NO span values differed by 3 percent or less due to temperature effects over this range, using a 700 ppm span gas; and NO<sub>2</sub> span values differed by 7.5 percent or less, using a 140 ppm span gas.

The relative accuracy of the ECOM analyzers was 1.3 to 15.3 percent for NO, NO<sub>2</sub>, and NO<sub>x</sub>, in nearly all measurements on a gas rangetop, gas water heater, and a diesel engine at both idle and high RPM. The only exceptions were conditions in which NO or NO<sub>2</sub> were present at levels below 6 ppm. In those cases, the ECOM analyzers were accurate within about their 1 ppm measurement resolution at those low levels. Relative accuracy for NO<sub>x</sub> was 12.1 percent or better with all combustion sources, including one producing less than 10 ppm of NO<sub>x</sub>. In source testing, the two ECOM analyzers showed unit-to-unit agreement within 4.2 percent or less at NO<sub>x</sub> levels from about 7 ppm to over 450 ppm. The agreement between the two ECOM analyzers was actually better than that between the two reference analyzers.

Comparison of verification results from the two ECOM analyzers shows only slight differences in performance, which would be of negligible importance in actual sampling. The performance of the two analyzers tested was essentially the same.

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## Chapter 8 References

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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 Standard (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

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Test Method (CTM)-030, U.S. EPA, Office of Air Quality Planning and Standards, Emission Measurement Center, October 13, 1997.

**Appendix A  
Data Recording Sheets**



## Linearity Test Data Sheet

Date: \_\_\_\_\_ Vendor/Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

Pre-Test Z/Span: Unit A: Zero (NO/NO<sub>2</sub>)   /   Span (NO/NO<sub>2</sub>)   /  

Unit B: Zero (NO/NO<sub>2</sub>)   /   Span (NO/NO<sub>2</sub>)   /  

	NO Test		NO <sub>2</sub> Test	
Time Response	Unit A (NO/NO <sub>2</sub> )	Unit B (NO/NO <sub>2</sub> )	Unit A (NO/NO <sub>2</sub> )	Unit B (NO/NO <sub>2</sub> )
1.	<u>  /  </u>	<u>  /  </u>	1.	<u>  /  </u>
2.	<u>  /  </u>	<u>  /  </u>	2.	<u>  /  </u>
3.	<u>  /  </u>	<u>  /  </u>	3.	<u>  /  </u>
4.	<u>  /  </u>	<u>  /  </u>	4.	<u>  /  </u>
5.	<u>  /  </u>	<u>  /  </u>	5.	<u>  /  </u>
6.	<u>  /  </u>	<u>  /  </u>	6.	<u>  /  </u>
7.	<u>  /  </u>	<u>  /  </u>	7.	<u>  /  </u>
8.	<u>  /  </u>	<u>  /  </u>	8.	<u>  /  </u>
9.	<u>  /  </u>	<u>  /  </u>	9.	<u>  /  </u>
10.	<u>  /  </u>	<u>  /  </u>	10.	<u>  /  </u>
11.	<u>  /  </u>	<u>  /  </u>	11.	<u>  /  </u>
12.	<u>  /  </u>	<u>  /  </u>	12.	<u>  /  </u>
13.	<u>  /  </u>	<u>  /  </u>	13.	<u>  /  </u>
14.	<u>  /  </u>	<u>  /  </u>	14.	<u>  /  </u>
15.	<u>  /  </u>	<u>  /  </u>	15.	<u>  /  </u>
16.	<u>  /  </u>	<u>  /  </u>	16.	<u>  /  </u>
17.	<u>  /  </u>	<u>  /  </u>	17.	<u>  /  </u>
18.	<u>  /  </u>	<u>  /  </u>	18.	<u>  /  </u>
19.	<u>  /  </u>	<u>  /  </u>	19.	<u>  /  </u>
20.	<u>  /  </u>	<u>  /  </u>	20.	<u>  /  </u>
21.	<u>  /  </u>	<u>  /  </u>	21.	<u>  /  </u>

Post-Test Z/Span: Unit A: Zero (NO/NO<sub>2</sub>)   /   Span (NO/NO<sub>2</sub>)   /  

Unit B: Zero (NO/NO<sub>2</sub>)   /   Span (NO/NO<sub>2</sub>)   /

## Interrupted Sampling Data Sheet

Date: \_\_\_\_\_ Vendor/Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

Pre-Shut Down Z/Span:

Date: \_\_\_\_\_ Time: \_\_\_\_\_

Unit A (NO/NO<sub>2</sub>) Zero \_\_\_\_\_ / \_\_\_\_\_ Span \_\_\_\_\_ / \_\_\_\_\_

Unit B (NO/NO<sub>2</sub>) Zero \_\_\_\_\_ / \_\_\_\_\_ Span \_\_\_\_\_ / \_\_\_\_\_

Post-Shut Down Z/Span:

Date: \_\_\_\_\_ Time: \_\_\_\_\_

Unit A (NO/NO<sub>2</sub>) Zero \_\_\_\_\_ / \_\_\_\_\_ Span \_\_\_\_\_ / \_\_\_\_\_

Unit B (NO/NO<sub>2</sub>) Zero \_\_\_\_\_ / \_\_\_\_\_ Span \_\_\_\_\_ / \_\_\_\_\_

### Interference Test Data Sheet

Date: \_\_\_\_\_ Vendor/Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

<u>Interference Gas</u>	<u>Concentration</u>	<u>Response (NO/NO<sub>2</sub>)</u>	
		<u>Unit A</u>	<u>Unit B</u>
Zero	--	<u>/</u>	<u>/</u>
CO	496 ppm	<u>/</u>	<u>/</u>
Zero	--	<u>/</u>	<u>/</u>
CO <sub>2</sub>	5.03%	<u>/</u>	<u>/</u>
Zero	--	<u>/</u>	<u>/</u>
NH <sub>3</sub>	494 ppm	<u>/</u>	<u>/</u>
Zero	--	<u>/</u>	<u>/</u>
Hydrocarbons	590 ppm	<u>/</u>	<u>/</u>
Zero	--	<u>/</u>	<u>/</u>
SO <sub>2</sub>	501 ppm	<u>/</u>	<u>/</u>
Zero	--	<u>/</u>	<u>/</u>
SO <sub>2</sub> + NO	451 ppm + 393 ppm	<u>/</u>	<u>/</u>

## Flow Rate Sensitivity Data Sheet

Date: \_\_\_\_\_ Vendor/Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

Flow Rate Data:	Unit A <u>(ccm)</u>	Unit B <u>(ccm)</u>
Ambient P	_____	_____
+10 in H <sub>2</sub> O	_____	_____
-10 in H <sub>2</sub> O	_____	_____

Response Data:		Unit A <u>(NO/NO<sub>2</sub>)</u>	Unit B <u>(NO/NO<sub>2</sub>)</u>
Ambient P	Zero	/	/
	NO Span	/	/
	Zero	/	/
	NO <sub>2</sub> Span	/	/
	Zero	/	/
+10 in H <sub>2</sub> O	Zero	/	/
	NO Span	/	/
	Zero	/	/
	NO <sub>2</sub> Span	/	/
	Zero	/	/
-10 in H <sub>2</sub> O	Zero	/	/
	NO Span	/	/
	Zero	/	/
	NO <sub>2</sub> Span	/	/
	Zero	/	/

# Ambient Temperature Test Data Sheet

Date: \_\_\_\_\_ Vendor/Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

Room Temperature: \_\_\_\_\_

	<u>Response (NO/NO<sub>2</sub>)</u>	
	<u>Unit A</u>	<u>Unit B</u>
Zero	<u>/</u>	<u>/</u>
NO Span	<u>/</u>	<u>/</u>
NO <sub>2</sub> Span	<u>/</u>	<u>/</u>
Zero	<u>/</u>	<u>/</u>

Cold Chamber Temperature: \_\_\_\_\_

Zero	<u>/</u>	<u>/</u>
NO Span	<u>/</u>	<u>/</u>
NO <sub>2</sub> Span	<u>/</u>	<u>/</u>
Zero	<u>/</u>	<u>/</u>

Heated Chamber Temperature: \_\_\_\_\_

Zero	<u>/</u>	<u>/</u>
NO Span	<u>/</u>	<u>/</u>
NO <sub>2</sub> Span	<u>/</u>	<u>/</u>
Zero	<u>/</u>	<u>/</u>

Room Temperature: \_\_\_\_\_

Zero	<u>/</u>	<u>/</u>
NO Span	<u>/</u>	<u>/</u>
NO <sub>2</sub> Span	<u>/</u>	<u>/</u>
Zero	<u>/</u>	<u>/</u>

Accuracy Test Data Sheet: Rangetop Combustion

Date \_\_\_\_\_ Vendor Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

**Pre-Test Zero/Span**

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Unit 14A: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

Unit 10: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

	<u>Unit 14A</u> (NO/NO <sub>2</sub> /NO <sub>x</sub> )	<u>Unit 10</u> (NO/NO <sub>2</sub> /NO <sub>x</sub> )
1.	____/____/____	____/____/____
2.	____/____/____	____/____/____
3.	____/____/____	____/____/____
4.	____/____/____	____/____/____
5.	____/____/____	____/____/____
6.	____/____/____	____/____/____
7.	____/____/____	____/____/____
8.	____/____/____	____/____/____
9.	____/____/____	____/____/____

**Post-Test Zero/Span**

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Unit 14A: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

Unit 10: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

**Accuracy Test Data Sheet: Water Heater Combustion**

Date \_\_\_\_\_ Vendor Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

***Pre-Test Zero/Span***

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Unit A: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

Unit B: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

	<u>Unit A</u> (NO/NO <sub>2</sub> /NO <sub>x</sub> )	<u>Unit B</u> (NO/NO <sub>2</sub> /NO <sub>x</sub> )
1.	____/____/____	____/____/____
2.	____/____/____	____/____/____
3.	____/____/____	____/____/____
4.	____/____/____	____/____/____
5.	____/____/____	____/____/____
6.	____/____/____	____/____/____
7.	____/____/____	____/____/____
8.	____/____/____	____/____/____
9.	____/____/____	____/____/____

***Post-Test Zero/Span***

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Unit A: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

Unit B: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

**Accuracy Test Data Sheet: Diesel-Engine Combustion**

Date \_\_\_\_\_ Vendor Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

***Pre-Test Zero/Span***

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Unit 14A: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

Unit 10: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

	<u>Unit 14A</u> (NO/NO <sub>2</sub> /NO <sub>x</sub> )	<u>Unit 10</u> (NO/NO <sub>2</sub> /NO <sub>x</sub> )
1.	____/____/____	____/____/____
2.	____/____/____	____/____/____
3.	____/____/____	____/____/____
4.	____/____/____	____/____/____
5.	____/____/____	____/____/____
6.	____/____/____	____/____/____
7.	____/____/____	____/____/____
8.	____/____/____	____/____/____
9.	____/____/____	____/____/____

***Post-Test Zero/Span***

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Calibration Gas & Concentration: \_\_\_\_\_ Instrument Range: \_\_\_\_\_

Unit 14A: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_

Unit 10: Zero (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_ Span (NO/NO<sub>2</sub>/NO<sub>x</sub>) \_\_\_\_/\_\_\_\_/\_\_\_\_



**Measurement-Stability Test Data Sheet: Diesel-Engine Combustion**

Date \_\_\_\_\_ Vendor Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

Diesel-Engine Load: \_\_\_\_\_

<u>Time</u> (t+min#)	<u>Unit A</u> (NO/NO <sub>2</sub> /NO <sub>x</sub> )	<u>Unit B</u> (NO/NO <sub>2</sub> /NO <sub>x</sub> )
1.	____/____/____	____/____/____
2.	____/____/____	____/____/____
3.	____/____/____	____/____/____
4.	____/____/____	____/____/____
5.	____/____/____	____/____/____
6.	____/____/____	____/____/____
7.	____/____/____	____/____/____
8.	____/____/____	____/____/____
9.	____/____/____	____/____/____
10.	____/____/____	____/____/____
11.	____/____/____	____/____/____
12.	____/____/____	____/____/____
13.	____/____/____	____/____/____
14.	____/____/____	____/____/____
15.	____/____/____	____/____/____
16.	____/____/____	____/____/____
17.	____/____/____	____/____/____
18.	____/____/____	____/____/____
19.	____/____/____	____/____/____
20.	____/____/____	____/____/____
21.	____/____/____	____/____/____
22.	____/____/____	____/____/____
23.	____/____/____	____/____/____
24.	____/____/____	____/____/____
25.	____/____/____	____/____/____
26.	____/____/____	____/____/____
27.	____/____/____	____/____/____
28.	____/____/____	____/____/____
29.	____/____/____	____/____/____
30.	____/____/____	____/____/____

Measurement-Stability Test Data Sheet: Diesel-Engine Combustion

Date \_\_\_\_\_ Vendor Analyzer: \_\_\_\_\_

Form Filled Out By: \_\_\_\_\_

Diesel-Engine Load: \_\_\_\_\_

Time (t + min#)	Unit A (NO/NO <sub>2</sub> /NO <sub>x</sub> )	Unit B (NO/NO <sub>2</sub> /NO <sub>x</sub> )
31.	____/____/____	____/____/____
32.	____/____/____	____/____/____
33.	____/____/____	____/____/____
34.	____/____/____	____/____/____
35.	____/____/____	____/____/____
36.	____/____/____	____/____/____
37.	____/____/____	____/____/____
38.	____/____/____	____/____/____
39.	____/____/____	____/____/____
40.	____/____/____	____/____/____
41.	____/____/____	____/____/____
42.	____/____/____	____/____/____
43.	____/____/____	____/____/____
44.	____/____/____	____/____/____
45.	____/____/____	____/____/____
46.	____/____/____	____/____/____
47.	____/____/____	____/____/____
48.	____/____/____	____/____/____
49.	____/____/____	____/____/____
50.	____/____/____	____/____/____
51.	____/____/____	____/____/____
52.	____/____/____	____/____/____
53.	____/____/____	____/____/____
54.	____/____/____	____/____/____
55.	____/____/____	____/____/____
56.	____/____/____	____/____/____
57.	____/____/____	____/____/____
58.	____/____/____	____/____/____
59.	____/____/____	____/____/____
60.	____/____/____	____/____/____

**Appendix B**  
**External Technical Systems Audit Report**

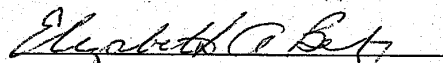
Environmental Technology Verification Program

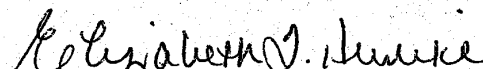
Advanced Monitoring Systems Pilot

Air Monitoring Systems

**NO/NO<sub>2</sub> Monitors Verification Test**  
**January 20-21, 1999 Audit**

Audit Report: ETVAMS001  
Revision 1

  
Elizabeth A. Betz

  
Elizabeth T. Hunike

## **1.0 Audit Information**

### **1.1 Auditors:**

Elizabeth A. Betz  
Human Exposure & Atmospheric Sciences Division  
U. S. EPA, NERL (MD-77)  
Research Triangle Park, NC 27711  
(919) 541-1535

Elizabeth T. Hunike  
Atmospheric Methods & Monitoring Branch  
Human Exposure & Atmospheric Sciences Division  
U. S. EPA, NERL (MD-46)  
Research Triangle Park, NC 27711  
(919) 541-3737

**1.2 Dates of Audit:** January 20-21, 1999

**1.3 Location of Audit:** Battelle Memorial Institute, Columbus, Ohio

### **1.4 Battelle Staff Interviewed and/or Observed:**

Karen Riggs	ETV AMS Pilot Manager
Susan Abbgly	QA/QC Reviewer
Sandy Anderson	QA Manager
Verification Test Team:	
Tom Kelly	Verification Test Leader
Joe Tabor	Laboratory Verification Testing
Jim Reuther	Emission Source Verification Testing
Steve Speakman	Operator, Emission Sources/Reference Method

## **2.0 Background**

Throughout its history, the U.S. EPA has evaluated technologies to determine their effectiveness in preventing, controlling, and cleaning up pollution. EPA has expanded these efforts by instituting the Environmental Technology Verification Program (ETV) to verify the performance of a larger number of innovative technical solutions to problems that threaten human health or the environment. The goal of ETV is to verify the environmental performance characteristics of commercial-ready technology through the evaluation of objective and quality assured data, so that potential purchasers and permittees are provided with an independent and credible assessment of what they are buying and permitting. The ETV Program Verification Strategy outlines the goals, operating principles, pilot selection criteria, and implementation activities. ETV includes twelve pilot projects. In these pilots, EPA is using the expertise of partner verification organizations to design efficient processes for conducting performance tests of innovative technologies. The implementation activities involve forming stakeholder groups who identify technologies needing verification, designing a generic verification protocol and then Test/QA

Plans for the specific technology to be verified. The verification tests are run on the identified technologies wishing to participate and verification statements based on the test results are generated.

One pilot, entitled Advanced Monitoring Systems (AMS), is to verify the performance of commercially available technologies used to monitor for environmental quality in air, water and soil. This pilot is managed by EPA's National Exposure Research Laboratory in Research Triangle Park, North Carolina and their verification partner for the AMS pilot project is Battelle Memorial Institute, Columbus, Ohio. This pilot has been divided into three sub-pilots, each looking at monitoring systems for a specific media, air, water and, eventually, soil. The Air AMS portion has evolved to the point of actually running verification tests on available air monitoring instrumentation.

### **3.0 Scope of Audit**

**3.1 Audit Preparation.** The auditors reviewed the following documents pertinent to the ETV AMS Pilot:

- a. *Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000), May 1998*
- b. *Environmental Technology Verification Program Quality Management Plan for the ETV Advanced Monitoring Systems Pilot, September 1998*
- c. *Test/QA Plan for Verification of Portable NO/NO<sub>2</sub> Emission Analyzers, December 4, 1998*
- d. *U. S. EPA Method 6C, Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)*
- e. *U. S. EPA Method 7E, Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)*

Based on the above material, a checklist was prepared. The U. S. EPA ETV AMS Pilot Manager, Robert G. Fuerst, was provided the checklist prior to the audit. The completed checklist for this audit is attached.

### **3.2 Audit Scope.**

The audit encompassed a technical systems audit of a verification test (VT) on nitrogen oxides monitors at Battelle. A technical systems audit is a qualitative onsite audit of the physical setup of the test. The auditors determine the compliance of testing personnel with the test/QA plan. The auditors were on site from Wednesday afternoon through Thursday afternoon. The technical systems audit was performed on the flow rate and ambient temperature of the laboratory portion of the VT and the relative accuracy tests with the gas cooktop, water heater and a portion of the lower range emissions of a diesel generator. No performance evaluations were conducted as a part of this audit.

### **4.0 Executive Summary**

4.1 The VT is well-managed, particularly considering its complexity. All personnel appeared to be well-trained for their particular duties. All involved showed enthusiasm and ingenuity during the VT.

4.2 The significant findings of this audit, cited in paragraph 5.0 below, had also been found by Battelle's QA staff during their audit earlier in the VT.

4.3 The technical systems audit showed that the VT personnel were very familiar with the Test/QA Plan. With one exception, differences for this VT from the original Test/QA Plan were well documented by deviation reports on file at Battelle. The deviation report format includes a date, cites the deviation, provides an explanation of the deviation and requires an approving Battelle signature. It was impressive that the deviation reports were present and were completed up front. The one difference from the VT that was not cited in a deviation report was that Battelle had intended to run an analyzer already on hand completely through the VT before the first vendor's analyzer. This was not done nor was a deviation report generated. The remaining differences were cited in the deviation reports.

## **5.0 Major Findings**

**5.1 Undocumented Deviation from the Test/QA Plan.** The undocumented deviation was from section 5.6, Test Schedule, and stated "to avoid bias in testing of the first analyzers through the sequence, Battelle's personnel will first conduct the entire test sequence using an analyzer already on hand at Battelle. Testing will then continue with analyzers named in section 2.4." Due to a delay in the arrival of the protocol gases used in the VT, Battelle did not run one of their instruments through the test sequence. As a result a leak in the gas supply system in the laboratory test portion was not detected before the first vendor started the VT sequence.

**5.2 Initial Calibration of Instruments for Emission Source Testing.** The Test/QA Plan states that "the chemiluminescent monitors to be used for Method 7E reference measurements will be subjected to a 4-point calibration with NO prior to the start of verification testing, on each measurement range to be used for verification." The initial Emission's portion of the VT was started on January 13, 1999. There was no 4-point calibration with NO recorded in the Emission's VT laboratory notebook prior to the January 13<sup>th</sup> testing. This finding is also a finding in Battelle's Internal Audit conducted during the first week of the VT.

## **6.0 Results of Technical Systems Audit**

**6.1 Organization.** The Battelle ETV AMS VT team consisted of four members. All team members were very knowledgeable of the procedures and helpful to the auditors. There are also two Battelle Quality Assurance staff members that are members of the ETV AMS team. Both were available and very helpful to the auditors. These Battelle QA staff members are responsible for running the internal audits required by the ETV related QMPs. One such audit was conducted the week prior to this EPA audit.

6.1.1 The Test/QA Plan stated that a Dr. Agnes Kovacs would be providing statistics and data analysis for this VT. One of the documented deviations was that Dr. Kovacs would not be participating in the VT as she has left Battelle. Although the deviation report stated that someone in the Statistics and Data Analysis Department would be taking her place, there was no indication in the deviation report as to who it would be.

**6.2 Gas Cylinder Certifications.** A review of the gas cylinder certifications uncovered some minor discrepancies. The expiration date on two of the cylinder certifications did not match the expiration date on the cylinders. The discrepancy was corrected by the gas manufacturer on the day of inspection. Battelle did not initially have certifications for the gas cylinders used in the source test. The gas manufacturer was contacted by phone and faxed in certifications for 3 of the 4 cylinders. The original certificates were later located on one of the team member's desk. The gas cylinder for one of the certificates reviewed was not found among the ETV VT equipment.

**6.3 Temperature Sensor Certification.** The certificate in the notebook maintained for the Laboratory Test Portion was for Model 402A, Serial # 40215 Temperature Indicator. This indicator was not seen by the Auditors. The Temperature Indicator used in the Laboratory Test portion to read the temperature of the monitors during the Ambient Test was Model 400A, decal # LN-560558. The certificate was not in the notebook, however, the indicator did have a label on it that stated that it was certified 1-7-99. Discussion with Susan Abby, after the audit, clarified that LN-560558 was an internal Battelle laboratory number and that the manufacturer's serial number on LN-560558 was 40215. However, the certificate did reflect an incorrect model number for Temperature Indicator Serial # 40215.

**6.4 Deviation Reports.** The dated reports cited the deviation, provided an explanation/justification of the deviation and required an approving Battelle signature. It was impressive that the deviations reports were present and were completed up front.

6.4.1 The Flow Rate Sensitivity Test procedure had three deviation reports. The Test/QA Plan called for the use of 60% span value during the test. A deviation report cited that this was changed to 70% span value to correlate to the Linearity Test. The two other reports related to the Flow Rate Sensitivity Test were very similar and called for a change in the order of the procedure to reduce the amount of plumbing changes required.

6.4.2 The Ambient Temperature Test had one deviation report. The order of the test was changed. The procedure called for doing a cooled chamber test first and then hot. The deviation report stated that all VTs will be done in the reverse order. The reason for the deviation was based on discussions with the vendors that indicated the rise in temperature after exposure to NO may cause more drift. The order was reversed to more clearly observe any drift.

6.4.2.1 During the Ambient Temperature Test observed, slight changes were made to accommodate the mass of the monitors. The vendor's monitors were larger than previous monitors and generated and held heat longer. The door to the heated chamber, once the monitors reached its temperature, had to remain slightly ajar to hold the chamber temperature at a constant value. The heated monitors were then placed in the cold chamber (a standard household refrigerator). The heat given off by the monitors raised the temperature in the refrigerator over 100°F. To obtain a cooled chamber reading the team members relocated the monitors to the outdoors which produced a cooled ambient temperature within the 45°F ±5°F for the one hour required for temperature equilibration and the additional time required to perform the zero and span check. This was a fine example of the ingenuity the VT team members showed to accommodate differences in monitors.

6.4.3 Interference Test. The mixture of SO<sub>2</sub> and NO for the Interference Test was changed from interferant levels of 250 ppm each of SO<sub>2</sub> and NO to interferant levels of 451 ppm SO<sub>2</sub> and 393



ppm NO. According to the deviation report, this change was made because the NO standard available wasn't at the anticipated concentration when the Test/QA Plan was written.

#### 6.4.4 Source Testing.

6.4.4.1 The Test/QA Plan cited the use of two diesel generators for the Source Test. The selection of these generators was made based on studies that Battelle had used in the past that provided a database of emission levels generated by these sources. However, these generators were property of the Air Force and were unavailable at the time of the VT due to military activities in the Middle East. Battelle substituted one generator they had on site and collected emission data at two speeds to provide two higher emission levels than previously provided by the cooktop or water heater. This substituted generator produced two levels of emissions; however, neither level was over 500 ppm of NO. The database that Battelle had on the originally planned generators showed that one model would produce ranges between 100-1000 ppm NO<sub>x</sub> and the second model would produce ranges between 600-2300 ppm NO<sub>x</sub>. The impact of this change is that there will be no verification for higher ranges.

6.4.4.2 The oxygen sensor was not used during the source test. This VT's focus was the verification of NO/NO<sub>2</sub> levels and not to compare oxygen data. Source stability will be documented by NO<sub>x</sub> measurements instead of oxygen measurements. The source stability for the water heater and the cooktop is also documented in two Battelle reports on data from these specific sources used in interlaboratory comparisons from 1994 through 1998. The initial generators planned for the VT also had similar data bases. The source stability of the generator actually used was verified by data collected in December and January prior to the VT. The actual data collected by the reference monitors during the VT also verified the source stability.

6.4.4.3 ThermoEnvironmental Models 14A and 10 NO/NO<sub>2</sub> analyzers were used for the reference method. The Test/QA Plan called for identical Beckman Model 955 monitors. The reason stated in the deviation report for the substitution was that the Thermo Instruments are newer and are in more current use.

6.4.4.4 Triplicate readings of calibration points were not run in the calibration of the reference method analyzers. Method 7E does not require triplicate readings of calibration points.

6.4.4.5 One deviation report addressed the use of unheated sample lines and poly tubing. The Test/QA Plan is based on EPA Method 7E but based on Battelle's own experience with the sources in the laboratory environment an unheated inlet was used. Additionally it should be noted that the VT is conducted inside in a laboratory setting with controlled temperature and humidity and Method 7E is for stack sampling. The only comment on this deviation report is that the originator of the deviation signed the report instead of obtaining an independent approval signature.

**6.5 Leak Detected in the System in the Laboratory Test Portion.** During the first vendors' laboratory test portion, a leak was detected in the system. The data sheets for the laboratory test portion of the first vendor's VT showed a note that a leak was detected and the vendor recorded oxygen levels. Also noted on the data sheet was a correction factor that would be used on the vendor's data that was made based on the vendor's oxygen readings. The correction factor notes were brought to the auditor's attention by Battelle's QA staff. Because the VT did no verification of oxygen levels,

the correction factor may be inaccurate. As part of the documentation for that VT, the accuracy of the oxygen readings by the vendor needs to be addressed.

**6.6 Initial Calibrations and Tests in the Source Laboratory.** As stated under major findings, paragraph 5.2 above, the initial calibrations of the chemiluminescent monitors used as the Method 7E references were not done before the first VT. In addition no interference test was conducted prior to 1-18-99 which was after the second VT. However, all subsequent VTs had the required initial calibration and interference tests. This was also a finding in Battelle's internal audit conducted a week earlier. Battelle will need to address this in the VT report.

**6.7 Corrections of Data Sheets.** In most instances, corrections made on the data sheets followed Good Laboratory Practices; however, some did not (i.e., one line was not drawn through the incorrect entry and the correction was not dated and initialed).

**6.8 Source Laboratory Notebook Entries.** The initial entries were difficult to follow because the writing was almost illegible and there were missing entries. However, with the exception of the first VT, the four-point initial calibrations are recorded and the time and dates of the VTs are also shown. The actual source test data are recorded on data sheets. The notebook is only used to record the calibration and interference test data on the reference monitors and to record the times, dates and comments on the VTs.

## Checklist for Verification Test (VT) of Portable NO/NO<sub>2</sub> Emission Analyzers

**Date(s):** January 20-21, 1999

**Location:** Battelle, Columbus, Ohio

**Personnel Involved in the Audit:**

	Titles	Names
EPA Auditor(s):		Elizabeth Betz
		Elizabeth Hunike
Battelle QA Rep present:	QA/QC Reviewer	Susan Abbgly
	QA Manager	Sandy Anderson
Battelle Auditees:	ETV AMS Pilot Manager	Karen Riggs
	Verification Test Leader	Tom Kelly
	Laboratory Verification Testing	Joe Tabor
	Emission Source Verification Testing	Jim Reuther
	Operator, Emission Sources/Reference Method	Steve Speakman
Vendor(s) Present:	Horiba	J. David Vojtko

General		Comments
Are the Testers familiar with:	ETV QMP	All staff seem familiar with the documents and there are copies of each in the ETV reference notebooks maintained in the Laboratory and Source Testing areas
	Verification Protocol	
	Test/QA Plan	
	QA Manager	
Generic Verification Protocol:	Finalized?	The Protocol has been finalized and is in the process of being placed on the web.
Test Plan:	Approved and Signed?	The test plan has been reviewed by the vendors. Approval signatures have been received as vendors have arrived to participate in the verification test

**Technologies:**

-Electrochemical (EC) sensors

**Testo's Model 350** electrochemical NO and NO<sub>2</sub> analyzer

Also by direct measurement: O<sub>2</sub>, CO, SO<sub>2</sub>, Stack Temperature, Stack Pressure

By calculation: CO<sub>2</sub>

**Energy Efficiency System's ENERAC 3000SEM** electrochemical NO & NO<sub>2</sub> analyzer

Also by direct measurement: O<sub>2</sub>, CO, SO<sub>2</sub>, CO<sub>2</sub>, Stack Temperature

**TSP's COMBUCHECK** electrochemical NO or NO<sub>2</sub> analyzer

**ECOM's A-Plus** electrochemical NO and NO<sub>2</sub> analyzer

Also by direct measurement: O<sub>2</sub>, CO, SO<sub>2</sub>, Stack Temperature, Stack Pressure

By calculation: CO<sub>2</sub>

-Chemiluminescence emitted from the reaction of NO with O<sub>3</sub> produced within the analyzer

**Horiba's Model PG-250** portable gas analyzer

Also by direct measurement: O<sub>2</sub>, CO, SO<sub>2</sub>, CO<sub>2</sub>

The audit was run during the second week of the Test Plan and the 4<sup>th</sup> vendor was being verified. The vendor was Horiba.

**Pre-Test Requirements:**

Dry Gas Meter:

Initial Calibration Date: See Below

Accurate within 1% and measured in ft<sup>3</sup>

Calibrated against a volumetric standard within 6 months preceding VT

During VT, checked at least once, against reference meter

In-Line Meter, Serial # 1036707, Rockwell R-275, certified 1/18/99

Reference Meter model DTM 115 certified 9/22/98

Temperature Sensor/Thermometers:

Initial Calibration Date: See Below

Calibrated against a certified temp. measurement standard within 6 months preceding VT

During VT, checked at least once, against an ASTM mercury-in-glass reference thermometer at ambient temperature and be within 2%.

Temperature Indicator, Serial #40215, Model 402A, certified 1/7/99, certificate available but didn't

locate this indicator. Temp indicator in Lab, LN-560558, Model 400A, certified 1/7/99.

Oxygen Monitor:

Initial Calibration Date: \_\_\_\_\_

Calibrated within the last six months

During VT, checked once every test day by sampling of ambient air

During operation of one combustion source, assessed for accuracy

Did not use as cited in a documented deviation report.

Chemiluminescent Monitors to be used for Method 7E

Initial Interference Response conducted prior to VT	Date: <u>See Below</u>
Measurement System Preparation prior to VT	Date: <u>See Below</u>
Analyzer Calibration Error prior to VT	Date: <u>See Below</u>
Sampling System Bias Check prior to VT	Date: <u>See Below</u>
NO <sub>2</sub> to NO Conversion Efficiency	Date: <u>See Below</u>

Calibrations Initial Calibration Date: See Below  
4-point calibration with NO & NO<sub>2</sub> prior to VT, on each measurement range

For Horiba's VT both were run 1/20/99, however neither were done before first VT. Interference response was conducted prior to Horiba's VT but not prior to the first VT.

Each point shall be prepared in triplicate - cited in a documented deviation report

Calibration error requirement:  $<\pm 2\%$  of span for the zero, midrange and high-range calibration gases.

Zero and Span checks done daily AM and PM during the VT

Observed AM checks before source test, not present for PM.

Gas Dilution System Initial Calibration Date: 12/16/98  
Flow measurement/control devices calibrated prior to VT by soap bubble flow meter.

Calibration Standards:

EPA Protocol 1 Gases (Calibration paperwork available):  
NO in N<sub>2</sub>, High Range: 80-100% of span  
Mid-Range: 40-60% of span  
Zero: Concentration  $\leq 0.25\%$  of span, ambient air

Protocol Cylinder # ALM057210 expiration date on certificate and cylinder tag did not match.

Cylinder # ALM017108 expiration date on certificate and cylinder tag did not match.

Certificate available for Cylinder # ALM036273 but could not locate cylinder.

Certificates for Source Lab cylinders (AAL14789, ALM014050, AAL17452, ALM015489) could not be initially located.

Sample Location:

Minimum of 8 duct diameters downstream and 2 duct diameters upstream of flow disturbances and center point of the flue vent

The minimal distances from flow disturbances cited in the Reference Method relate to particulate and are not critical for gases and were not used. Vendor's instrument sampling tubes were placed beside those for the reference instruments.

**Day One - Laboratory Tests:**

**Linearity: (response over the full measuring range) - Not Observed**

21 measurements for each analyte (NO, NO<sub>2</sub> or NO<sub>x</sub>)

Zero six times, each other three times

Calibration points used: 0, 10, 20, 40, 70 and 100% of the analyzer's measuring range

Horiba: 0-25, 0-50, 0-100, 0-250, 0-500, 0-1000, 0-2500

0, 250, 500, 1000, 1750 for 0-2500

Initial Zero and Span check?

After every three points, pure dilution gas provided and the analyzers' readings recorded?

Is the order of concentration points followed?

Final Zero and Span Check?

Linearity test was not observed; however, data sheets were examined. The 100% span used for the Horiba was 500 ppm. The laboratory log sheets verified that 21 measurements were made, the order of concentration points cited was used, and that initial and final Zero and Span checks were done.

**Response Time Determinations - Not Observed**

Analyzer's response recorded at 10 second intervals during Response Time check (estimated to be 30 readings)

**Detection Limit - Not Observed**

Detection limit is based on data from zero and 10% readings during Linearity test (9 readings)

**Interrupted Sampling (four readings total) - Not Observed**

Zero and Span recorded at end of Linearity Test on Day One

**Day Two - Laboratory Tests**

**Interrupted Sampling continued** - Not Observed

Zero and Span are recorded after analyzer has been powered up before any adjustments

Same Span from previous day is used

**Interference Tests:** - Not Observed

Actual concentrations were obtained from the data sheets. A documented deviation cited the change in the SO<sub>2</sub> and NO interferant concentrations.

Interferant	Interferant Concentration	Target Analyte
CO	500 ppm - Actual concentration used - 496 ppm	NO, NO <sub>2</sub> , NO <sub>x</sub>
CO <sub>2</sub>	5% - Actual percentage used - 5.03%	NO, NO <sub>2</sub> , NO <sub>x</sub>
SO <sub>2</sub>	500 ppm - Actual concentration used - 501 ppm	NO, NO <sub>2</sub> , NO <sub>x</sub>
NH <sub>3</sub>	500 ppm - Actual concentration used - 494 ppm	NO, NO <sub>2</sub> , NO <sub>x</sub>
Hydrocarbon Mixture	~ 500 ppm C <sub>1</sub> , ~ 100 ppm C <sub>2</sub> , ~ 50 ppm C <sub>3</sub> and C <sub>4</sub> Hydrocarbon concentration used - 590 ppm	NO, NO <sub>2</sub> , NO <sub>x</sub>
SO <sub>2</sub> and NO	250 ppm each - Actual concentration used - 451 ppm SO <sub>2</sub> & 393 ppm NO	NO, NO <sub>2</sub> , NO <sub>x</sub>

Analyzer zeroed first and recorded

Interferant gas supplied, analyzer stabilized and analyte concentrations recorded (6 readings)

**Flow Rate Sensitivity** (9 readings) - Not Observed

Type of flow measuring device: automated bubble flowmeter, rotameter, or other

Ambient atmosphere and ambient flow rate recorded

Zero gas provided and recorded, span gas provided and recorded, zero provided again and recorded

Adjust pressure in system to +10" of water, record flow rate, repeat zero, span and zero

Adjust pressure in system to -10" of water, record, flow rate, repeat zero, span and zero

A leak was detected during the running of the flow rate test for the first vendor. The data sheets reflect this and also indicate a correction factor would be used in the calculations. The correction factor was based on the O<sub>2</sub> value recorded on the vendor's monitors.

**Ambient Temperature** (12 readings)

Room Temperature recorded (assumed to be above 45°F and below 105°F)

Zero and Span and Zero done at each temperature

Instrument allowed to equilibrate to chamber temperature for 1 hour

The ambient temperature test was observed. Room temperature readings were done first. Then the monitors were placed in a heated chamber at 105°F at 13:24 and first readings were at 14:45. The chamber door had to remain slightly ajar to keep the temperature constant. Next the monitors were placed in the cooling chamber which was a household refrigerator. The heated monitors kept overheating the refrigerator. After the initial hour to equilibrate the monitors, the refrigerator temperature was at 110° F. To obtain the cooled ambient temperature needed for the test, the monitors were placed out the laboratory window onto the adjacent roof for an hour and were brought to 47°F. The cooling chamber test readings were taken from 6:38 pm to 6:43 pm. This showed great ingenuity of the laboratory test staff to obtain the required ambient conditions for the test.



## Day Three and Four - Source Tests

### Method 7E

#### **Measurement System Performance - Chemiluminescent Monitors**

Thermo Environmental Instruments Model 10 and Model 14A. Data were recorded off a voltage meter attached to each instrument and voltage readings were then converted to concentrations. The Fluke voltage meter attached to Model 14A was calibrated 11/2/98 and the one attached to Model 10 was calibrated 11/3/98.

Zero Drift:  $\leq \pm 3\%$  of the span over the period of each run

Calibration Drift:  $\leq \pm 3\%$  of the span over the period of each run

Interference Check:  $\leq \pm 7\%$

#### **Measurement System Specifications:**

A documented deviation cited changes to the sample probe and lines initially indicated to be allowed by EPA Method CTM-022 but later revised per July 16, 1999 letter from Battelle indicating the changed was based on Battelle's own experience with the sources used in the laboratory environment.

Sample Probe - Glass, stainless steel, or equivalent

Sample Line - Heated stainless steel or Teflon tubing

Sample Transport Lines - Stainless Steel or Teflon tubing

Calibration Valve Assembly - 3-way valve assembly or equivalent

Moisture Removal System - refrigerator-type condenser or similar device(?) - Ice Chest was used.

Particulate Filter - borosilicate or quartz glass wool or glass fiber mat, non-reactive with NO<sub>x</sub>,  
in-stack or heated out-of-stack

Sample Pump - Leak free pump of any non-reactive material

Sample Flow Rate Control - control valve and rotameter or equivalent

Sample Gas Manifold - any non-reactive material

Data Recorder - strip chart recorder, analog computer or digital recorder;  
resolution shall be 0.5% of span

A data recorder was not used. The test data was recorded on log sheets, one filled out by the vendor on his monitors and one filled out by source laboratory operator for the reference monitors. Calibrations prior to VT are recorded in a bound notebook. Entries are also made to indicate the date and times the VTs in the source laboratory were run.

#### **Sampling:**

Measurements obtained only after twice the response time has elapsed

Zero and Calibration Drift tests performed immediately preceding and following every run

Adding zero gas & calibration gas (closely approximates the source) at calibration valve

Sampling continues only when zero and calibration drift are within specifications

#### **Emission Calculations: - No calculations were observed**

Concentrations are: avg readings (initial & final sampling system bias checks are averaged)  
adjusted for the zero and upscale sampling system bias checks

**Relative Accuracy Tests**

**Low NO<sub>x</sub> Sources**

Gas Cooktop: NO and NO<sub>2</sub> ranges 1-9 ppm  
 Must operate continuously during test (can't cycle off)  
 Must operate at steady-state (See Page 8 or 9)

Condition/Specification	Comments
Analyzers (two each) zeroed and span checked initially only	✓ - Span was 20 ppm NO and 10 ppm NO <sub>2</sub>
Sampling probes of analyzers placed beside reference method probe	✓ - Lines to instruments are then connected into a metal tube to top of stove top.
Analyzers are allowed to stabilize	✓
After initial readings, probes are switched to ambient air and stabilized	✓
Sample Probes are returned to source for a total of nine samplings	✓
Final zero and span check conducted on analyzer after each source, using the same span as initial check	✓

The cooktop used in the VT has been used by Battelle in a previous study. The data on the source levels generated by the cooktop are documented in a Battelle report entitled "An Interlaboratory Program to Validate a Protocol for the Measurement of NO<sub>2</sub> Emissions from Rangetop Burners." The data covers 1994 through 1998.

The gas supply for the cooktop is from a certified cylinder without sulfur.

Water Heater: NO and NO<sub>2</sub> ranges 10-80 ppm

Must operate continuously during test (can't cycle off)

Must operate at steady-state (See Page 8 or 9)

Condition/Specification	Comments
Analyzers (two each) zeroed and span checked initially only	✓ - Span was 100 ppm NO and 15 ppm NO <sub>2</sub>
Sampling probes of analyzers placed beside reference method probe	✓ - connect in a "T" together
Analyzers are allowed to stabilize	✓
After initial readings, probes are switched to ambient air and stabilized	✓
Sample Probes are returned to source for a total of nine samplings	✓
Final zero and span check conducted on analyzer after each source, using the same span as initial check	✓

The water heater used in the VT has been used by Battelle in a previous study. The data on the source levels generated by the water heater is documented in a Battelle report entitled "An Interlaboratory Study to Determine the Precision of an Emission Measurement Protocol for Residential Gas Water Heaters." The data covers 1994 through 1998.

The gas supply for the water heater was from the city gas supply. However, Battelle has a gas chromatograph monitoring the concentration of the gas daily.

## Medium NO<sub>x</sub> Source

First Diesel Generator: NO and NO<sub>2</sub> ranges 100-1000 ppm NO<sub>x</sub>  
 Must operate at steady-state

Condition/Specification	Comments
Analyzers (two each) zeroed and span checked initially only	✓ - Generator was run at high RPM Span was 200 ppm NO and 50 ppm NO <sub>2</sub>
Sampling probes of analyzers placed beside reference method probe	✓
Analyzers are allowed to stabilize	✓
After initial readings, probes are switched to ambient air and stabilized	✓
Sample Probes are returned to source for a total of nine samplings	✓ - initial sampling observed only, auditors departed
Analyzers are evaluated at three separate load conditions per generator	
Extended sampling interval (one hour) is conducted during one load condition	See Note Below
Final zero and span check conducted on analyzer after each source, using the same span as initial check	

Note: The Test/QA Plan called for two specific generators from the Air Force that were unavailable at the time of the VT. A generator on-site was modified to be both the medium and high source. This generator was run at a high RPM for the medium source and at idle for the high source. Because of the noise level at the high RPM, most of the extended sampling interval (one hour) was done during the high source test and not the medium source. One vendor chose to not submit its monitors to the high source so its extended sampling interval was done during the medium source (high RPM).

Steady-State:

Temperature changes in the center position of the exhaust of not more than  $\pm 10^{\circ}\text{F}$ ;

NO<sub>x</sub> changes at the center of the exhaust duct of  $\leq \pm 5\%$  relative to the mean over the 15 minute interval as determined using the EPA reference method

O<sub>2</sub> changes, at the center of the exhaust duct of  $\leq \pm 0.50\%$  absolute ( $\pm 5000$  ppm) from the mean sampled over the 15 minute interval.

**High NO<sub>x</sub> Source - Not Observed**

Second Diesel Generator: NO and NO<sub>2</sub> ranges 600-2300 ppm NO<sub>x</sub>  
 Must operate at steady-state

Condition/Specification	Comments
Analyzers (two each) zeroed and span checked initially only	
Sampling probes of analyzers placed beside reference method probe	
Analyzers are allowed to stabilize	
After initial readings, probes are switched to ambient air and stabilized	
Sample Probes are returned to source for a total of nine samplings	
Analyzers are evaluated at three separate load conditions per generator	
Extended sampling interval (one hour) is conducted during one load condition	
Final zero and span check conducted on analyzer after each source, using the same span as initial check	

Note: Instead of a second generator, the generator was run at idle to produce a span of 400 ppm NO and 100 ppm NO<sub>2</sub>.

Steady-State:

Temperature changes in the center position of the exhaust of not more than  $\pm 10^{\circ}\text{F}$ ;

NO<sub>x</sub> changes at the center of the exhaust duct of  $\leq \pm 5\%$  relative to the mean over the 15 minute interval as determined using the EPA reference method

O<sub>2</sub> changes, at the center of the exhaust duct of  $\leq \pm 0.50\%$  absolute ( $\pm 5000$  ppm) from the mean sampled over the 15 minute interval.