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Environmental Technology Verification Report

TSI COMBUCHECK
SINGLE GAS MONITOR

Prepared by

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Advanced Monitoring Systems

TSI COMBUCHECK
Single Gas Monitor

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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 permitters, 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.

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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_2	carbon dioxide
DC	direct current
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FID	flame ionization detector
ft^3	cubic feet
gpm	gallons per minute
kW	kilowatt
LOD	limit of detection
lpm	liters per minute
m^3	cubic meters
NH_3	anhydrous ammonia
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO_x	nitrogen oxides
NO_2	nitrogen dioxide
O_2	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	SCAQMD Air Quality Management District
SCR	selective catalytic reduction
SO_2	sulfur dioxide
UHP	ultra-high purity

Chapter 1
Background

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

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

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle 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 TSI COMBUCHECK Model 8750 Single Gas monitor.

Chapter 2
Technology Description

The objective of the ETV Advanced Monitoring Systems (AMS) pilot is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for verification testing of COMBUCHECK Model 8750 electrochemical NO and NO_2 single gas monitors, manufactured by TSI, Inc., St. Paul, Minn. The following is a description of the TSI single gas monitors based on information provided by the vendor.

The TSI COMBUCHECK is a hand-held single gas monitor with interchangeable electrochemical sensors to measure carbon monoxide (CO), oxygen (O_2), nitric oxide (NO), nitrogen dioxide (NO_2), or sulfur dioxide (SO_2). The range of the COMBUCHECK is 0 to 2000 ppm for carbon monoxide and nitric oxide, 0 to 100 ppm for nitrogen dioxide, 0 to 1000 ppm for sulfur dioxide, and 0 to 30 percent for oxygen. Only the capabilities for NO and NO_2 measurement were evaluated in this test.

The COMBUCHECK monitor can be used in a variety of environments and for many applications, including measuring flue gas concentrations to optimize combustion efficiency, sampling gas levels near combustion appliances, and monitoring ambient concentrations. A backlit display is provided for use in poor lighting areas. The COMBUCHECK gas sensors are interchangeable with a simple field calibration. The Model 8750 COMBUCHECK monitor has a built-in pump to provide a fast response to changes in gas concentrations. The flexible stainless steel probe has a liquid/particulate filter. The COMBUCHECK will operate under conditions from 0 to 50°C (32 to 122°F), while sources up to 540°C (1,000°F) can be sampled. An optional portable printer is also available to provide hard copy documentation of readings while in the field.

Figure 2-1. COMBUCHECK

The COMBUCHECK weighs 0.84 pound and measures 4.0" x 6.6" x 1.5". It can be operated for over 24 hours on four AA alkaline batteries. An optional AC adapter is also available.

As the product name implies, the COMBUCHECK is intended primarily for rapid inspection and maintenance checks of heaters, furnaces, and boilers. It is not intended for long-term or continuous monitoring. This instrument is a new product for TSI, and its verification testing was intended partly to determine how well a low-end single gas monitor would stand up to emission analyzer conditions.

In this verification test, four COMBUCHECK monitors were used, two for NO and two for NO_2. In all testing, the two NO (or NO_2) analyzers were operated simultaneously to assess unit-to-unit repeatability. The four units were operated on AC power throughout verification testing.

Chapter 3
Test Design and Procedures

3.1 Introduction

The verification test described in this report was conducted in January 1999 on commercial portable nitrogen oxide monitors. The tests were conducted at Battelle in Columbus, Ohio, according to procedures specified in the *Test/QA Plan for Verification of Portable NO/NO$_2$ Emission Analyzers*.(1) Verification testing of the monitors involved the following tests:

1. A series of laboratory tests in which certified NO and NO$_2$ standards were used to challenge the monitors over a wide concentration range under a variety of conditions.

2. Tests using three realistic combustion sources, in which data from the monitors undergoing testing were compared to chemiluminescent NO and NO$_x$ measurements made following the guidelines of EPA Method 7E.(2)

These tests are listed in Table 3-1.

Table 3-1. Identity and Schedule of Verification Tests Conducted on TSI COMBUCHECK Single Gas Monitors

Test Activity	Date Conducted
Laboratory Tests	
Linearity	January 15, 1999, p.m.
Interrupted Sampling	January 15, p.m. – January 16, a.m.
Interferences	January 16, a.m.
Pressure Sensitivity	January 16, a.m.
Ambient Temperature	January 16, p.m.
Source Tests	
Gas Rangetop	January 17, a.m.
Gas Water Heater	January 17, a.m.
Diesel Generator High RPM	January 17, p.m.

To assess inter-unit variability, four identical TSI COMBUCHECK monitors, two with NO sensors and two with NO$_2$ sensors, were tested simultaneously. These four monitors were designated as Unit A NO, Unit A NO_2, Unit B NO, and Unit B NO_2 throughout all testing. The commercial monitors were operated at all times by a representative of TSI so that each monitor's performance could be assessed without concern about the familiarity of Battelle staff with the monitors. At all times, however, the TSI representative was supervised by Battelle staff. Displayed NO and NO_2 readings from the monitors (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 TSI operator recorded data. This approach was taken because visual display of measured NO and NO_2 (or NO_x) concentrations was the "least common denominator" of data transfer among several NO/NO_2 monitors 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 TSI staff setting up and checking out the four TSI monitors in the laboratory at Battelle. Once vendor staff were satisfied with the operation of the monitors, the laboratory tests were begun. These tests were carried out in the order specified in the test/QA plan.(1) Upon completion of laboratory tests, the monitors 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_x concentration and proceeded to sources emitting progressively more NO_x. In all source sampling, the monitors being tested sampled the same exhaust gas as did the reference analyzers. This was accomplished by inserting the TSI monitors' 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 monitors over their full nominal response ranges, which for the TSI COMBUCHECK monitors were 0 to 2,000 ppm for NO and 0 to 100 ppm for NO_2. The lab tests were aimed at quantifying the full range of performance of the monitors.

Laboratory tests were conducted using certified standard gases for NO and NO_2, and a gas dilution system with flow calibrations traceable to the National Institute of Standards and Technology (NIST). The NO and NO_2 standards were diluted in high purity gases to produce a range of accurately known concentrations. The NO and NO_2 standards were EPA Protocol 1 gases, obtained from Scott Specialty Gases, of Troy, Michigan. As required by the EPA Protocol(3) 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_2 standard (Scott Cylinder Number ALM 019660) was 493.2 ppm. These concentrations were confirmed in a performance evaluation audit performed 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 respective ranges of 10, 10, 1, and 0.1 lpm. 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 monitors 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: $SO_2 < 0.1$ ppm, $NO_x < 0.1$ ppm, $CO < 0.5$ ppm, $CO_2 < 1$ 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 monitors from the Environics 2020, using a simple manifold that allowed the monitors 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 monitors, and the third provided a connection for a Magnehelic differential pressure gauge (±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 monitors. 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 ±10 inches of water, while maintaining excess flow of the gas mixtures to the manifold. The arrangement shown in Figure 3-1 was used in all laboratory tests, with the exception of interference testing. For most interference testing, gas standards of the appropriate concentrations were supplied directly to the manifold, without use of the Environics 2020 diluter.

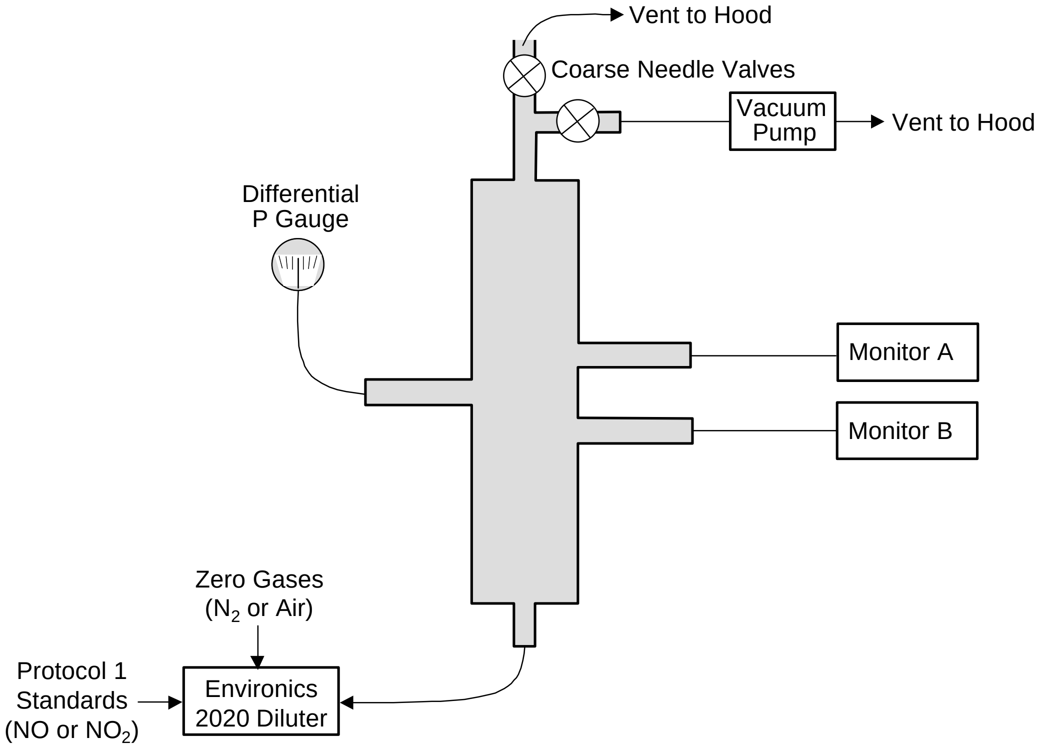

Figure 3-1. Manifold Test Setup

Laboratory testing consisted of a series of separate tests evaluating different aspects of monitor 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

At the request of the TSI representative, before starting the linearity test the TSI NO monitors were calibrated with a 200 ppm NO concentration, and the TSI NO_2 monitors were calibrated with a 25 ppm NO_2 concentration. Both of these calibration mixtures were prepared using the EPA Protocol Gases and Environics calibrator.

The linearity of monitor response was then tested by wide-range multipoint calibrations with NO and NO_2. Linearity testing consisted of a 21-point response check for NO, and for NO_2. At the start of this check, the TSI monitors were provided with the appropriate zero gas, and then with an NO or NO_2 span gas concentration at the respective nominal full scale of the monitors (i.e., 2,000 ppm NO or 100 ppm NO_2). No adjustment was made to the monitors to match that span value, and 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.(1) Following completion of all 21 points, the zero and 100 percent spans were repeated, also without adjustment of the monitors. This entire procedure was performed for NO and then for NO_2.

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_2 detection limits of the monitors, using a statistical procedure defined in the test/QA plan.(1)

3.2.3 Response Time

During the NO and NO_2 linearity tests, upon switching from zero gas to an NO or NO_2 concentration of 70 percent of the respective full scale (i.e., about 1,400 ppm NO or 70 ppm NO_2), the monitors' responses were recorded at 10-second intervals until fully stabilized. These data were used to determine the response times for NO and for NO_2, 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 TSI monitors were shut down (i.e., their electrical power was turned off overnight), ending the first day of laboratory testing. The next morning the monitors were powered up, and the same zero gas and span concentrations were run without adjustment of the monitors. Comparison of the NO and NO_2 zero and span values before and after shutdown indicated the extent of zero and span drift resulting from the shutdown. Full-scale NO and NO_2 levels (i.e., 2,000 ppm NO and 100 ppm NO_2) were used as the span values in this test.

3.2.5 Interferences

Following monitor 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 TSI monitors to species other than NO and NO_2. The potential interferants listed in Table 3-2 were supplied to the monitors one at a time, and the NO and NO_2 readings of the monitors were recorded. The potential interferants were single components, except for a mixture of SO_2 and NO, which was intended to assess whether SO_2 in combination with NO produced a bias in NO response.

Table 3-2. Summary of Interference Tests Performed

Interferant	Interferant Concentration
CO	496 ppm
CO_2	5.03%
SO_2	501 ppm
NH_3	494 ppm
Hydrocarbon Mixture*	485 ppm C_1, 98 ppm C_2, 48 ppm $C_3 + C_4$
SO_2 and NO	451 ppm SO_2 + 383 ppm NO

*C_1 = methane; C_2 = ethane; and $C_3 + C_4$ = 24 ppm propane + 24 ppm n-butane.

The CO, CO_2, SO_2, and NH_3 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 ± 2 percent, based on analysis. The CO, CO_2, and NH_3 mixtures were all in Ultra-High Purity (UHP) air, and the SO_2 mixture was in UHP nitrogen. The SO_2/NO mix listed in Table 3-2 was prepared by diluting the SO_2 standard with the NO Protocol Gas using the Environics 2020.

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 (± 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 TSI monitors. 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 monitor 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_2 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 monitors, and on the NO and NO_2 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; 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 monitors. Zero gas was supplied to the manifold at ambient pressure, and the monitor'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 monitor'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 monitor, and the flow measurements were repeated.

The dependence of NO and NO_2 response on pressure was determined by sampling the appropriate zero gas, and an NO or NO_2 span gas equivalent to 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 monitors, first for NO at all three pressures, and then for NO_2 at all three pressures. The data at different pressures were used to assess zero and span drift resulting from the sample pressure differences.

3.2.7 Ambient Temperature

The purpose of the ambient temperature test was to quantify zero and span drift that may occur as the monitors are subjected to different temperatures during operation. This test involved providing the monitors with zero and span gases for NO and NO_2 (at the same 70 percent of nominal range values used in the pressure test) 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^3 steel and glass laboratory chamber, thermostated at 41°C (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^3.

The general procedure was to provide zero and span gas for NO, and then for NO_2, to the monitors at room temperature, and then to place the monitors 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. After 1 hour or more of stabilization in the heated chamber, the zero and span tests were repeated. The monitors, manifold, and other connections were then transferred to the refrigerator. After a 1-hour stabilization period of 1 hour or more, the zero and span checks were repeated at the reduced temperature. The monitors were returned to the laboratory bench; and, after a 1-hour stabilization period, the zero and span checks were repeated a final time.

3.3 Combustion Source Tests

3.3.1 Combustion Sources

Three combustion sources (a gas rangetop, a gas residential water heater, and a diesel engine) were used to generate NO_x emissions from less than 10 ppm to over 150 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.(4,5)

3.3.1.1 Rangetop

The low-NO_x 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 6 to 7 ppm, and NO_2 in the range of about 2 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_2 emissions.(4)

Rangetop NO_x 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).(6) 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_x 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_x 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 80 to 120 ppm, and NO_2 in the range of 5 to 15 ppm. NO_x emissions dropped as the water temperature rose after ignition, stabilizing at the lower end of the ranges 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.(5)

Water heater NO_x 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_x 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_x 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). In testing of the TSI COMBUCHECK monitors, this device generated NO_x emissions up to about 150 ppm, during operation at high load (3,500 RPM). About 60 to 70 ppm of the NO_x was NO_2. 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_x 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).(9) 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_x 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.

3.3.2.1 Sampling Systems

Prior to sampling, the TSI representative inserted the four monitors' probes into the exhaust duct of the rangetop, water heater, or diesel engine. The TSI probes were located closely together in pairs, 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. Because of the small size of the TSI monitors, the lengths of sample-transfer tubing required to connect the TSI instruments to the rangetop, water heater, and diesel engine were all less than 4 feet. 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 TSI monitors used unheated 1/8" sample probes. 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 fiber filter.

3.3.2.2 Reference Method

The reference method of NO determination against which the commercial monitors were compared was the ozone chemiluminescence method for NO that forms the basis of EPA Method 7E.(2) The reference measurements were made using a Model 10 and a Model 14A source-level NO_x 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 650ºC (1,202°F) for reduction of NO_2 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_x, so display of both readings required manual switching of sampling modes on both instruments. This requirement resulted in the NO and NO_x 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_2 on the applicable ranges, using the EPA Protocol 1 gases. The ratio of the linear regression slope of the NO_2 calibration to that of the NO calibration determined the NO_2 conversion efficiency. For the TSI source tests, which took place on January 17, 1999, calibration data from January 16 were applied. Conversion efficiency values of 91.8 percent and 90.6 percent were found for the Model 14A and Model 10 monitors, respectively.

3.3.2.3 Calibration Gas Supply

Before and after sampling of each combustion source, both the monitors undergoing testing and the reference analyzers were supplied with zero gas and with standard NO and NO_2 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.

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

Source	NO Span Level (ppm)	NO_2 Span Level (ppm)
Gas Rangetop	20	10
Gas Water Heater	100	15
Diesel–High RPM	200	50

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_x emission. For the rangetop, steady-state was achieved after about 15 minutes, when the water began to boil. For the water heater, steady-state was achieved in about 15 minutes, when its water was fully heated. Because the water heater tank had a thermostat, cycling would have occurred had about 3 gpm of hot water not been continuously drained out of the tank.

For the diesel engine, steady-state was achieved in about 10 minutes of operation. The diesel was operated at full speed (3,500 RPM) to achieve its lowest NO_x emissions.

The order of operation of the combustion sources was (1) rangetop, (2) water heater, and (3) diesel engine. This allowed the monitors to be exposed to continuously increasing NO and

NO_2 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 monitors sampling the source emissions, the TSI operator indicated when he was ready to take the first set of readings (a set of readings consisting of the NO and NO_2 responses on the four TSI monitors). At that time the Battelle operator of the reference analyzers also took corresponding readings. The monitors undergoing testing were then disconnected from the source, and allowed to sample room air until readings dropped well below the source emissions levels. The monitors were then reconnected to the source, and after stabilizing another set of readings was taken. There was no requirement that monitor 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 monitors. 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 monitors 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. The COMBUCHECK single gas monitors are not intended for extended continuous sampling of combustion sources, and so had not been tested in this application. However, with the agreement of the TSI operator, the monitors were subjected to the extended sampling test.

Chapter 4
Quality Assurance/Quality Control

Quality control (QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS pilot(7) and the test/QA plan(1) 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 demonstration technologies. The results of the review of the reference analysis 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_2 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_2 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_x 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 the experience of Battelle staff in sampling the combustion sources used in this test, and other combustion sources.

Table 4-1. Results of QC Procedures for Reference NO_x Analyzers for Testing TSI COMBUCHECK Monitors

NO_2 conversion efficiency	91.8% for Model 14A in 100 ppm and 1,000 ppm ranges				
NO_2 conversion efficiency	90.6% 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 (r2 > 0.9999)				
Calibration of reference method using four points at 0, 30, 60, 100% for NO2	Meets criteria (r2 > 0.9999)				
Calibrations (100 ppm range)	Meets ± 2% requirement (relative to span)	Model 10		Model 14A	
		NO		NO	
		Error, % of Span	% of Scale	Error, % of Span	% of Scale
		0.5%	30%	0.9%	30%
		0.4%	60%	0.4%	60%
		NO_2		NO_2	
		Error, % of Span	% of Scale	Error, % of Span	% of Scale
		0.3%	30%	0.2%	30%
		0.7%	60%	0.5%	60%
Zero drift	Meets ± 3% requirement (relative to span) on all combustion sources				
Span drift	Meets ± 3% requirement (relative to span) on all combustion sources				
Interference check	< ± 7% (No interference response observed)				

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. This deviation has no impact on the final data, for the reasons 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.

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. 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_2 calibration gases independent of the test calibration standards containing certified concentrations of NO and NO_2. Accuracy of the reference analyzers was determined by comparing the measured NO/NO_2 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_2 was a commercial standard of 50.5 ppm NO_2 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
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 15th and 16th.	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.
From Pressure Sensitivity Test conducted 1/12/99 an explanation is needed of correction factor to be applied to data.	The O_2 sensors of the vendor's monitors showed the presence of O_2 in the sample gas at a time when only NO in pure N_2 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_2 level observed, and exactly accounted for an apparently low NO response from the vendor's monitors. That is, the O_2 data were used to correct the observed NO responses to what they would have been with no air leakage. The leakage was corrected, and did not occur in testing of the TSI monitors.
Start and stop time for instruments to equilibrate at each temperature is not noted on data sheets.	Added start and stop time to data sheets as a method to document equilibration.
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.	All source tests with the TSI monitors met the 3% requirement (see Table 4-1). No impact on final data.
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.	Comparison of drift is easily made visually; written comments will be added if termination of a test is called for.
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.	This test was terminated. Notes were added as suggested and the test was later repeated in its entirety. No impact on TSI test.

Table 4-4. Performance Evaluation Results

		Reading (V)	Zero (V)	Zero Corrected	Apparent Concentration*	Percent Difference**	Limits
Unit 14A	NO in N_2 (ppm)						
Test Std	3,925	9.92	0.01	9.91	3905.3	0.5%	± 2%
PE Std	3,988	10.13	0.01	10.12			
Unit 10	NO in N_2 (ppm)						
Test Std	3,925	1.01	-0.01	1.03	3895.7	0.7%	± 2%
PE Std	3,988	1.04	-0.01	1.05			
Unit 14A	NO_2 in Air (ppm)						
Test Std	50.0***	4.40	0.01	4.39	48.7	2.5%	± 5%
PE Std	50.5	4.56	0.02	4.54			
Unit 10	NO_2 in Air (ppm)						
Test Std	50.0***	0.44	-0.01	0.45	50.0	0.1%	± 5%
PE Std	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_2 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.

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*(7), the *Test/QA Plan for Verification of Portable NO/NO$_2$ Emission Analyzers,*(1) and *U.S. EPA Method 7E Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).*(2) 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 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 analyzer does not affect any of the verification test data since initial tests were repeated after full calibrations had been completed. There is no impact on the TSI test data from either of these factors.

Chapter 5
Statistical Methods

5.1 Laboratory Tests

The monitor 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 TSI monitor. The calibration model used was

$$Y_c = h(c) + error_c \tag{1}$$

where Y_c is the monitor'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 (σ_c) of the measured concentration values (c) was modeled by the following relationship,

$$\sigma_c^2 = \alpha + kc^{\beta} \tag{2}$$

where α, k, and β 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.

$$weight = w_c = \frac{1}{\sigma_c^2} \tag{3}$$

The form of the linear regression model fitted was $h(c) = \alpha_o + \alpha_1 c$. In the concentration subregion 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

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

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

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

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

$\bar{Y}_{ci}$ is the average of the n_{ci} analyzer responses at the i^{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.

$$\sum_{i=l}^{n}\sum_{j=l}^{n_{ci}} (Y_{cij} - \alpha_0 - \alpha_1 c_i)^2 \; w_{ci} = \sum_{i=l}^{n}\sum_{j=l}^{n_{ci}} (Y_{ci} - \bar{Y}_{ci})^2 \; w_{ci} + \sum_{i=1}^{n} (\bar{Y}_{cij} - \alpha_0 - \alpha_1 c_i)^2 \, n_{ci} w_{ci}$$

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 a monitor's expected response exceeds the calibration curve at zero concentration by three times the standard deviation of the monitor'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

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

where σ_o is the estimated standard deviation at zero concentration. The LOD is estimated as $LOD = 3\hat{\sigma}_0 / \hat{a}_0$. 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 monitors 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 monitor to the calibration gas and R_z is the final response of the monitor to the zero gas. The monitor 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:

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

where $\text{time}_{95\%}$ is the time at which Response_{RT} occurred and Time_I 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 monitor to the interferant species, relative to its sensitivity to NO or NO_2. The relative sensitivity is defined as the ratio of the observed NO/NO_2/NO_x response of the monitor to the actual concentration of the interferant. For example, a monitor 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 monitor 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 sample flow rate, the response on zero gas, and the response on span gas were measured for each monitor. 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 monitor 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:

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

$t = \hat{b} / (0.07071\hat{s}(c))$ 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 monitor 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:

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

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

5.2 Combustion Source Tests

5.2.1 Accuracy

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

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

where *d* refers to the difference between the average of the two reference units and one of the tested units and $\bar{x}$ 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^{α}_{n-1} is the t value for the 100(1 - α)th percentile of the distribution with n - 1 degrees of freedom. The relative accuracy was determined for an α 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 monitor $|\bar{d}|/\bar{x}$, where the bar indicates the average value of the differences or of the reference values.

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

$$\hat{SE} \cong \frac{S_d}{\sqrt{n}\,x} \sqrt{0.3634 + \left(t_{n-1}^{a}\right)^2 \frac{1}{2(n-1)}} \times 100\% \qquad (8)$$

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 monitor response in extended sampling from a combustion source was assessed by means of a trend analysis on 60 minutes of data obtained continuously using the diesel generator as the source. The existence of a difference in trend between the test unit and the average of the reference units was assessed by fitting a linear regression line with the difference between the measured concentration for a test unit and the average of the reference units as the dependent variable, and time as the independent variable. Subtracting the average reference unit values adjusts for variation in the source output. The slope and the standard error of the slope are reported. The null hypothesis that the slope of the trend line on the difference is zero was tested using a one-sample two-tailed t-test with n - 2 = 58 degrees of freedom.

5.2.4 Inter-Unit Repeatability

The purpose of this comparison was to determine if any significant differences in performance exist between two identical monitors operating side by side. In tests in which monitor performance was verified by comparison with data from the reference method, the two identical units of each type of monitor 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 monitor 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 a monitor 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.

Chapter 6
Statistical Results

6.1 Laboratory Tests

6.1.1 Linearity

Tables 6-1a and b list the data obtained in the linearity tests for NO and NO_2, respectively. Table 6-2 shows the results of the linear calibration curve fits for each unit, based on the data shown in Tables 6-1a and b.

Table 6-1a. Data from NO Linearity Test of TSI COMBUCHECK Monitors

Reading	Actual NO (ppm)	Unit A NO (ppm)	Unit B NO (ppm)
1	0.0	11	13
2	2002.0	2103	2063
3	189.2	200	243
4	493.4	505	578
5	0.0	15	33
6	1396.0	1542	1563
7	392.1	473	461
8	189.2	247	236
9	0.0	20	18
10	392.1	437	436
11	493.4	556	552
12	1399.0	1576	1555
13	0.0	28	25
14	2002.0	2259	2215
15	1399.0	1600	1573
16	493.4	585	572
17	0.0	32	28
18	388.4	454	444
19	189.2	228	220
20	2002.0	2287	2228
21	0	34	30

Table 6-1b. Data from NO_2 Linearity Test of TSI COMBUCHECK Monitors

Number	Actual NO_2 (ppm)	Unit A NO_2 (ppm)	Unit B NO_2 (ppm)
1	0.0	0.2	0.2
2	100.1	135.4	135.4
3	10.0	15.7	16.6
4	40.1	52.7	51.9
5	0.0	0.2	0.5
6	70.1	88	86.8
7	20.0	26.2	26.8
8	10.0	13.9	14.4
9	0.0	0.7	1.6
10	20.0	24.4	23.9
11	40.1	47.4	45.9
12	70.1	84.5	82.8
13	0.0	1.3	2.4
14	100.1	121.4	119.2
15	70.1	85	84.6
16	40.1	49.9	49.7
17	0.0	1.3	2.6
18	20.0	23.7	23.5
19	10.0	13.2	13.7
20	100.1	116.7	113.8
21	0.0	1.6	2.9

Table 6-2. Statistical Results for Test of Linearity

	Unit A		Unit B	
Linear Regression	**NO**	**NO_2**	**NO**	**NO_2**
Intercept (ppm) (Std Err)	22.292(3.599)	0.972 (0.236)	23.844(2.627)	1.854 (0.410)
Slope (Std Err)	1.101 (0.011)	1.218 (0.015)	1.100 (0.005)	1.184 (0.018)
R^2	0.9981	0.9972	0.9996	0.9956

The results in Table 6-2 indicate that the TSI monitors responded approximately linearly to the NO and NO_2 concentrations provided, but with slopes that differed substantially from 1. The R^2 values for all four monitors exceed 0.99, but the slopes are 1.1 for both NO monitors and about 1.2 for the NO_2 monitors. This observation appears to result from error or instability in the calibration of the TSI units. As noted in Section 3.2.1, the TSI NO and NO_2 monitors were provided before the linearity test with 200 ppm NO and 25 ppm NO_2, respectively, and their responses were calibrated to those standards. Shortly thereafter, when NO and NO_2 concentrations were provided over the full nominal ranges of the monitors, the responses obtained were consistently high. This is clearly evident in Tables 6-1a and b, and also was apparent in the pre- and post-test span gas responses. The 2,000 ppm NO span gas produced responses of 2,099 and 2,023 ppm on Units A and B, respectively, before the linearity test, and 2,242 and 2,182 ppm after the test. Similarly, the 100 ppm NO_2 span gas produced readings of 123.4 and 122.7 ppm before the linearity test, and 113 and 109.5 ppm after the test. Thus, the linearity test results shown in Tables 6-1a and b and 6-2 indicate that the TSI monitors may provide linear response over their full nominal ranges for NO and NO_2, but that instability in calibration may be a concern.

Table 6-1a also indicates that the readings of the TSI NO monitor on zero gas increased considerably during the linearity test, to 30 ppm or more. This observation clearly indicates a "memory" effect, in which the response of the monitor remains elevated following exposure to high NO levels. In practice, TSI recommends that the user re-zero the monitor after a high NO exposure, or wait a sufficient time (an hour or so) for the monitor to return to baseline while sampling clean, dry air. Neither of those approaches was feasible in this test.

Although the TSI operator was allowed to judge when the TSI monitors had stabilized on zero gas, and to record readings at that time, Table 6-1a indicates that much longer stabilization times would have been needed for readings to return to baseline. The conclusion is that measurement of low NO concentrations should not be attempted following high NO exposures, unless substantial restabilization times are feasible.

6.1.2 Detection Limit

Table 6-3 shows the estimated detection limits for each test unit and each analyte, determined from the data obtained in the linearity test.

Table 6-3. Estimated Detection Limits for TSI COMBUCHECK Monitors

	Unit A		**Unit B**	
	NO	**NO_2**	**NO**	**NO_2**
Estimated Detection Limit (ppm)	25.661	1.490	20.774	2.877
(Standard Error) (ppm)	(8.119)	(0.472)	(6.570)	(0.911)

Table 6-3 shows that calculated detection limits were about 1.5 and 2.9 ppm for the two NO_2 monitors, but about 26 and 21 ppm for the two NO analyzers. The higher detection limits for NO result directly from the much greater variability of the NO readings on zero air in the linearity test (Table 6-1a), and are probably not a good indication of the NO detection limits achievable with the COMBUCHECK monitors. Zero readings from the two NO analyzers increased consistently over the duration of the linearity test, from about 12 ppm to over 30 ppm. This increase is thought to be due to a memory effect, i.e., the NO sensors do not fully return to zero after sampling of relatively high NO levels. Thus, the higher detection limits for NO are probably due at least in part to the much greater calibration range used in the linearity test for NO, relative to the range used for NO_2. Clearly, when measurements are being made over the full NO range of the monitors, care must be taken that the baseline is fully stabilized before making measurements in the low end of the range. When fully stabilized to a near-zero baseline, the detection limits for the NO and NO_2 monitors should be comparable to the measurement resolution of the monitors, i.e., about 1 ppm for NO and 0.1 to 0.2 ppm for NO_2.

6.1.3 Response Time

Table 6-4 lists the data obtained in the response time test of the TSI COMBUCHECK Monitors. Table 6-5 shows the response times of the monitors to a step change in analyte concentration, based on the data shown in Table 6-4.

Table 6-5 shows that the TSI COMBUCHECK monitors provide substantially faster responses for NO than for NO_2, with some difference in time response between different monitors.

The Unit A NO monitor showed a response time of 65 seconds, whereas Unit B responded in less than half that time. For NO_2, the response times of both monitors were 2 minutes or more, and were closely similar. All the response times in Table 6-5 are within the 4-minute time response stated in the SCAQMD test protocol,(8) and also agree well with the 90 percent response times stated in the COMBUCHECK specifications.

Table 6-4. Response Time Data for TSI COMBUCHECK Monitors

Time (sec)	Unit A NO (ppm)	Unit A NO_2 (ppm)	Unit B NO (ppm)	Unit B NO_2 (ppm)
0	14	0.2	33	0.5
10	88	57.1	1252	81.9
20	1358	110.0	1431	99.9
30	1398	81.3	1499	78.6
40	1415	81.6	1508	78.1
50	1423	82.0	1514	78.5
60	1434	82.3	1514	78.8
70	1444	82.4	1518	79.2
80	1452	82.3	1520	79.2
90	1454	82.3	1524	79.2
100	1459	82.3	1526	79.2
110	1463	82.4	1526	79.7
120	1470	83.0	1528	80.1
130	1470	83.4	1531	80.7
140	1476	83.8	1532	81.1
150	1481	84.3	1534	81.8
160	1482	84.5	1536	82.1
170	1482	85.1	1538	82.6
180	1489	85.5	1538	83.0
190	1490	86.1	1529	83.5
200	1493	86.3	1544	83.2
210	1495	86.4	1542	84.0
220	1498	86.8	1544	84.4
230	1503	86.8	1544	84.6
240	1504	87.0	1544	85.0
250	1505	87.0	1545	85.0
260	1505	87.3	1545	85.2
270	1505	87.3	1545	85.2
280	1509	87.6	1548	85.2
290	1510	87.6	1548	85.3
300	1514	87.6	1547	85.5

Table 6-5. Response Time Results for TSI COMBUCHECK Monitors

	Unit A		Unit B	
	NO	NO_2	NO	NO_2
Response Time* (sec)	65	126	26	142

* 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 2,000 ppm NO and 100 ppm NO_2 were used for this test. Zero differences were less than 3 ppm for the two NO_2 monitors, and 20 to 30 ppm for the two NO monitors. For all four monitors, the change in zero readings was downward from pre- to post-shutdown, and in fact zero readings on all four monitors were essentially zero after the shutdown. This observation shows that the zero readings pre-shutdown were elevated due to the NO and NO_2 exposures during the linearity test, and that the monitors returned to zero after the several hours of shutdown, i.e., the elevation of zero gas readings was reversible. The span differences in Table 6-7 are in opposite directions for the NO and NO_2 analyzers. NO span readings decreased by about 6 percent of the 2,000 ppm span value, whereas NO_2 span readings increased by 7.9 and 12.2 percent of the 100 ppm span value.

Table 6-6. Data from Interrupted Sampling Test with TSI COMBUCHECK Monitors

	Unit A NO	Unit A NO_2	Unit B NO	Unit B NO_2
Pre-Shutdown Date:	**1/15/99**	**Time:**	**17:00**	
Pre-Shutdown Zero (ppm):	22	1.6	30	2.9
Pre-Shutdown Span (ppm):	2242	113	2182	109.5
Post-Shutdown Date:	**1/16/99**	**Time:**	**09:25**	
Post-Shutdown Zero (ppm):	0.5	0	0.5	0
Post-Shutdown Span (ppm):	2118	120.9	2054	121.7

Table 6-7. Pre- to Post-Test Differences as a Result of Interruption of Operation of TSI COMBUCHECK Monitors

	Unit A		Unit B	
Pre-Shutdown—Post-Shutdown	NO	NO_2	NO	NO_2
Zero Difference (ppm)	21.5	1.6	29.5	2.9
Span Difference (ppm)	124	-7.9	128	-12.2

6.1.5 Interferences

Table 6-8 lists the data obtained in the interference tests. Table 6-9 summarizes the sensitivity of the monitors to interferant species, based on the data from Table 6-8. Table 6-9 shows both the absolute differences observed for each interferant relative to the preceding zero reading, and the resulting relative sensitivity to each interferant, in percent of the NO sensitivity. For the SO_2/NO mixture, the entries indicate the impact of the SO_2 on the response to NO. Thus, the ppm values show the difference between NO response and the expected 383 ppm value, and the relative sensitivity is based on the 451 ppm SO_2 concentration.

Table 6-8. Data from Interference Tests on TSI COMBUCHECK Monitors

Interferant Gas	Interferant, Conc. (ppm)		Response (ppm equivalent)		
		Unit A NO	Unit A NO_2	Unit B NO	Unit B NO_2
Zero		3	0.3	6	0.9
CO	496 ppm	5	0.6	26	1
Zero		2	0.4	3	0.9
CO_2	5.03%	2	0.4	3	0.9
Zero		2	0.2	2	0.4
NH_3	494 ppm	2	0.2	2	0.5
Zero		2	0.4	2	0.7
HCs	590 ppm	2	0.2	3	0.5
Zero		2	0.2	2	0.2
SO_2	501 ppm	3	-1.0	2	-2.2
Zero		2.5	0	3.4	0
SO_2 + NO	451+383 ppm	395	2.5	409	3.4

Table 6-9. Results of Interference Tests of TSI COMBUCHECK Monitors

	Unit A Response ppm (% relative sensitivity)		Unit B Response ppm (% relative sensitivity)	
Interferant	NO	NO_2	NO	NO_2
CO (496 ppm)	2 (0.49%)	0.3 (< 0.1%)	20 (4%)	0.1 (< 0.1%)
CO_2 (5.03%)	0	0	0	0
NH_3 (494 ppm)	0	0	0	0.1 (< 0.1%)
HCs (590 ppm)	0	-0.2 (< 0.1%)	1 (0.2%)	-0.2 (< 0.1%)
SO2 (501 ppm)	1 (0.2%)	-1.2 (0.2%)	0	-2.4 (0.5%)
SO2 (451 ppm) + NO (383 ppm)	9.5 (2.1%)	2.5 (0.6%)	22.6 (5.0%)	3.4 (0.8%)

Table 6-9 shows that, with one exception, none of the individual interferants caused a response greater than about +/- 2 ppm on any of the monitors. Thus, interference from these gases is negligible. The one exception is that on NO Unit B, CO at 496 ppm caused an increased response above zero of 20 ppm. If real, this result implies an interference from CO equal to about 4 percent of the sensitivity to an equal concentration of NO.

The SO_2/NO mixture in Table 6-9 resulted in responses slightly higher (by 9.5 and 22.6 ppm, respectively) than those expected for the 383 ppm NO level. These results indicate an enhancement of the NO response due to the SO_2 present; at the levels tested the effect of the SO_2 equals 2 to 5 percent of the response to an equal concentration of NO. These percentages are comparable to the span drift observed with the TSI NO monitors (see Section 6.1.8), and do not strongly indicate an interference from SO_2 in the presence of NO.

The SO_2/NO mixture also produced a slight increase in response (2.5 and 3.4 ppm, respectively) on the two TSI NO_2 monitors. It is not known whether this represents a cross-sensitivity of the NO_2 sensors to NO, or an effect of the SO_2 present. SO_2 alone produced a very slight reduction in response of the two NO_2 monitors (Table 6-9). If it is assumed that only the NO in the SO_2/NO mixture effects the NO_2 monitors, then the result places an upper bound on the cross-sensitivity to NO of the NO_2 monitors. That is, the NO sensitivity of Units A and B of the TSI NO_2 monitors cannot exceed 2.5/383 = 0.65 percent and 3.4/383 = 0.89 percent, respectively.

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 monitor flow rates at the different duct gas pressures.

No significant effect of duct pressure on zero and span values was seen with any of the TSI COMBUCHECK monitors. This conclusion is based on using the response variability determined in the linearity test. Zero readings of the NO_2 monitors changed by less than 1 ppm, whereas those of the NO monitors changed by about 8 to 20 ppm. Table 6-10 clearly shows that the zero readings of the NO monitors were elevated by several ppm at any pressure, as a result of exposure to the 1,400 ppm NO span gas used in this test. The span differences shown in Table 6-11 for the NO_2 monitors are equivalent to about 7 to 14 percent of the 70 ppm NO_2 span gas concentration. The span differences in Table 6-11 for the Unit A NO monitor are equivalent to about 1 percent or less of the 1,400 ppm NO span gas used. Those for the Unit B NO monitor are 3.5 to 4 percent of that span concentration.

Tables 6-10 and 6-11 also indicate that the sample gas flow rates drawn by the TSI monitors are highly dependent on the duct pressure, and that this effect is highly different from one monitor to another. Sample flow rates at +10 inches of water exceeded those at ambient pressure by 34 to 84 percent; flow rates at -10 inches of water were reduced by 14 to 47 percent. This behavior occurs because no effort is made to regulate the sample flow of the COMBUCHECK monitors, since the response of the NO and NO_2 sensors is essentially insensitive to flow rate. This lack of flow rate dependence is confirmed by the data in Tables 6-10 and 6-11 and the discussion above.

Table 6-10. Data from Pressure Sensitivity Test for TSI COMBUCHECK Monitors

Pressure		Unit A NO	Unit A NO_2	Unit B NO	Unit B NO_2
Ambient	Flow rate (ccm)	658	594	638	620
	Zero (ppm)	0		0	
	NO span (ppm)	1465		1437	
	Zero (ppm)	11	0.4	14	0.4
	NO_2 span (ppm)		86.3		81.7
	Zero (ppm)		1		1.1
+10 in. H_2O	Flow rate (ccm)	1030	1090	852	1087
	Zero (ppm)	9		13	
	NO span (ppm)	1470		1486	
	Zero (ppm)	19	0.5	30	0.8
	NO_2 span (ppm)		94.5		91.6
	Zero (ppm)		1.1		1.5
-10 in. H_2O	Flow rate (ccm)	560	418	551	328
	Zero (ppm)	16		25	
	NO span (ppm)	1449		1493	
	Zero (ppm)	29	0.9	29	1.1
	NO_2 span (ppm)		92.8		86.8
	Zero (ppm)		1.2		1.5

Table 6-11. Pressure Sensitivity Results for TSI COMBUCHECK Monitors

		Unit A		Unit B	
		NO	NO_2	NO	NO_2
Zero	High–Ambient (ppm diff*)	8.5	0.1	14.5	0.4
	Low–Ambient (ppm diff)	17	0.35	20	0.55
	Significant Pressure Effect	N	N	N	N
Span	High–Ambient (ppm diff)	5	8.2	49	9.9
	Low–Ambient (ppm diff)	-16	6.5	56	5.1
	Significant Pressure Effect	N	N	N	N
Flow Rate	High–Ambient (ccm diff*)	372	496	214	467
	Low–Ambient (ccm diff)	-98	-176	-87	-292

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

6.1.7 Ambient Temperature

Table 6-12 lists the data obtained in the ambient temperature test with the TSI COMBUCHECK monitors.

Table 6-12. Data from Ambient Temperature Test of TSI COMBUCHECK Monitors

Condition	Unit A NO (ppm)	Unit A NO_2 (ppm)	Unit B NO (ppm)	Unit B NO_2 (ppm)
(Room Temp.)				
Temp. 22.8°C (73°F)				
Zero	7		6	
NO span	1476		1487	
Zero		1.2		1.4
NO_2 span		87.2		81.7
(Heated)				
Temp. 40°C (104°F)				
Zero	10		24	
NO span	1459		1467	
Zero	27	1.2	39	1.5
NO_2 span		92.8		86.7
(Cooled)				
Temp. 6.7°C (44°F)				
Zero	7		6	
NO span	1483		1442	
Zero	16	2.9	12	3.5
NO_2 span		85.6		80.9
(Room Temp.)				
Temp. 22.2°C (72°F)				
Zero	4		6	
NO span	1455		1441	
Zero		1.7		1.6
NO_2 span		93.4		85

Table 6-13 summarizes the sensitivity of the monitors to changes in ambient temperature. This table is based on the data shown in Table 6-12, where the span values are 1,400 ppm for NO and 70 ppm for NO_2.

Table 6-13. Ambient Temperature Effects on TSI COMBUCHECK Monitors

		Unit A		Unit B	
		NO	**NO_2**	**NO**	**NO_2**
Zero	Heat - room (ppm diff*)	4.5	-0.25	18	0
	Cool - room (ppm diff)	1.5	1.45	0	2.0
	Significant Temp. Effect	N	N	N	N
Span	Heat - room (ppm diff)	-6.5	2.5	3	3.35
	Cool - room (ppm diff)	17.5	-4.7	-22	-2.45
	Significant Temp. Effect	N	N	N	N

* ppm difference between heated/cooled and room temperatures. The differences were calculated using the average of the pre-span zero responses recorded at room temperature.

Table 6-13 shows that no significant dependence on ambient temperature was found for the TSI monitors. Changes in zero readings with temperature were a few ppm, except that the TSI Unit B NO monitor showed a zero drift of 18 ppm in moving from room temperature to the heated chamber. Span values showed some variation during the test, but no consistent pattern with temperature. The span differences shown in Table 6-13 for the NO monitors amount to 0.2 to 1.6 percent of the 1,400 ppm span concentration. The span differences shown for the NO_2 monitors amount to 3.5 to 6.7 percent of the 70 ppm NO_2 span.

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. The NO and NO_2 span concentrations used in the linearity test were 2,000 ppm and 100 ppm, respectively; those in the temperature test were 1,400 ppm and 70 ppm, respectively. Table 6-15 shows that for both the NO and NO_2 monitors, zero and span drift were both much larger as a result of the linearity test than as a result of the temperature test. This may be due to the higher NO and NO_2 concentrations and longer duration of sampling in the linearity test. Note that the manufacturer recommends allowing the instrument baseline time to return fully to its initial value after prolonged exposure (i.e., >3 to 5 minutes) to high concentrations of analyte. However, NO_2 monitor zero levels dropped during the linearity test, whereas those of the two NO monitors rose 20 and 30 ppm, respectively. Zero readings changed by 3 ppm or less on all four TSI monitors as a result of the ambient temperature test.

The span drift observed for the NO monitors in the linearity test (Table 6-15) is equivalent to 7 to 8 percent of the 2,000 ppm NO span value. The corresponding span drift for the NO_2 monitors is equivalent to 10 to 13 percent of the 100 ppm NO_2 span value.

Table 6-14. Data from Linearity and Ambient Temperature Tests Used to Assess Zero and Span Drift of the TSI COMBUCHECK Monitors

Test		Unit A NO (ppm)	Unit A NO_2 (ppm)	Unit B NO (ppm)	Unit B NO_2 (ppm)
Linearity	Pre-Test Zero	2	10.4	0	10.4
	Pre-Test Span	2099	123.4	2023	122.7
	Post-Test Zero	22	1.6	30	2.9
	Post-Test Span	2242	113	2182	109.5
Ambient Temperature	Pre-Test Zero	7	1.2	6	1.4
	Pre-Test Span	1476	87.2	1487	81.7
	Post-Test Zero	4	1.7	6	1.6
	Post-Test Span	1455	93.4	1441	85

Table 6-15. Zero and Span Drift Results for the TSI COMBUCHECK Monitors

		Unit A		Unit B	
Pre- and Post-Differences		NO (ppm)	NO_2 (ppm)	NO (ppm)	NO_2 (ppm)
Linearity Test	Zero	-20	8.8	-30	7.5
	Span	-143	10.4	-159	13.2
Ambient Temperature Test	Zero*	3	-0.45	0	-0.2
	Span	21	-6.2	46	-3.3

* Drift is the difference (pre-monitoring minus post-monitoring) between the first and last zero response at room temperature.

The span drift observed for the NO monitors in the ambient temperature test (Table 6-15) is equivalent to 1.5 to 3.3 percent of the 1,400 ppm NO span value. The corresponding span drift for the NO_2 monitors is equivalent to 4.7 to 8.9 percent of the 70 ppm NO_2 span value.

6.2 Combustion Source Tests

The following sections describe the results of the combustion source tests with the TSI COMBUCHECK monitors. After these tests were performed, TSI staff reported an error in operating their NO_2 monitors in that the in-line water traps used in the sample intake lines had been mislabeled and, consequently, were installed backward. This error may have had a severe effect on TSI's NO_2 measurements and, in turn, on NO_x levels calculated from the NO_2 data. The potential impact of this error on TSI's source testing results is noted in the following sections, but cannot be quantified or corrected.

6.2.1 *Relative Accuracy*

Tables 6-16a through c list the measured NO, NO_2, and NO_x data obtained in sampling of the four combustion sources. Note that the TSI monitors measure either NO or NO_2, and the indicated NO_x totals are the sum of those data from the respective pairs of monitors designated A or B; in contrast, the reference monitors measure NO and NO_x, and NO_2 is determined by difference. Tables 6-16a through c show that a wide range of NO and NO_2 concentrations was emitted by the three sources.

Table 6-17 displays the relative accuracy (in percent) of the TSI monitors for NO, NO_2, and NO_x for each of the 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. In considering the relative accuracy results, it should be noted that the COMBUCHECK specifications indicate accuracy for NO of 5 ppm or 5 percent of reading, whichever is greater, and for NO_2 of 3 ppm or 5 percent of reading, whichever is greater.

At the request of the TSI representative, the TSI NO and NO_2 monitors were calibrated with 200 ppm NO and 25 ppm NO_2, respectively, prepared using the EPA Protocol Gases and Environics dilution system, before starting the source sampling portion of the verification test. The monitors were adjusted to match those respective standard concentrations. The span gas concentrations listed in Table 3-3 were then provided to the TSI monitors before and after sampling of each respective combustion source, but no adjustment of the TSI monitors was made. As will be discussed in Section 6.2.2, the TSI readings observed in sampling of those span gases do not show close quantitative agreement with the span values, indicating that the calibration of the monitors was not stable after adjustment to the 200 ppm NO and 25 ppm NO_2 calibration gases.

One possible explanation for this is the finding, after these tests were completed, that the in-line water traps used with the TSI NO_2 monitors were labelled incorrectly, and consequently were installed backward in the sample lines. In this backward configuration, the traps would collect particles and not allow condensed water to reach the reservoir. The collected particles and water might have been an effective trap for NO_2, contributing to the variability observed in NO_2 measurements. The general effect of operating with the water trap reversed has been demonstrated by TSI in the laboratory, but it is impossible to determine the quantitative effect on the test results. In most of the combustion tests, the TSI NO_2 monitors read high relative to the reference analyzers, whereas in TSI's tests reversal of the water trap was found to first increase, then sharply decrease, the NO_2 response.

Table 6-16a. Data from the Gas Rangetop in Verification Testing of TSI COMBUCHECK Monitors

	TSI Monitor Data						Reference Analyzer Data					
	Unit A NO (ppm)	Unit A NO_2 (ppm)	Unit A NO_x (ppm)	Unit B NO (ppm)	Unit B NO_2 (ppm)	Unit B NO_x (ppm)	14A NO (ppm)	14A NO_2 (ppm)	14A NO_x (ppm)	10 NO (ppm)	10 NO_2 (ppm)	10 NO_x (ppm)
1	5	3.2	8.2	6	6.3	12.3	6.1	2.2	8.3	5.8	1.9	7.7
2	7	3.7	10.7	5	6.9	11.9	6.3	2.4	8.7	6.0	2.2	8.2
3	4	4.7	8.7	5	7.7	12.7	6.4	2.5	8.9	6.0	2.3	8.3
4	4	4.7	8.7	5	7.1	12.1	6.5	2.4	8.8	6.2	2.1	8.3
5	4	5.3	9.3	5	8.5	13.5	6.5	2.4	8.9	6.2	2.1	8.3
6	4	5.7	9.7	5	8.4	13.4	6.4	2.5	8.9	6.1	2.4	8.5
7	4	6	10	5	9.2	14.2	6.5	2.5	9.0	6.2	2.3	8.5
8	5	6.5	11.5	5	9.4	14.4	6.5	2.4	8.9	6.2	2.2	8.4
9	4	5.9	9.9	5	8.7	13.7	6.5	2.3	8.8	6.2	2.2	8.4

Table 6-16b. Data from Gas Water Heater in Verification Testing of TSI COMBUCHECK Monitors

	TSI Monitor Data						Reference Analyzer Data					
	Unit A NO (ppm)	Unit A NO_2 (ppm)	Unit A NO_x (ppm)	Unit B NO (ppm)	Unit B NO_2 (ppm)	Unit B NO_x (ppm)	14A NO (ppm)	14A NO_2 (ppm)	14A NO_x (ppm)	10 NO (ppm)	10 NO_2 (ppm)	10 NO_x (ppm)
1	85	16.7	101.7	89	13.6	102.6	122.9	2.5	125.4	112.5	7.4	119.9
2	86	16.1	102.1	89	14.8	103.8	120.9	4.6	125.5	112.5	7.9	120.4
3	88	15.3	103.3	91	16.8	107.8	118.9	6.7	125.6	112.2	7.5	119.7
4	79	14.9	93.9	84	18.8	102.8	103.2	15.4	118.6	96.6	14.8	111.4
5	67	13.2	80.2	72	23.3	95.3	93.0	7.2	100.2	87.2	7.8	95.0
6	57	13.8	70.8	64	15.4	79.4	83.8	5.5	89.3	78.4	6.9	85.4
7	61	12.8	73.8	63	17.1	80.1	82.5	5.0	87.5	77.7	6.3	84.0
8	58	12.7	70.7	62	17.4	79.4	81.4	6.6	87.9	76.7	7.0	83.8
9	57	12.7	69.7	63	18.3	81.3	81.3	5.8	87.1	76.3	7.2	83.5

Table 6-16c. Data from the Diesel Generator at High RPM in Verification Testing of TSI COMBUCHECK Monitors

	TSI Monitor Data						Reference Analyzer Data					
	Unit A NO (ppm)	Unit A NO_2 (ppm)	Unit A NO_x (ppm)	Unit B NO (ppm)	Unit B NO_2 (ppm)	Unit B NO_x (ppm)	14A NO (ppm)	14A NO_2 (ppm)	14A NO_x (ppm)	10 NO (ppm)	10 NO_2 (ppm)	10 NO_x (ppm)
1	84	150.9	234.9	100	256.3	356.3	87.9	65.8	153.7	91.7	67.1	158.8
2	88	73	161	101	95.7	196.7	80.6	66.0	146.6	86.7	69.3	156.0
3	86	44.1	130.1	94	41	135	83.3	65.5	148.8	90.7	68.2	158.9
4	77	20.7	97.7	63	41.2	104.2	78.6	62.7	141.3	86.7	67.1	153.8
5	74	146.5	220.5	69	216.7	285.7	78.8	62.2	141.0	84.7	68.2	152.9
6	72	144.9	216.9	73	209	282	77.5	62.5	140.0	82.7	64.8	147.5
7	76	145.1	221.1	73	203.6	276.6	80.3	61.9	142.2	85.7	66.0	151.6
8	76	95.2	171.2	71	144.1	215.1	77.5	61.1	138.6	82.7	64.8	147.5
9	80	57.3	137.3	75	69.4	144.4	78.4	61.6	140.0	82.7	66.0	148.6

Table 6-17. Relative Accuracy of TSI COMBUCHECK Monitors

	Unit A			Unit B		
Source	NO (ppm)	NO_2 (ppm)	NO_x (ppm)	NO (ppm)	NO_2 (ppm)	NO_x (ppm)
Gas Rangetop (6 ppm NO, 2 ppm NO_2)***	40.43* (4.79)**	156.62 (12.49)	21.31 (3.09)	23.85 (2.00)	284.68 (12.23)	60.94 (2.61)
Gas Water Heater (90 ppm NO, 7 ppm NO_2)	29.52 (1.37)	128.62 (12.50)	19.53 (0.85)	25.39 (1.52)	169.13 (12.21)	14.90 (1.77)
Diesel Generator–High RPM (80 ppm NO, 65 ppm NO_2)	8.56 (1.38)	110.50 (21.91)	44.60 (9.17)	15.11 (4.04)	216.23 (35.48)	93.02 (15.69)

*Relative accuracy, percent relative to mean of two reference analyzers.
**Standard error of the relative accuracy value.
***Approximate NO and NO_2 levels from each source are shown; see Tables 6-16a through c.

Consistent with the hypothesis that the improperly functioning water traps affected the validity of the NO_2 measurements, Table 6-17 shows that the relative accuracy of the TSI monitors in sampling the gas rangetop emissions was better for NO than for NO_2. For NO, TSI Unit A read about 2 ppm low, and Unit B over 1 ppm low, relative to the reference analyzers (Table 6-16a). These results are within the 5 ppm accuracy specification for NO noted above. At the low NO levels present, these readings result in relative accuracies of about 40 percent and 24 percent, respectively. For NO_2, both TSI units read considerably higher than the 2 to 2.5 ppm levels recorded by the reference analyzers, and the two TSI units did not agree closely with one another. Although usually within the 3 ppm NO_2 accuracy specification, relative accuracies of over 150 percent and nearly 300 percent resulted for NO_2 Units A and B, respectively. Relative accuracies of 21 and 61 percent for NO_x resulted from the combined relative accuracies of the pairs of units designated A and B, respectively.

Tables 6-17 and 6-16b show a similar pattern in sampling of the gas water heater. The two TSI NO monitors read consistently low relative to the reference analyzers (Table 6-16b), resulting in relative accuracies of about 30 and 25 percent, respectively (Table 6-17). The two TSI NO_2 monitors read consistently high relative to the reference analyzers, resulting in relative accuracies of about 130 and 170 percent for NO_2 Units A and B. Neither the NO nor the NO_2 monitors showed accuracies consistent with their specifications, which were noted above. The overall relative accuracies for NO_x were about 20 and 15 percent, respectively.

In sampling of the highest NO_x levels, from the diesel generator (Table 6-16c), the TSI monitors showed good relative accuracy for NO. As Table 6-17 shows, relative accuracy for the NO Units A and B was 8.6 and 15.1 percent, respectively. Both these values are well within the 20 percent relative accuracy value stated in the SCAQMD protocol.(8) However, for NO_2, the TSI monitors exhibited readings generally much higher than those from the reference analyzers, and also much more variable (Table 6-16c). The two TSI NO_2 analyzers also did not agree closely with one another in this test. As a result, relative accuracy for the two NO_2 analyzers was about

110 and 215 percent, respectively. These NO_2 results are thought to be caused by improper NO_2 sampling, due to the reversal of the water traps used with the monitors.

6.2.2 Zero and Span Drift

Table 6-18 shows all the data used to evaluate zero and span drift of the TSI COMBUCHECK monitors from the combustion source tests. These values are from the zero and span gases provided to the TSI monitors before and after sampling of the indicated combustion source. As noted above, prior to the combustion source sampling the TSI monitors were calibrated with 200 ppm NO and 25 ppm NO_2. Thus, the zero and span gas results shown in Table 6-18 were obtained without adjustment of the monitors.

Table 6-18. Data Used to Assess Zero and Span Drift for TSI COMBUCHECK Monitors on Combustion Sources

Source		Unit A NO (ppm)	Unit A NO_2 (ppm)	Unit B NO (ppm)	Unit B NO_2 (ppm)
Gas Rangetop*	Pre-Test Zero	0	0	0	-0.3
	Pre-Test Span	10	12.4	10	12.6
	Post-Test Zero	0	0	0	0
	Post-Test Span	15	12.7	12	12.9
Gas Water Heater**	Pre-Test Zero	0	0	0	0
	Pre-Test Span	95	18.4	96	18.5
	Post-Test Zero	0	0.2	0	1.2
	Post-Test Span	90	22.9	92	23.7
Diesel–High RPM***	Pre-Test Zero	-3	0	0	0
	Pre-Test Span	187	74.8	189	80
	Post-Test Zero	0	0.4	3	0.7
	Post-Test Span	176	67.2	171	79.1

* Span values 20 ppm NO and 10 ppm NO_2.
** Span values 100 ppm NO and 15 ppm NO_2.
*** Span values 200 ppm NO and 50 ppm NO_2.

Table 6-19 summarizes the zero and span drift results from the combustion source tests. This table shows that zero drift for the NO_2 monitors was always within 1.2 ppm over the combustion source sampling, and that zero drift for the NO monitors was always within 3 ppm. Span drift for the NO_2 monitors was usually smaller in an absolute sense (i.e., in ppm) than that of the NO monitors, perhaps because of the lower span gas concentrations for NO_2. With the gas rangetop the NO_2 span drift values are equivalent to 3 percent of the 10 ppm NO_2 span level; the NO span drift values equal 10 and 25 percent, respectively, of the 20 ppm NO span level.

Table 6-19. Results of Zero and Span Drift Evaluation for TSI COMBUCHECK Monitors

		Unit A		Unit B	
Pre-Test—Post-Test		**NO (ppm)**	**NO_2 (ppm)**	**NO (ppm)**	**NO_2 (ppm)**
Gas Rangetop*	Zero	0	0	0	0
	Span	-5	-0.3	-2	-0.3
Gas Water Heater**	Zero	0	-0.2	0	-1.2
	Span	5	-4.5	4	-5.2
Diesel Generator–High RPM***	Zero	-3	-0.4	-3	-0.7
	Span	11	7.6	18	0.9

* Span values 20 ppm NO and 10 ppm NO_2.
** Span values 100 ppm NO and 15 ppm NO_2.
*** Span values 200 ppm NO and 50 ppm NO_2.

With the gas water heater, NO_2 span drift equaled 30 to 35 percent of the 15 ppm span value, and NO span drift equaled 4 to 5 percent of the 100 ppm NO span value. With the diesel generator, NO_2 span drift was 1.8 to 15 percent of the 50 ppm span value, and NO span drift was 5.5 to 9 percent of the 200 ppm span value.

Note that most of the span readings shown in Table 6-18 do not agree closely with the known span values provided. This behavior parallels that found in the source test results discussed under Relative Accuracy (Section 6.2.1). For example, the TSI responses to span gases in the gas rangetop testing are low for NO and high for NO_2 (Table 6-18). This observation suggests that calibration drift in the TSI monitors, following adjustment to the 200 ppm NO and 25 ppm NO_2 calibration gases, was a factor in the results obtained during the combustion source tests. As noted above, improper installation of the water traps was likely one contributor to span drift for NO_2.

6.2.3 Measurement Stability

Table 6-20 shows the data obtained in the extended sampling test, in which the TSI COMBUCHECK and reference monitors sampled diesel emissions for a full hour without interruption or sampling of ambient air. It must be stressed that the COMBUCHECK monitors are not designed or intended to sample a combustion source for more than a few minutes at a time. Thus the extended sampling test was not appropriate for these monitors. Nevertheless, the TSI operator agreed to participate, and the TSI 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 TSI monitors 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_2, and NO_x data with time. Also shown in Table 6-21 is an indication of whether the slopes indicated by the TSI monitors differed from those observed by the reference analyzers.

Table 6-20. Data from Extended Sampling Test with Diesel Generator at Idle, Using TSI COMBUCHECK Monitors

	TSI Analyzer Data						Reference Analyzer Data					
	Unit A NO (ppm)	Unit A NO_2 (ppm)	Unit A NO_x (ppm)	Unit B NO (ppm)	Unit B NO_2 (ppm)	Unit B NO_x (ppm)	14A NO (ppm)	14A NO_2 (ppm)	14A NO_x (ppm)	10 NO (ppm)	10 NO_2 (ppm)	10 NO_x (ppm)
1	80	57.3	137.3	75	69.4	144.4	79.0	62.0	141.0	84.7	69.3	154.0
2	85	36.7	121.7	78	45.4	123.4	75.2	65.8	141.1	85.7	63.7	149.4
3	83	25.7	108.7	78	35.5	113.5	76.6	60.4	137.0	81.6	66.0	147.6
4	87	21.5	108.5	83	27.7	110.7	79.1	61.8	140.9	83.7	67.1	150.7
5	83	16.3	99.3	81	25.2	106.2	74.5	63.8	138.2	80.6	68.2	148.8
6	88	15	103	87	21.8	108.8	78.9	62.6	141.5	83.7	68.2	151.8
7	86	7.5	93.5	86	19	105	76.2	61.4	137.6	81.6	68.2	149.8
8	88	5.2	93.2	89	17.2	106.2	75.6	66.5	142.1	79.6	70.4	150.0
9	87	4.4	91.4	89	16.1	105.1	78.0	63.0	141.0	83.7	64.8	148.5
10	87	6.9	93.9	88	14.8	102.8	76.1	61.4	137.5	82.7	62.6	145.3
11	88	58.7	146.7	90	16	106	78.6	63.5	142.0	83.7	64.8	148.5
12	86	9.1	95.1	89	13	102	78.9	60.0	138.9	83.7	62.6	146.3
13	87	3.7	90.7	90	15.1	105.1	76.2	61.5	137.7	80.6	64.8	145.5
14	85	3.2	88.2	90	15.3	105.3	79.0	61.2	140.1	81.6	69.3	150.9
15	87	3.3	90.3	91	13.7	104.7	76.5	64.8	141.3	81.6	66.0	147.6
16	87	3.1	90.1	92	13.1	105.1	78.6	62.4	141.0	82.7	66.0	148.6
17	86	3.1	89.1	90	12.4	102.4	78.1	60.0	138.1	81.6	66.0	147.6
18	87	7.9	94.9	91	14.8	105.8	79.1	62.9	142.1	82.7	67.1	149.7
19	87	87.3	174.3	89	8	97	78.8	60.1	138.9	81.6	68.2	149.8
20	88	68.8	156.8	93	12.6	105.6	79.6	62.0	141.6	81.6	69.3	150.9
21	85	10.3	95.3	94	15.5	109.5	78.7	61.9	140.6	84.7	63.7	148.4
22	86	3.1	89.1	91	12.4	103.4	77.0	61.0	138.0	83.7	62.6	146.3
23	86	2.4	88.4	91	10.8	101.8	79.0	62.8	141.8	82.7	64.8	147.5
24	86	2.3	88.3	90	13.4	103.4	78.0	61.0	139.0	83.7	62.6	146.3
25	87	2.3	89.3	93	15.8	108.8	79.5	60.6	140.1	82.7	61.5	144.2
26	84	2.7	86.7	90	13.8	103.8	79.7	60.1	139.9	81.6	64.8	146.5
27	85	3.1	88.1	93	13.4	106.4	79.1	60.3	139.5	82.7	61.5	144.2
28	84	3.4	87.4	92	14.6	106.6	79.0	63.3	142.2	81.6	64.8	146.5
29	85	3.4	88.4	90	12.4	102.4	79.3	58.6	137.9	82.7	62.6	145.3
30	84	12.9	96.9	92	12.8	104.8	79.2	60.2	139.5	82.7	63.7	146.4

Table 6-20. Data from Extended Sampling Test with Diesel Generator at Idle, Using TSI COMBUCHECK (continued)

	TSI Analyzer Data						Reference Analyzer Data					
	Unit A NO (ppm)	Unit A NO_2 (ppm)	Unit A NO_x (ppm)	Unit B NO (ppm)	Unit B NO_2 (ppm)	Unit B NO_x (ppm)	14A NO (ppm)	14A NO_2 (ppm)	14A NO_x (ppm)	10 NO (ppm)	10 NO_2 (ppm)	10 NO_x (ppm)
31	85	37.2	122.2	92	9	101	78.7	63.5	142.1	83.7	63.7	147.4
32	86	29.4	115.4	93	11.5	104.5	78.0	63.9	141.9	82.7	64.8	147.5
33	85	53.1	138.1	91	10.7	101.7	78.5	65.0	143.5	83.7	64.8	148.5
34	85	13.5	98.5	93	4.2	97.2	78.0	60.9	138.9	82.7	63.7	146.4
35	85	3.4	88.4	93	47.4	140.4	79.0	62.2	141.3	84.7	61.5	146.2
36	86	2.7	88.7	93	15.4	108.4	78.2	60.8	138.9	83.7	61.5	145.2
37	85	2.7	87.7	93	5.3	98.3	79.0	62.0	141.0	84.7	61.5	146.2
38	84	2.8	86.8	93	31.1	124.1	79.3	60.4	139.8	83.7	63.7	147.4
39	85	4.2	89.2	93	13.9	106.9	78.8	60.2	139.0	82.7	62.6	145.3
40	82	4.3	86.3	89	4.7	93.7	79.4	63.2	142.6	83.7	64.8	148.5
41	86	3.4	89.4	93	31.3	124.3	78.2	62.6	140.8	82.7	62.6	145.3
42	82	3.3	85.3	93	15	108	79.3	63.4	142.7	83.7	63.7	147.4
43	86	3.3	89.3	93	4.7	97.7	80.0	63.0	143.0	84.7	63.7	148.4
44	85	5.1	90.1	94	8.7	102.7	79.0	62.6	141.7	83.7	63.7	147.4
45	87	3.8	90.8	93	12.2	105.2	81.0	61.5	142.5	83.7	64.8	148.5
46	83	3	86	94	4.5	98.5	80.4	59.1	139.5	84.7	62.6	147.3
47	84	3	87	91	4.4	95.4	81.0	61.8	142.8	84.7	63.7	148.4
48	87	2.8	89.8	95	45.9	140.9	80.6	62.4	143.0	84.7	64.8	149.5
49	84	3.4	87.4	93	9.2	102.2	80.0	61.8	141.8	84.7	63.7	148.4
50	84	5.2	89.2	93	4.4	97.4	81.8	60.6	142.4	85.7	63.7	149.4
51	85	2.4	87.4	94	4.7	98.7	82.1	61.2	143.3	85.7	62.6	148.3
52	85	2.3	87.3	89	60.4	149.4	81.4	61.4	142.8	84.7	62.6	147.3
53	85	2.1	87.1	93	13.5	106.5	81.8	60.4	142.2	83.7	64.8	148.5
54	84	9.5	93.5	91	5.1	96.1	80.4	61.5	141.9	82.7	66.0	148.6
55	83	4.8	87.8	91	4.5	95.5	81.8	60.4	142.2	85.7	63.7	149.4
56	82	3.7	85.7	93	11.4	104.4	82.3	60.6	142.9	85.7	63.7	149.4
57	82	2.3	84.3	92	29.2	121.2	81.7	60.0	141.8	84.7	63.7	148.4
58	83	2.1	85.1	92	6.9	98.9	81.8	61.0	142.8	83.7	64.8	148.5
59	83	4	87	93	45	138	81.0	62.5	143.5	84.7	63.7	148.4
60	87	140.8	227.8	99	210	309	81.7	60.9	142.6	86.7	61.5	148.2

Inspection of Table 6-20 shows that while the TSI NO monitors gave stable performance, the TSI NO_2 monitors showed erratic performance during the extended sampling test. NO_2 readings from both TSI units were often low relative to the reference analyzers, but were highly variable, and excursions to high readings on one unit were not usually coincident with excursions on the other unit. This behavior has been explained by the finding that the in-line water traps used in the TSI monitors were labeled incorrectly during production, and consequently were installed backwards in the sample lines to the monitors. In this reversed configuration, the traps would block both water and soot particles, creating an efficient system for removing NO_2. Thus the NO_2 results in Table 6-20 are not considered a fair example of the performance of the TSI NO_2 monitors. The NO_x results from the TSI monitors are subject to the same conclusion.

However, despite not being designed for extended sampling, the TSI NO monitors showed good performance, consistent with the relative accuracy values found for NO on the diesel source (Table 6-17). As shown in Table 6-21, Unit A showed a slight decrease in NO over the 1-hour sampling period, and Unit B a slight increase, the latter being consistent with the indication of the reference analyzers. The trends in NO were significantly different for both Units A and B from that of the reference analyzers. However, the actual differences in NO trends were fairly small. For exmple, Unit A showed an NO slope of -0.038 ppm/min (-2.3 ppm/hr), and Unit B a slope of 0.163 ppm/min (+9.8 ppm/hr), compared to the reference analyzer slope of 0.064 ppm/min (+3.8 ppm/hr). Thus, over the one-hour sampling period, the different trends in NO amounted to about a 6 ppm deviation from the trend of the reference analyzers, or roughly 7 percent of the NO level in the diesel exhaust. This degree of performance is good considering that the NO monitors are not intended for this application.

6.2.4 Inter-Unit Repeatability

The repeatability of test results between the TSI monitors 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 TSI COMBUCHECK NO or NO_2 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 measurement stability.

The unit-to-unit differences found in the source combustion tests are related to two factors. One is the failure of the monitors to provide accurate readings even on NO and NO_2 span gases, despite having been calibrated with similar mixtures prepared from the identical sources. This observation is described in Sections 6.2.1 and 6.2.2. The second factor is the widely variable readings obtained from the two NO_2 monitors in source sampling, which is discussed in Sections 6.2.1 through 6.2.3, and which was likely caused by the reversed installation of the in-line water traps. This factor invalidates the NO_2 and NO_x data from the combustion source tests, and may have been a cause of the unstable span responses.

Table 6-21. Results of Evaluation of Measurement Stability for TSI COMBUCHECK Monitors

	Unit A			Unit B			Reference Units Average		
	NO	NO_2	NO_x	NO	NO_2	NO_x	NO	NO_2	NO_x
Slope (Std Err)	-0.038 (0.012)	-0.168 (0.184)	-0.206 (0.187)	0.163 (0.023)	0.171 (0.213)	0.334 (0.212)	0.064 (0.007)	-0.045 (0.010)	0.019 (0.011)
Difference in Slopes from the Average of the Reference Units (Std Err)	-0.102 (0.015) *	-0.123 (0.183)	-0.225 (0.184)	0.099 (0.025) *	0.216 (0.213)	0.315 (0.211)	---	---	---

* Statistically significant different slopes between test unit and the average of the reference units at the 5% significance level.

Table 6-22. Summary of Repeatability

Unit A vs. Unit B			NO	NO_2	NO_x
Linear Regression	Intercept	t-statistic	-0.348	-1.863	---
		p-value*	0.734	0.092	---
	Slope	t-statistic	0.168	1.456	---
		p-value	0.870	0.176	---
Detection Limit		t-statistic	0.468	-1.352	---
		p-value	0.644	0.186	---
Relative Accuracy	Gas Rangetop	t-statistic	1.644	32.195	10.932
		p-value	0.139	**<0.001**	**<0.001**
	Gas Water Heater	t-statistic	8.222	2.326	4.842
		p-value	**<0.001**	**<0.048**	**<0.001**
	Generator–High RPM	t-statistic	0.204	3.896	3.583
		p-value	0.843	**<0.005**	**<0.007**
Measurement Stability	Slope	t-statistic	-11.638	-2.038	3.266
		p-value	**<0.001**	**0.046**	**0.002**

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

6.3 Other Factors

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

6.3.1 Cost

The cost of each single gas monitor as tested in this verification test was approximately $700.

6.3.2 Data Completeness

The data completeness in the verification tests was 100 percent for all four units of the TSI COMBUCHECK.

6.3.3 Maintenance/Operational Factors

The short duration of the verification tests prevented assessment of long-term maintenance costs, durability, etc. The TSI monitors are hand-held devices, readily portable and easy to calibrate and operate. They require minimal setup or take-down time. Their main operational limitation is that they are single-gas analyzers; thus, multiple units would be needed to determine multiple gases.

Chapter 7
Performance Summary

As discussed elsewhere in the report, the TSI COMBUCHECK is a low-cost, versatile single-gas detector designed for spot-checking, short-measurement applications. It is not intended to be used for long-term measurements of combustion. The primary analytes are CO and oxygen; those two versions of the COMBUCHECK were not tested in this study. Performance of the NO and NO_2 monitors tested herein may not be representative of the product line in general. The testing performed in this study indicates that the manufacturer's cautions against prolonged exposure to high concentrations certainly hold true for the NO and NO_2 versions of the instrument.

The TSI COMBUCHECK monitors are capable of providing linear response over their full ranges of 0 to 2,000 ppm NO and 0 to 100 ppm NO_2, provided that stable calibration is achieved. High correlation of TSI response to calibration concentration was observed, but slopes of about 1.1 to 1.2 were found for NO and NO_2, respectively. This finding is related to the failure of the monitors to provide accurate readings on span gases after calibration at 200 ppm NO and 25 ppm NO_2. Detection limits determined from the calibration data were about 20 to 25 ppm for NO and 1.5 to 3 ppm for NO_2. These values are undoubtedly inflated by the monitors' slow rate of return to a baseline reading, after exposure to a high NO or NO_2 level. Care must be taken after conducting high level measurements to allow for an extended stabilization period on clean, dry air, before attempting relatively low measurements.

No substantial interference was observed with either the NO or NO_2 monitors from 496 ppm CO, 5.03 percent CO_2, 494 ppm NH_3, 590 ppm of total hydrocarbons, 501 ppm of SO_2, or 451 ppm SO_2 in the presence of 383 ppm NO.

Response times for NO for two units tested were 65 and 26 seconds, respectively; response times for NO_2 for two units tested were 126 and 142 seconds, respectively. Zero drift was less than 3 ppm for all four TSI monitors in sampling combustion sources and in most laboratory testing. Zero drift in the NO monitors was 20 to 30 ppm, in laboratory testing of linearity over the full 2,000 ppm measurement range of the monitors. Span drift varied widely depending on the type of test being conducted and the levels of span gases provided. In laboratory testing with span gases of 1,400 to 2,000 ppm, NO span drift was 2 to 8 percent of the span level. Corresponding NO_2 span drift, with span gases of 70 to 100 ppm, was 5 to 13 percent of the span level. In source testing, with span gases of 20 to 200 ppm, NO span drift was 4 to 25 percent of the span level; for NO_2 with span gases of 10 to 50 ppm, span drift was 2 to 35 percent of the span value. No significant additional drift occurred when the TSI monitors were shut down completely overnight.

Over a 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 TSI monitors. The ambient temperature over the range of 7 to 41°C (45 to 105°F) also had no significant effect on the zero and span readings.

Relative accuracy for NO for the two tested monitors was within the manufacturer's stated 5 ppm tolerance with NO levels below 10 ppm, but ranged from 8.6 to 40.4 percent, over three combustion sources having NO emissions from about 6 to 100 ppm. Highly variable and inconsistent readings were observed from the NO_2 monitors in some tests, apparently as a result of the incorrect installation of the in-line water traps in the monitors. As a result, relative accuracy results obtained for NO_2 and NO_x are not considered a valid assessment of analyzer performance. The variability of the monitors was such that the two TSI NO monitors, and the two TSI NO_2 monitors, performed significantly differently from one another in all the tests conducted with combustion sources.

Chapter 8
References

1. *Test/QA Plan for Verification of Portable NO/NO_2 Emission Analyzers*, Battelle, Columbus, Ohio, December 1998.

2. *U.S. EPA Method 7E, Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)* Code of Federal Regulations, 40 CFR, Ch. 1, Part 60, Appendix A (1991).

3. *Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors: Protocol Number 1*, Research Triangle Park, NC: U.S. Environmental Protection Agency, Quality Assurance Division, June 1978.

4. *Interlaboratory Program to Validate a Protocol for the Measurement of NO_2 Emissions from Rangetop Burners*, GRI-94/0458, Gas Research Institute, Chicago, Illinois, December 1994.

5. *Interlaboratory Study to Determine the Precision of an Emission Measurement Protocol for Residential Gas Water Heaters*, GRI-96-0021, Gas Research Institute, Chicago, Illinois, March 1996.

6. American National 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_x Analyzer Evaluation for Alternative Nitrogen Oxide Emission Rate Determination at Process Units*, Source Testing and Engineering Branch, SCAQMD 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).

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$_2$) ___/___ Span (NO/NO$_2$) ___/___

Unit B: Zero (NO/NO$_2$) ___/___ Span (NO/NO$_2$) ___/___

		NO Test			NO$_2$ Test	
		Unit A (NO/NO$_2$)	Unit B (NO/NO$_2$)		Unit A (NO/NO$_2$)	Unit B (NO/NO$_2$)
	1.	/	/	1.	/	/
	2.	/	/	2.	/	/
	3.	/	/	3.	/	/
	4.	/	/	4.	/	/
	5.	/	/	5.	/	/
Time Response	6.	/	/	6.	/	/
	7.	/	/	7.	/	/
	8.	/	/	8.	/	/
	9.	/	/	9.	/	/
	10.	/	/	10.	/	/
	11.	/	/	11.	/	/
	12.	/	/	12.	/	/
	13.	/	/	13.	/	/
	14.	/	/	14.	/	/
	15.	/	/	15.	/	/
	16.	/	/	16.	/	/
	17.	/	/	17.	/	/
	18.	/	/	18.	/	/
	19.	/	/	19.	/	/
	20.	/	/	20.	/	/
	21.	/	/	21.	/	/

Post-Test Z/Span: Unit A: Zero (NO/NO$_2$) ___/___ Span (NO/NO$_2$) ___/___

Unit B: Zero (NO/NO$_2$) ___/___ Span (NO/NO$_2$) ___/___

Interrupted Sampling Data Sheet

Date: ____________________ Vendor/Analyzer: ___________________________

Form Filled Out By: ____

Pre-Shut Down Z/Span:
Date: ___________________________ Time: ___________________________

Unit A (NO/NO_2) Zero ____/____ Span ______/_______

Unit B (NO/NO_2) Zero ____/____ Span ______/_______

Post-Shut Down Z/Span:
Date: ___________________________ Time: ___________________________

Unit A (NO/NO_2) Zero ____/____ Span ______/_______

Unit B (NO/NO_2) Zero ____/____ Span ______/_______

Interference Test Data Sheet

Date: ____________________ Vendor/Analyzer: ___________________________

Form Filled Out By: ____

Interference Gas	Concentration	Response (NO/NO_2) Unit A	 Unit B
Zero	--	__/__	__/__
CO	496 ppm	__/__	__/__
Zero	--	__/__	__/__
CO_2	5.03%	__/__	__/__
Zero	--	__/__	__/__
NH_3	494 ppm	__/__	__/__
Zero	--	__/__	__/__
Hydrocarbons	590 ppm	__/__	__/__
Zero	--	__/__	__/__
SO_2	501 ppm	__/__	__/__
Zero	--	__/__	__/__
SO_2 + NO	451 ppm + 393 ppm	__/__	__/__

Flow Rate Sensitivity Data Sheet

Date: ______________ Vendor/Analyzer: ____________________

Form Filled Out By: ____

Flow Rate Data:

	Unit A (ccm)	Unit B (ccm)
Ambient P		
+10 in H_2O		
-10 in H_2O		

Response Data:

		Unit A (NO/NO_2)	Unit B (NO/NO_2)
Ambient P	Zero	/	/
	NO Span	/	/
	Zero	/	/
	NO_2 Span	/	/
	Zero	/	/
+10 in H_2O	Zero	/	/
	NO Span	/	/
	Zero	/	/
	NO_2 Span	/	/
	Zero	/	/
-10 in H_2O	Zero	/	/
	NO Span	/	/
	Zero	/	/
	NO_2 Span	/	/
	Zero	/	/

Ambient Temperature Test Data Sheet

Date: ____________________ Vendor/Analyzer: ____________________________

Form Filled Out By: ____

Room Temperature: ____________	Response (NO/NO$_2$)	
	Unit A	Unit B
Zero	/	/
NO Span	/	/
NO$_2$ Span	/	/
Zero	/	/
Cold Chamber Temperature: ____________		
Zero	/	/
NO Span	/	/
NO$_2$ Span	/	/
Zero	/	/
Heated Chamber Temperature: ____________		
Zero	/	/
NO Span	/	/
NO$_2$ Span	/	/
Zero	/	/
Room Temperature: ____________		
Zero	/	/
NO Span	/	/
NO$_2$ Span	/	/
Zero	/	/

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_2/NOx) ____/____/_____ Span (NO/NO_2/NOx) ____/____/_____

Unit 10: Zero (NO/NO_2/NOx) ____/____/_____ Span (NO/NO_2/NOx) ____/____/_____

	Unit 14A (NO/NO_2/NOx)	Unit 10 (NO/NO_2/NOx)
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_2/NOx) ____/____/_____ Span (NO/NO_2/NOx) ____/____/_____

Unit 10: Zero (NO/NO_2/NOx) ____/____/_____ Span (NO/NO_2/NOx) ____/____/_____

Mod-1: 01/17/99

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$_2$/NOx) ____/____/_____ Span (NO/NO$_2$/NOx) ____/____/_____

Unit B: Zero (NO/NO$_2$/NOx) ____/____/_____ Span (NO/NO$_2$/NOx) ____/____/_____

	Unit A (NO/NO$_2$/NOx)	Unit B (NO/NO$_2$/NOx)
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$_2$/NOx) ____/____/_____ Span (NO/NO$_2$/NOx) ____/____/_____

Unit B: Zero (NO/NO$_2$/NOx) ____/____/_____ Span (NO/NO$_2$/NOx) ____/____/_____

Mod-1: 01/17/99

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_2/NOx) ____/____/_____ Span (NO/NO_2/NOx) ____/____/_____

Unit 10: Zero (NO/NO_2/NOx) ____/____/_____ Span (NO/NO_2/NOx) ____/____/_____

	Unit 14A (NO/NO_2/NOx)	Unit 10 (NO/NO_2/NOx)
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_2/NOx) ____/____/_____ Span (NO/NO_2/NOx) ____/____/_____

Unit 10: Zero (NO/NO_2/NOx) ____/____/_____ Span (NO/NO_2/NOx) ____/____/_____

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$_2$/NOx)	Unit B (NO/NO$_2$/NOx)
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_2/NOx)	Unit B (NO/NO_2/NOx)
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_2 Monitors Verification Test
January 20-21, 1999 Audit

Audit Report: ETVAMS001
Revision 1

Elizabeth A. Betz
Elizabeth A. Betz

Elizabeth T. Hunike
Elizabeth T. Hunike

1.0 Audit Information

1.1 Auditors:

Elizabeth A. Betz
Human Exposure & Atmospheric Sciences Division
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(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 Abbgy	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 permitters 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_2 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 13th 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 Abbgy, 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_2 and NO for the Interference Test was changed from interferant levels of 250 ppm each of SO_2 and NO to interferant levels of 451 ppm SO_2 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_x and the second model would produce ranges between 600-2300 ppm NO_x. 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_2 levels and not to compare oxygen data. Source stability will be documented by NO_x 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_2 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's 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_2 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 Abbgy
	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_2 analyzer
Also by direct measurement: O_2, CO, SO_2, Stack Temperature, Stack Pressure
By calculation: CO_2

Energy Efficiency System's ENERAC 3000SEM electrochemical NO & NO_2 analyzer
Also by direct measurement: O_2, CO, SO_2, CO_2, Stack Temperature

TSI's COMBUCHECK electrochemical NO or NO_2 analyzer

ECOM's A-Plus electrochemical NO and NO_2 analyzer
Also by direct measurement: O_2, CO, SO_2, Stack Temperature, Stack Pressure
By calculation: CO_2

-Chemiluminescence emitted from the reaction of NO with O_3 produced within the analyzer

Horiba's Model PG-250 portable gas analyzer
Also by direct measurement: O_2, CO, SO_2, CO_2

The audit was run during the second week of the Test Plan and the 4th 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^3
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: See Below
Measurement System Preparation prior to VT Date: See Below
Analyzer Calibration Error prior to VT Date: See Below
Sampling System Bias Check prior to VT Date: See Below
NO_2 to NO Conversion Efficiency Date: See Below

Calibrations Initial Calibration Date: See Below
4-point calibration with NO & NO_2 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: <±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_2, 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_2 or NO_x)
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_2 and NO interferant concentrations.

Interferant	Interferant Concentration	Target Analyte
CO	500 ppm - Actual concentration used - 496 ppm	NO, NO_2, NO_x
CO_2	5% - Actual percentage used - 5.03%	NO, NO_2, NO_x
SO_2	500 ppm - Actual concentration used - 501 ppm	NO, NO_2, NO_x
NH_3	500 ppm - Actual concentration used - 494 ppm	NO, NO_2, NO_x
Hydrocarbon Mixture	~ 500 ppm C_1, ~ 100 ppm C_2, ~ 50 ppm C_3 and C_4 Hydrocarbon concentration used - 590 ppm	NO, NO_2, NO_x
SO_2 and NO	250 ppm each - Actual concentration used - 451 ppm SO_2 & 393 ppm NO	NO, NO_2, NO_x

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_2 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: ≤± 3% of the span over the period of each run
Calibration Drift: ≤± 3% of the span over the period of each run
Interference Check: ≤±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_x, 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_x Sources

Gas Cooktop: NO and NO_2 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_2
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_2 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_2 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_2
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_x Source

First Diesel Generator: NO and NO_2 ranges 100-1000 ppm NO_x
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_2
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 ±l0°F;

NO_x 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_2 changes, at the center of the exhaust duct of $\leq \pm 0.50\%$ absolute (±5000 ppm) from the mean sampled over the 15 minute interval.

High NO_x Source - Not Observed

Second Diesel Generator: NO and NO_2 ranges 600-2300 ppm NO_x
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_2.

Steady-State:

Temperature changes in the center position of the exhaust of not more than ±l0°F;

NO_x 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_2 changes, at the center of the exhaust duct of $\leq \pm 0.50\%$ absolute (±5000 ppm) from the mean sampled over the 15 minute interval.