REFINEMENT AND DEMONSTRATION OF A NEW INDOOR CONTINUOUS NITROGEN DIOXIDE MONITOR

FINAL REPORT
Contract Number 99-327

Prepared for:

California Air Resources Board

California Environmental Protection Agency

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ACKNOWLEDGEMENTS

We gratefully acknowledge the participation of Patricia Holowecky, Patrick Hoffman and Thomas Kelly of Battelle. We also thank Jeff Yanosky, Dorothy Shimer and Peggy Jenkins of the California Air Resources Board for their involvement in this work. This report was submitted in fulfillment of Contract 99-327 – Refinement and Demonstration of a New Indoor Continuous Nitrogen Dioxide Monitor.

ABSTRACT

This is the Final Report on California Air Resources Board (CARB) Contract No. 99-327 – Refinement and Demonstration of a New Indoor Continuous Nitrogen Dioxide Monitor. This work builds on CARB Contract No. 96-312 (Kelly and Myers, 1999). Under that contract, a small, quiet, portable instrument was developed to measure nitrogen dioxide (NO_2) and nitrous acid (HONO) in indoor air. Indoor sources of these toxic compounds include emissions from combustion sources, such as cooking appliances, portable heaters, and tobacco smoking. The NO_2/HONO instrument is a fully self-contained continuous monitor, based on a miniature commercial electrochemical cell that responds to both NO_2 and HONO. In this project, investigators further refined the four electrochemical NO_2/HONO monitors developed under the previous program, assembled one additional monitor, and improved the data reduction process. The monitors were fitted with improved electronics, new pump mufflers, and a tamper proof front cover. The monitors were tested in the laboratory and in test chambers at Battelle and were evaluated by CARB staff in Sacramento, California. The refinement produced a small, quiet, portable, easy to use, linear, and repeatable monitor that is able to record concentrations below 15 ppbv.

EXECUTIVE SUMMARY

Background

There is a critical need for accurate, real-time indoor nitrogen dioxide (NO_2) measurements in field studies. Indoor air quality and exposure field studies conducted to date have had to rely on modeled results or data from passive NO_2 samplers that provide only long-term (3-7 day) average results. Those average data do not reflect the very high indoor levels of NO_2 that can occur over short time periods with the use of combustion sources such as gas stoves and heaters. Preliminary results from California Air Resources Board (CARB) Children's Epidemiology Study identified NO_2 as a major contributor to respiratory impacts in children; however, the investigators had to rely on modeled estimates of indoor NO_2 in analyzing exposures.

Under CARB Contract No. 96-312 (Kelly and Myers, 1999), Battelle successfully developed a shoe-box sized, real-time, indoor monitor that used a commercially available electrochemical sensor to measure both NO_2 and its indoor reaction product nitrous acid (HONO) with good accuracy and precision. Battelle recommended refinements to the monitor to streamline data reduction and improve operation of the monitor. Monitors developed under the original program required expertise to obtain, install, and calibrate the electrochemical sensors used in the monitor, and to reduce the data generated from the monitor. The electrochemical sensors required frequent recalibration (approximately every 2 weeks) and had to be replaced periodically (every six to twelve months) due to gradually declining sensitivity. The real-time data were downloaded and analyzed using commercially available software. The monitor appeared to provide good measurements in the laboratory and field, but additional testing in California homes and in ambient air was deemed to be needed. In particular, the indoor NO_2 and HONO levels encountered in previous field testing rarely approached the 250ppbv level set for the California one-hour NO_2 standard (Kelly and Myers, 1999). The work on this project (99-327) further refined the existing indoor NO_2/HONO monitors and field tested the improved monitors in a California home.

Refinement and Testing Efforts

The printed circuit board (PCB) that amplifies and conditions the signal generated by the electrochemical sensor in the NO_2/HONO monitor was redesigned. A PCB provided by the manufacturer of the electrochemical sensor, TSI Inc., originally performed this function. Because of the specific requirements of the nitrogen dioxide monitor used in this project, the original PCB was found to be inadequate and a PCB with greater gain and signal to noise ratio was developed. Steps were taken to reduce the pump noise from the monitors, a tamper-proof front cover was designed, and a more sophisticated software interface was developed for downloading data from the monitors.

At CARB's request, a set of guidelines were established that allow the monitor's operator to determine if the monitors are operating properly. Typical monitor performance had been characterized in previous routine operation in field locations. While extensive testing has been done to determine the monitors’ behavior, such as sensitivitr.5(s)-10.10.1(e) tr atmo, st   aiv titr.5(s)-7(a

Conclusions

The monitor refinements performed on this project were successfully implemented. The printed circuit board redesign greatly reduced the signal noise, provided an extra signal to record sampling mode valve position, and allowed the operator to boost the output signal for a given concentration by a factor of three by selecting the high gain setting. The noise reduction efforts allowed the monitors to operate below the recommended decibel level, and tamper proof covers were fitted to each of the monitors. Additional data analysis software was developed that allows users to easily convert recorded signals to concentration units. Finally the monitors were successfully evaluated by CARB staff and field demonstrated by Battelle staff in a Sacramento, CA home.

LIST OF ABBREVIATIONS

CARB	California Air Resource Board
dB	Decibel
F	Degrees Fahrenheit
HONO	Nitrous acid
mV	Millivolts
NO_2	Nitrogen dioxide
PCB	Printed circuit board
ppbv	Parts per billion by volume (in air)
RH	Relative humidity
V	Volts

INTRODUCTION

This is the Final Report on California Air Resources Board (CARB) Contract No. 99-327 – Refinement and Demonstration of a New Indoor Continuous Nitrogen Dioxide Monitor. The primary objectives of this project were to further refine electrochemical nitrogen dioxide (NO_2) and nitrous acid (HONO) monitors developed under CARB Contract No. 96-312 (Kelly and Myers, 1999) and to document the performance of the enhanced monitors in a California home at elevated NO_2 levels. The main tasks of this work were to refine the four monitors developed under the previous program; to assemble another monitor, equivalent to the four improved units; to deliver the monitors to CARB; and to review operating, data acquisition, and data reduction procedures with CARB staff. CARB staff were to evaluate the monitors and operate them alongside a reference monitor in a California home at elevated NO_2 levels. This report discusses the refinements made to the monitors, and provides the results of a laboratory evaluation conducted by CARB staff, and of a field test performed in Sacramento, California.

Background

There is a critical need for accurate, real-time indoor nitrogen dioxide (NO_2) measurements in field studies. Indoor air quality and exposure field studies conducted to date have had to rely on modeled results or data from passive NO_2 samplers that provide only long-term (3-7 day) average results. Those average data do not reflect the very high indoor levels of NO_2 that can occur over short time periods with the use of gas stoves and heaters. Preliminary results from CARB's Children's Epidemiology Study identified NO_2 as a major contributor to respiratory impacts in children; however, the investigators had to rely on modeled estimates of indoor NO_2 in analyzing exposures.

Under CARB Program No. 96-312, Battelle successfully developed a shoe-box sized, real-time, indoor monitor that used a commercially available electrochemical sensor to measure both NO_2 and its indoor reaction product HONO with good accuracy and precision (Kelly and Myers, 1999). Battelle recommended refinements to the monitor to streamline data reduction and improve operation of the monitor. Monitors developed under the original program required expertise to obtain, install, and calibrate the electrochemical sensors used in the monitor, and to reduce the data generated from the monitor. The electrochemical sensors required frequent recalibration fairly often (approximately every two weeks) and had to be replaced periodically (every six to twelve months) due to gradually declining sensitivity. The real-time data were downloaded and analyzed using commercially available software. The monitor appeared to provide good measurements in the laboratory and field, but additional testing in California homes and in ambient air was deemed to be needed. In particular, the indoor NO_2 and HONO levels encountered in previous field testing rarely approached the 250ppbv level set for the California one-hour NO_2 standard (Kelly and Myers, 1999). The work on this project further refined the existing indoor NO_2 monitors and field tested the improved monitors in an indoor California residential environment. Specifically, the following tasks were completed:

1. Refinement of the four NO_2/HONO monitors developed under CARB Contract No. 96-312
    a. Added an extra channel to each HOBO data logger to record valve position
    b. Improved the electronic circuits used to operate the electrochemical sensors by increasing sensitivity and adding a low/high range switch
    c. Changed pumps and added muffling to quiet monitor operation
    d. Improved data handling process
    e. Built an additional NO_2/HONO monitor that matched the existing four improved units

2. Delivered all five monitors to CARB staff and trained them on operation and data reduction procedures

3. Complete an independent-party evaluation of the performance of the monitor including accuracy, reliability, and ease of use in residential environments at sustained NO_2 concentrations above 250 ppb

4. Demonstrated performance during field test in a residence in Sacramento, California

5. Developed operating manual and performance guidelines.

The subsequent sections of this report present the final products of each of these tasks.

1.0 MONITOR REFINEMENTS AND FABRICATION

1.1 Electronics Refinement

The PCB that amplifies and conditions the signal generated by the electrochemical sensor in the NO_2/HONO monitor was redesigned. A PCB provided by the manufacturer of the electrochemical sensor, TSI Inc., originally performed this function. Because of the specific requirements of the nitrogen dioxide monitor used in this project, the original PCB was found to be inadequate and a PCB with greater gain and signal to noise ratio was developed.

As part of this design, several pieces of electronics such as the valve switching relay, the voltage controller for the digital front-panel display, and the output voltage resistorcapacitor filter, that were originally mounted separately from the TSI Inc. PCB were replaced with solid state components and moved onto the new PCB. This saved space within the monitor and reduced the cost of those electronic parts. Additionally, an extra signal was added to the HOBO data recorder input as Channel 2. This input records to Channel 2 a high voltage (1V) when the valve controlling the flow path of inlet air through a CO_3 filter is activated (indicating the NO_2 measurement mode) and a low signal (0.005 V) when the valve is deactivated (indicating the NO_2 + HONO measurement mode). This additional signal was added so that the user could clearly identify, from the Channel 2 data, whether the monitor was operating in the NO_2 or NO_2+HONO mode.

1.2 Monitor Reassembly

Once the redesigned PCB was fabricated, the new part had to be retrofitted into the existing monitors. The new PCB effected several improvements over the original monitor design. First, the relay, front panel display controller, and capacitance filters were moved from three separate locations in the old monitor, onto the new PCB. This helped decrease the amount of wiring and electrical noise, and freed up space within the monitor housing. Second, the new PCB was fitted with a switch that allows the user to change the gain of the amplifier, thereby changing the operational range of the monitor.

The air pumps were also replaced with more appropriately sized pumps, thus reducing the wear on the pumps and quieting the monitor. In addition, the monitors were fitted with a particulate filter that was applied at the inlet port. This particulate filter protected the monitors from particulate matter that might be generated near indoor combustion sources. Finally, a cover was fabricated so that the front panel switches and displays are protected from accidental interference during extended in-home use.

1.3 Monitor Calibration

After the PCBs had been tested to ensure proper electrical behavior, the monitors were calibrated for HONO and NO_2. Figure 1 shows a schematic of the experimental setup. The calibration for HONO was done using a permeation tube of HNO_3, by converting HNO_3 to HONO through contact with a bed of solid $NaNO_2$ coated on glass beads. The HNO_3 permeation tube (VICI Metronics, Part # 100-070-0160) was 7cm long and had a certified permeation rate of 950 ng/min/cm (± 15%,) at 90 °C. The tube was held in the oven of a Metronics 340 dynamic calibrator and supplied with purified dry air. The output of the calibrator was sent via a 45°C heated line to a glass trap containing the 5mm $NaNO_2$ coated glass beads. The glass beads completely converted HNO_3 to HONO and the resulting air stream containing HONO vapor was humidified (by mixing with a separate stream of humid air) and delivered to each of the four monitors, one at a time. The HONO concentration was confirmed with a Monitor Labs Model 8840 nitrogen oxides monitor that incorporated a heated molybdenum NO_x converter. The HONO source provided only enough flow to calibrate one NO_2/HONO monitor at a time.

The NO_2 calibration was done using a similar experimental setup, except that the Metronics 340 calibrator and glass beads were replaced with an Environics Model 1010 gas dilution system and cylinder of NO_2. This system diluted purified dry air with a 37.7

ppm gas standard of NO_2 to achieve the desired concentration. During this calibration there was sufficient volumetric flow to supply all of the monitors simultaneously; therefore all four monitors were calibrated at once instead of one at a time as was the case during the HONO calibrations.

A humidity generator was used to add a small amount of humidified air to the dry air from the Metronics 340 or the Environics 1010. This was done to ensure that the sensor heads remained within the recommended operating range of 15%-85% RH. For all calibrations, the humidity was maintained at approximately 23%RH and the temperature was room temp, or 80 F.

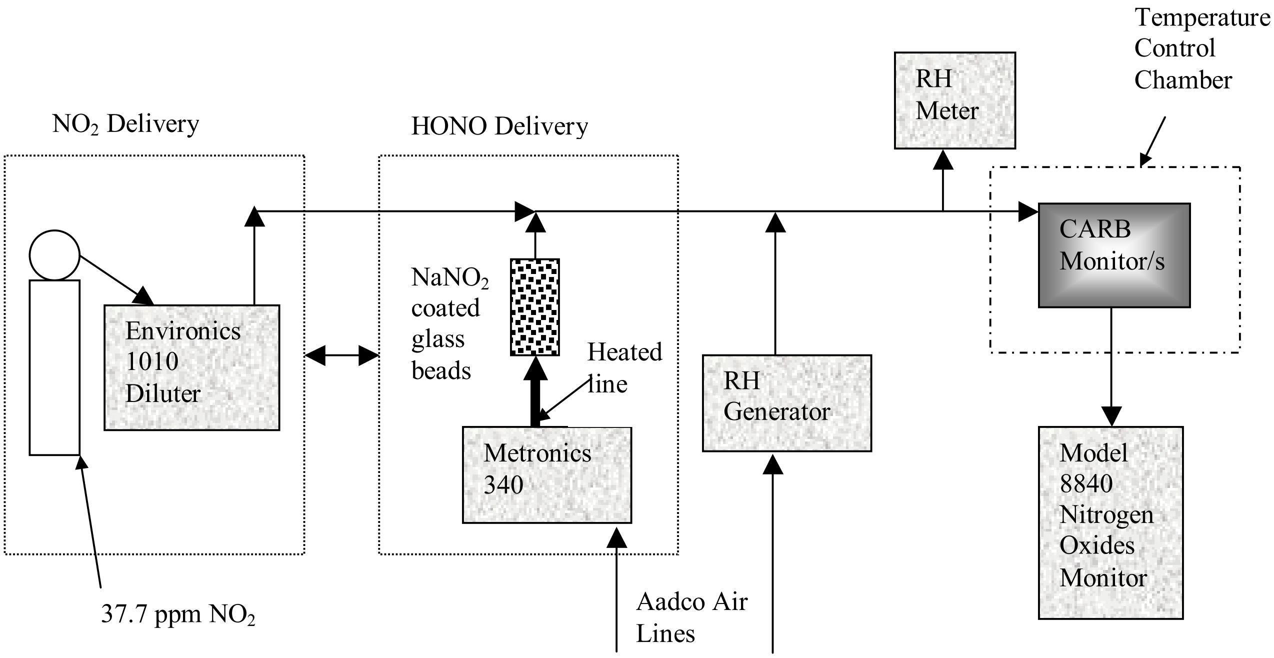


FIGURE 1. SCHEMATIC OF EXPERIMENTAL SETUP FOR NO_2 and HONO CALIBRATIONS.

1.4 Calibration Results

The four monitors were given designations of A,B,C, and D and were calibrated separately for NO_2 and HONO, each using the low gain setting, and then were calibrated again for NO_2 using the high gain setting. Table 1 shows the results of the NO_2 calibrations for all four monitors over the range of 0 to 950 ppbv, and Table 2 shows the results of the HONO calibration over a range of 1 to 130 ppbv, each using the low gain setting. Table 3 shows the NO_2 calibration results over a range of 0 to 100 ppbv, using the high gain setting. In each table the calibration results are shown in terms of the respective monitor's output scale factor, in mV of output signal per ppbv of NO_2 or

HONO. Tables 1 and 3 show the NO_2 response in both modes of each monitor, since NO_2 is measured in both modes.

TABLE 1. SCALE FACTORS FOR NO_2 – LOW GAIN SETTING

	Monitor A		**Monitor B**		**Monitor C**		**Monitor D**	
Channel	NO_2+HONO	NO_2	NO_2+HONO	NO_2	NO_2+HONO	NO_2	NO_2+HONO	NO_2
Scale factor (mV/ppbv)	1.7	1.3	1.0	0.9	1.1	1.0	1.4	1.3

TABLE 2. SCALE FACTORS FOR HONO – LOW GAIN SETTING

	Monitor A	**Monitor B**	**Monitor C**	**Monitor D**
Scale factor (mV/ppbv)	11.4	6.2	8.3	11.5

TABLE 3. SCALE FACTORS FOR NO_2 – HIGH GAIN SETTING

	Monitor A		**Monitor B**		**Monitor C**		**Monitor D**	
Channel	NO_2+HONO	NO_2	NO_2+HONO	NO_2	NO_2+HONO	NO_2	NO_2+HONO	NO_2
Scale factor (mV/ppbv)	4.1	2.9	2.7	2.4	2.4	2.1	3.5	3.1

It can been seen from these calibration results that the monitors were approximately six to eight times as sensitive to HONO as to NO_2 and that the high gain setting produces a scale factor approximately 2.5 times that of the low gain setting. In all cases the NO_2 scale factor was higher in the NO_2+HONO (i.e. unfiltered) mode than in the NO_2 (i.e. filtered) mode. This may reflect differences in flow in the two paths, but is not due to the

After the calibration was performed, the monitors were calibrated again for NO_2 at two different temperatures and two different humilities to evaluate the effect that changing environmental conditions have on the monitor's performance. The monitors were calibrated under a constant temperature of 80 F and a relative humidity of 23%, then the relative humidity was adjusted to 75% and the monitors were recalibrated. Then this procedure was repeated the same RH values at a temperature of 110 F. Scale factors for NO_2 for each monitor were determined for each of the experimental conditions. Table 4 shows the summary of these tests, in terms of NO_2 response for each monitor relative to the lowest temperature and RH conditions.

TABLE 4. SUMMARY OF TEMPERATURE AND RH EFFECTS ON NO_2/HONO MONITORS

Temp/RH	**Relative NO_2 Response**[a]			
	Monitor A	**Monitor B**	**Monitor C**	**Monitor D**
80 F/23%	1.00	1.00	1.00	1.00
80 F/75%	1.08	1.11	1.00	1.00
110 F/23%	1.23	1.11	1.20	1.31
110 F/75%	1.23	1.22	1.30	1.31

a: Results normalized to lowest T and RH =1.00

The results from this test show that the monitors had an average response change of approximately 0.7%/°F and an average response change of 0.1%/%RH, over the ranges tested.

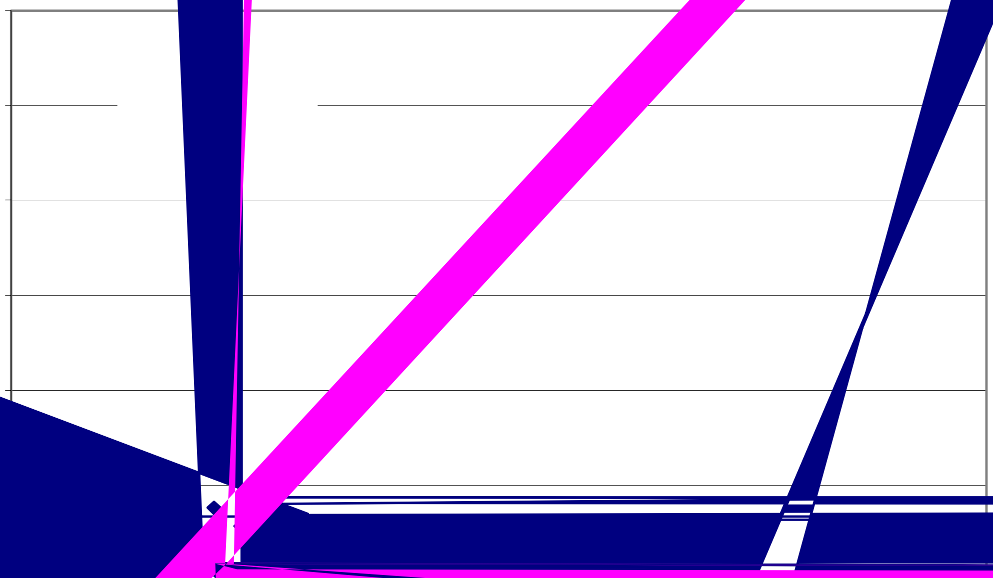
1.6 Interference Tests

Two interference gas tests were conducted on successive days in a 0.4 m^3 chamber in which several target species and potential interferants were injected together into the chamber. These tests were conducted to make sure that the monitors were not adversely affected when used in an environment containing other gases potentially found in indoor air. The gases NO_2, NO, CO, and CO_2 were introduced into the chamber using compressed gas standards and the Environics 1010 gas dilution system. The flow rate and the duration of flow determined the final chamber concentration. Ozone was introduced by a brief injection of dry air through a commercial corona discharge ozone source. HONO was introduced using the Metronics 340 and the same method described in Section 1.3. Table 5 summarizes the mixture tests, showing the gases, the prepared concentrations and the time at which each gas was injected into the test chamber.

TABLE 5. SUMMARY OF GAS INTERFERENCE TESTS

	Species	**Concentration Prepared (ppbv)**	**Time Introduced**
Test 1	NO_2	150	13:20
	CO	100	14:00
	CO_2	1000	14:18
	NO	500	14:35
Test 2	NO_2	250	12:06
	CO	100	12:18
	CO_2	1000	12:32
	HONO	100	12:50
	O3	100	13:10

Each test began with the monitors sampling humidified zero air from the chamber. Then, during the first test, NO_2, CO, CO_2, and NO were subsequently added to the chamber, while recording each monitor's response. Then the test was repeated the next day except that HONO was included as a target gas, and O_3 replaced NO. The results from the two tests for monitor A are shown in Figures 2 and 3, which exemplify the results of these tests for all the monitors. The output responses on mV from both the NO_2 and the NO_2+HONO channels of the monitors are shown in Figures 2 and 3



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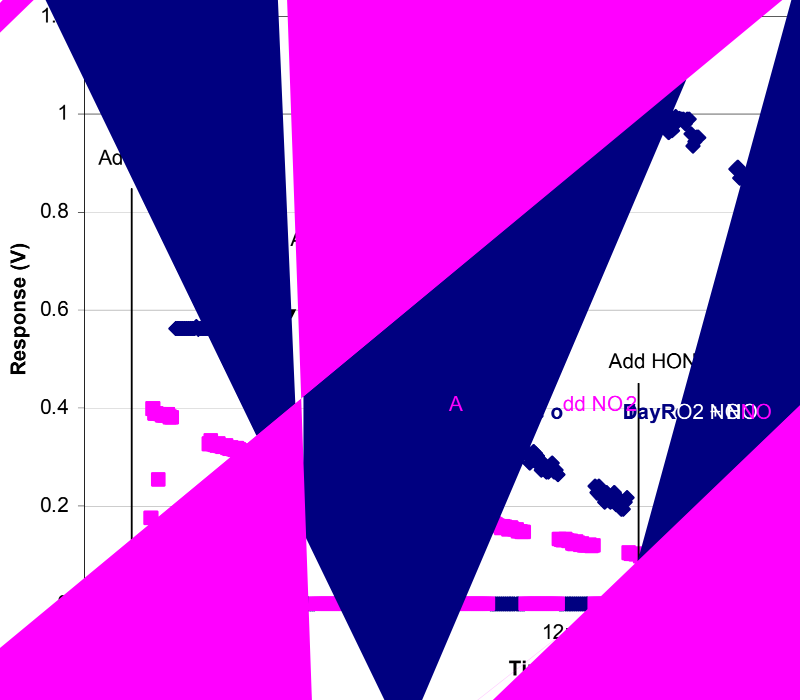

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It can be seen that the NO_2+HONO channel of Monitor A is more sensitive to NO_2 than is the NO_2 channel alone, consistent with Tables 1 and 3. Furthermore, in both tests the monitor responded to the addition of NO_2 and HONO in the chamber, but the addition of potential interference gases had no visible effect on the monitor's ability to properly monitor the target compounds. It can also be seen that the monitor is more sensitive to HONO than to NO_2 since the voltage signal increase due to the addition of HONO is greater than that seen with the addition of NO_2 even though the concentration of NO_2 is 250 ppbv and the HONO concentration is 100 ppbv. These results confirm the results of similar interference tests done in the original development of the NO_2/HONO monitors (Kelly and Myers, 1999). Of particular interest is the absence of response to ozone (Figure 3), which indicates that the addition of an ozone scrubber to the monitor design is not necessary. This finding is contrary to the findings by CARB staff after ozone was introduced directly into the monitor at a concentration of 699 ppbv. It appears that at typical indoor concentrations, and when present in a mixture of gases, the interference due to ozone is minimal.

1.7 Pump Modifications

A review of common sound pressure levels showed that in an average office environment, 50 dB is expected. Tests conducted at Battelle confirmed this level, showing that Battelle has an average noise level of 47.7 dB. Tests conducted to determine the noise of the running pump resulted in an average of 54.9 dB, with the pump unenclosed and unmuffled. Repeating the tests with a muffled, insulated pump reduced the noise levels to 48.6 dB with an average background noise of 47.5 dB. Table 6 summarizes these results.

TABLE 6. NOISE LEVELS FOR UNENCLOSED AND ENCLOSED PUMP

Background (dB)	Pump-unenclosed, unmuffled (dB)	Pump-enclosed, muffled (dB)	Difference (dB)
47.7	54.9		7.2
47.5		48.6	1.1

A similar insulation was retrofitted to the existing monitors and designed into the final monitor, therefore reducing the audible impact of operating the monitors in a classroom

1.8 Data Reduction Improvements

Efforts have been made to develop a user interface that will allow the monitor operator to more easily analyze the data stored in the on-board HOBO datalogger. To accomplish this, a JAVA-based package allows the user to choose a raw data file, in volts, that has been recorded by the monitor, and stepwise enter calibration information, and temperature and relative humidity information, to arrive at a final concentration data file. A disk with the executable file accompanies the monitors.

The user begins by choosing an output file name and location that will store the processed data. Next, the user chooses the method of inputting the scale factors that convert the voltage information to concentrations. This is done using information from a calibration that the user has recently performed. Then the user is prompted to input the name and location of the raw data from the HOBO, both concentration and temperature and RH. Next, the user decides whether or not to apply temperature and relative humidity corrections to the data. Finally, the software displays the processed data and stores it in the previously determined file. This data is then suitable for display in any charting software, such as Microsoft Excel. Detailed instructions for using this software are included in the Operating Manual in Appendix A

2.0 DELIVER MONITORS TO CARB

Battelle delivered four monitors to CARB on July 31, 2001 for evaluation by the Monitoring Laboratory Division (MLD) of CARB. In attendance for the delivery and training were several CARB staff members, including Peggy Jenkins, Dorothy Shimer, Tom Phillips, Clint Taylor, Mac McDougall, Jeff Yanosky, Scott Fruin, Reggie Smith, and Susan Lum. The purpose of the training was to explain to CARB staff the refinements and modifications incorporated into this latest monitor design and to answer questions about its operation.

After a discussion describing the operating procedure of the monitor, several monitor-related items were identified for Battelle to provide additional information.

First, because the MLD does not have the capability to deliver HONO, it was suggested the monitors would not be used in that configuration. As indicated above, the calibration for HONO was done using a permeation tube of HNO_3 and converting nitric acid (HNO_3) to HONO. Because of the limited capabilities of the MLD, another possible method for delivering HONO was suggested. HONO can be delivered by slowly (i.e., with a syringe pump) adding sodium nitrite solution to a flask of sulfuric acid, and sweeping the HONO vapors out of the flask with a flow of clean air or nitrogen. However, this method results in HONO with lower purity than with the nitric acid permeation tube, and the production rate is not as constant. Consequently, production of HONO was not part of the CARB evaluation of the monitor reported in Appendix B.

Second, during the training period, it was brought to Battelle's attention that the monitors were exceedingly noisy and produced an audible high pitched sound that needed to be quieted before final delivery. The audible sound produced by the monitors is a result of the pump that is used to pull air through the system. It was suggested that the pump noise be reduced to a level of 55 dB at a distance of 3ft. This design criteria, however, was only to be used as a guideline and not a firm requirement. To this end, pump housing modifications, exhaust muffling, and alternative pumps were successfully investigated to reduce the pump noise, as described in Section 1.7.

Third, it was determined that additional documentation was needed to operate the monitor. The needed documentation includes instructions for downloading the data stored in the onboard HOBO datalogger, and a written description of how to operate the monitor with emphasis on the calculations used to convert the voltages stored on the HOBO to concentrations of NO_2. The operating manual that provides this needed documentation is attached as Appendix A of this report.

3.0 CARB EVALUATION

After the electrochemical sensors were replaced in each of the monitors and the monitors were calibrated during November 2002, the monitors were sent to CARB for an evaluation period in December 2002. During this evaluation period, Jeff Yanosky of CARB evaluated the monitors and wrote a summary report of his findings. The ARB evaluation of the monitors were very favorable. The accuracy of each indoor NO_2 monitor was generally good, measuring on average between 80% and 92% of the concentration measured by the reference NO_x monitor. The precision of the indoor NO_2 monitors was high, with within- and between-instrument differences representing less than 6% of the measured concentrations on average. The response of each indoor NO_2 monitor was highly linear across the range from zero to 699 ppb NO_2, with values for the coefficient of determination (R^2) greater than 0.99 for each monitor. The sensitivity of the indoor NO_2 monitors was found to be very high, with a level of 15 ppb NO_2 being clearly detectable. The indoor NO_2 monitors also exhibited very little drift over the testing period, staying within 1 ppb NO_2 of the initial value on average when supplied with zero air. Additional findings from this report are discussed in this section and the final version of this report is included as Appendix B.

The evaluation of the monitors by CARB focused on documenting the performance of the monitor including accuracy, reliability, and ease of use in residential environments at sustained NO_2 concentrations above 250 ppbv. Therefore, all of the steps required to successfully measure NO_2 were performed, including calibration, data downloading, and data interpretation. The monitors were calibrated at the beginning of the evaluation period to determine the response to NO_2. Then the monitors were evaluated to determine the effect of RH on the response to NO_2. Several performance evaluations were completed that tested the monitors' accuracy, precision and linearity. Finally the monitors were calibrated again to determine the extent of calibration drift. A qualitative assessment of “ease of use” was also performed. Note that at the time of the evaluation, the additional data analysis software was not in place.

The monitors were calibrated against a ThermoEnvironmental chemiluminescence NOx monitor in January 2003 over an NO_2 range of 0 to 699 ppbv, at room temperature and 40% RH. Calibration points of 0, 50, 200, 400 and 699 ppbv were performed with the monitors operating in their low gain setting. Table 7 shows the scale factors that result from a least squares fit of the calibration data.

TABLE 7. SCALE FACTORS FOR NO_2 – LOW GAIN SETTING, FROM CARB EVALUATION OF FOUR MONITORS[a]

	Monitor A	**Monitor B**	**Monitor C**	**Monitor D**
Scale factor (mV/ppbv)	2.3	1.6	2.8	1.2

a: All data in NO_2 measurement mode.

During the evaluation period, the output of one of the monitors, Monitor C, was saturated when elevated concentrations (greater than approximately 700 ppb) of NO_2 were delivered to it. Therefore only the calibration data below 700 ppb were used to calculate the scale factor in Table 7 for Monitor C. This monitor was returned to Battelle so that a cause for the saturation could be discovered. Upon investigation, it was determined that the saturation is the result of a very sensitive (2.8 mV/ppbv) electrochemical cell in that unit, which produces full scale output at lower than expected NO_2 levels. Thus this behavior is an artifact of the high sensitivity, and not a malfunction of the monitor.

During the evaluation period, two of the monitors experienced pump failures and the pumps were repaired by cleaning and lubricating the diaphragms. In addition, the operator recommended that the fittings that connected the tubing to the pump be secured because the tubing connections on Unit B and Unit D were loose. It is not anticipated that these pumps will need to be cleaned before each field test. The pumps are expected to last 2000 hours without needing to be replaced. A copy of the report delivered on this evaluation is included in Appendix B

4.0 DEMONSTRATION IN SACRAMENTO FIELD TEST

Battelle performed an in home field test from February 17 to February 20, 2003, in which the monitors were calibrated and then operated continuously in a Sacramento, CA home for two days. During the in-home portion of the demonstration, the monitors were placed in the kitchen of the residence while the gas oven and range top were operated according to a scripted routine. Unit C was not available for the test and therefore only Unit A, B and D results are shown.

A calibration of the monitors was performed before the field demonstration. This calibration against a ThermoEnvironmental (TECO) chemiluminescence monitor was performed at room temperature and 40% RH. Calibration points of 0, 50, 180, 370 and 660 ppbv were performed with the monitors operating on their low gain setting. The data from this calibration are shown in Figure 4. Table 8 shows the scale factors that result from a least squares fit of the calibration data. Note that these values closely agree with the calibrations performed on the corresponding monitors by CARB staff in January (Table 7).

TABLE 8. SCALE FACTORS FOR NO_2 – LOW GAIN SETTING, SACRAMENTO TEST[a]

	Monitor A	**Monitor B**	**Monitor D**
Scale factor (mV/ppbv)	2.3	1.6	1.2

a: All data in NO_2 measurement mode.

Once calibrated, the monitors and the TECO reference monitor were placed in a residence in Sacramento, CA. The partial floor plan for the home is shown in Figure 5, and a detailed floor plan of the kitchen is shown in Figure 6. The monitors were placed near the oven with the inlet lines attached to the oven vent, as shown in Figure 5, near the breathing zone height of a standing adult.

Testing began the evening of February 19 at approximately 6 pm. During this time the monitors recorded every minute, while the TECO measurements were recorded approximately every half hour while the operator was present. While the monitors were recording NO_2 measurements, the operator was manipulating the operation of the oven and range top to simulate typical cooking conditions. The occupants of the home also used the gas range for unscripted activities. Table 9 shows the scripted actions performed during the test and Figures 7 and 8 show the results from Units A, B, and D as well as the TECO monitor on the first and second day of testing, respectively. Unit A experienced a pump failure during the night between Day 1 and Day 2 and therefore no data are available for Day 2. This unit was returned to Battelle for repair after the test.

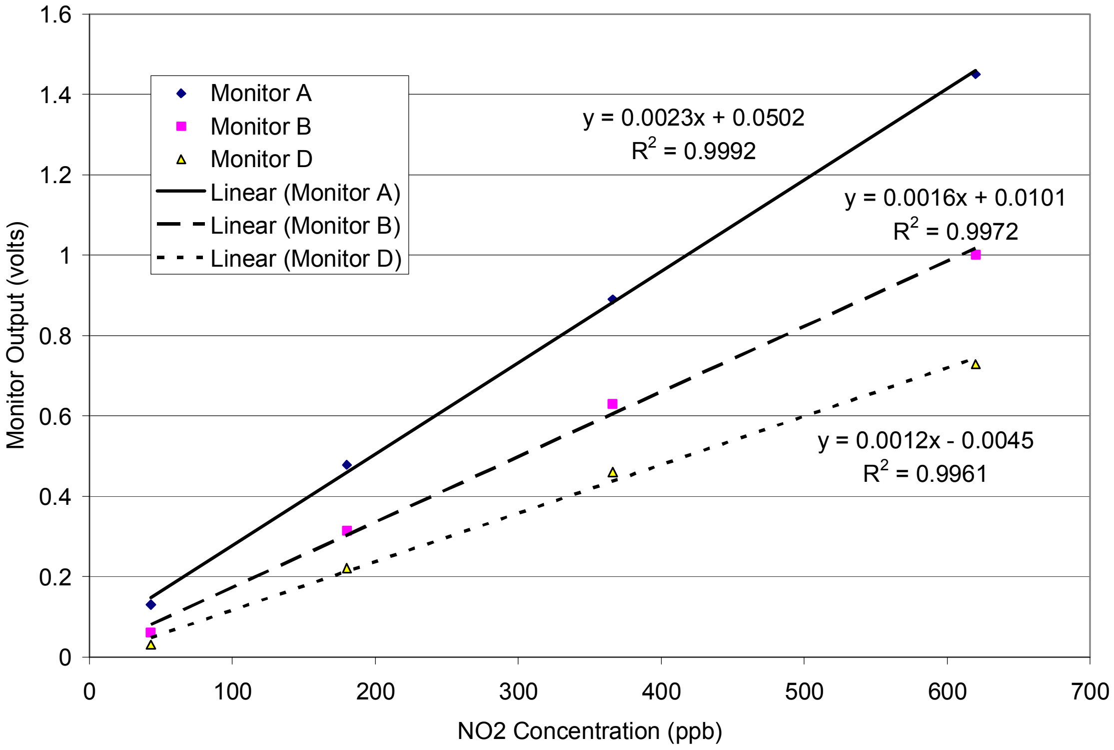


FIGURE 4. RESPONSE OF NO_2 MONITORS DURING CALIBRATION FOR SACRAMENTO FIELD TEST

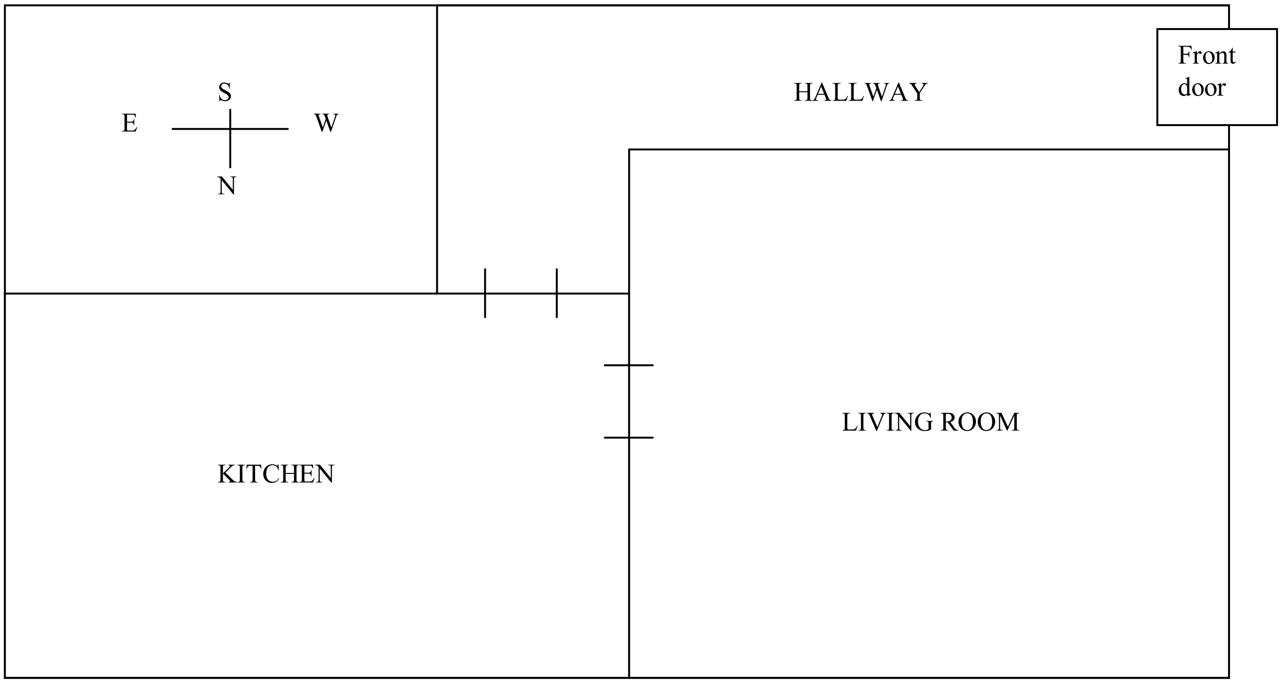


FIGURE 5. SCHEMATIC OF THE FLOOR PLAN FOR THE HOME

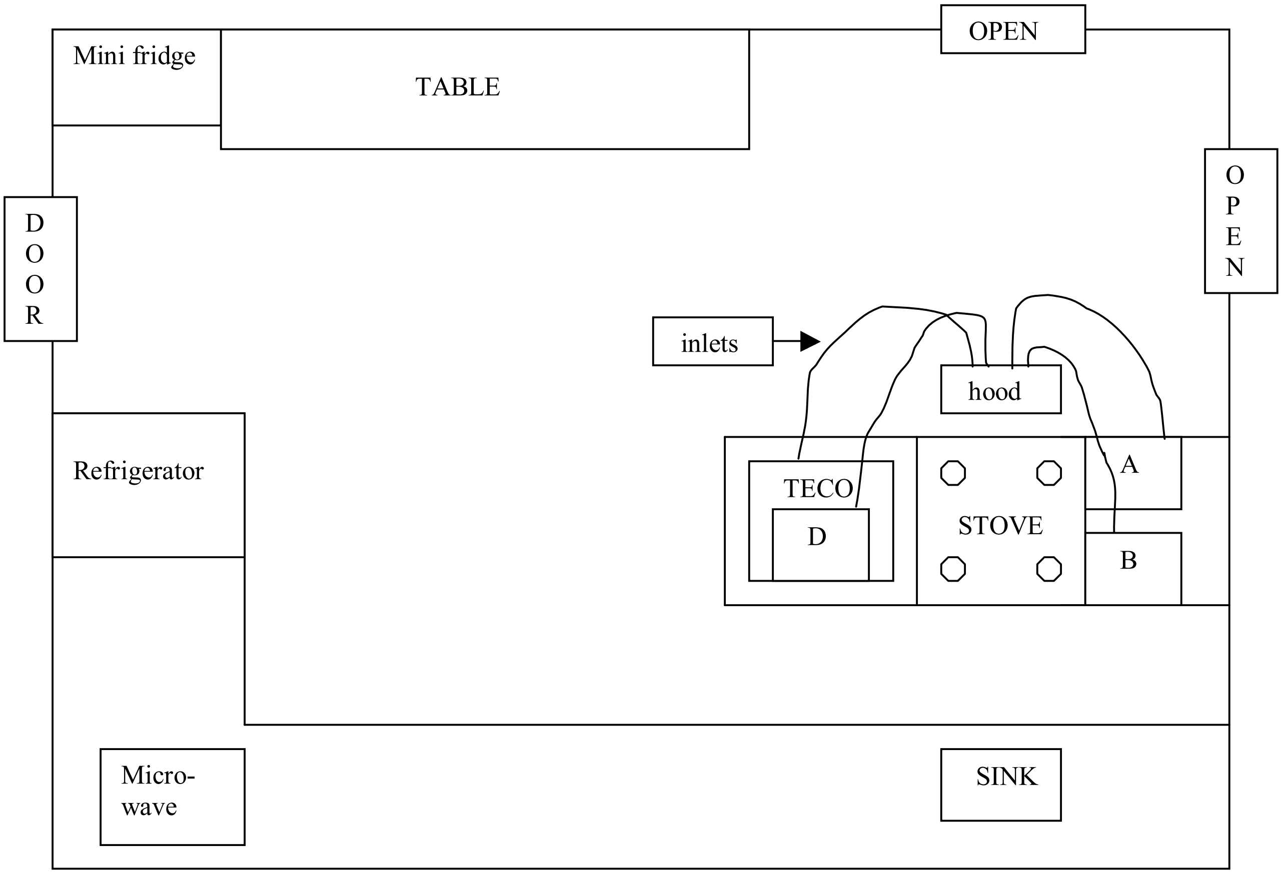
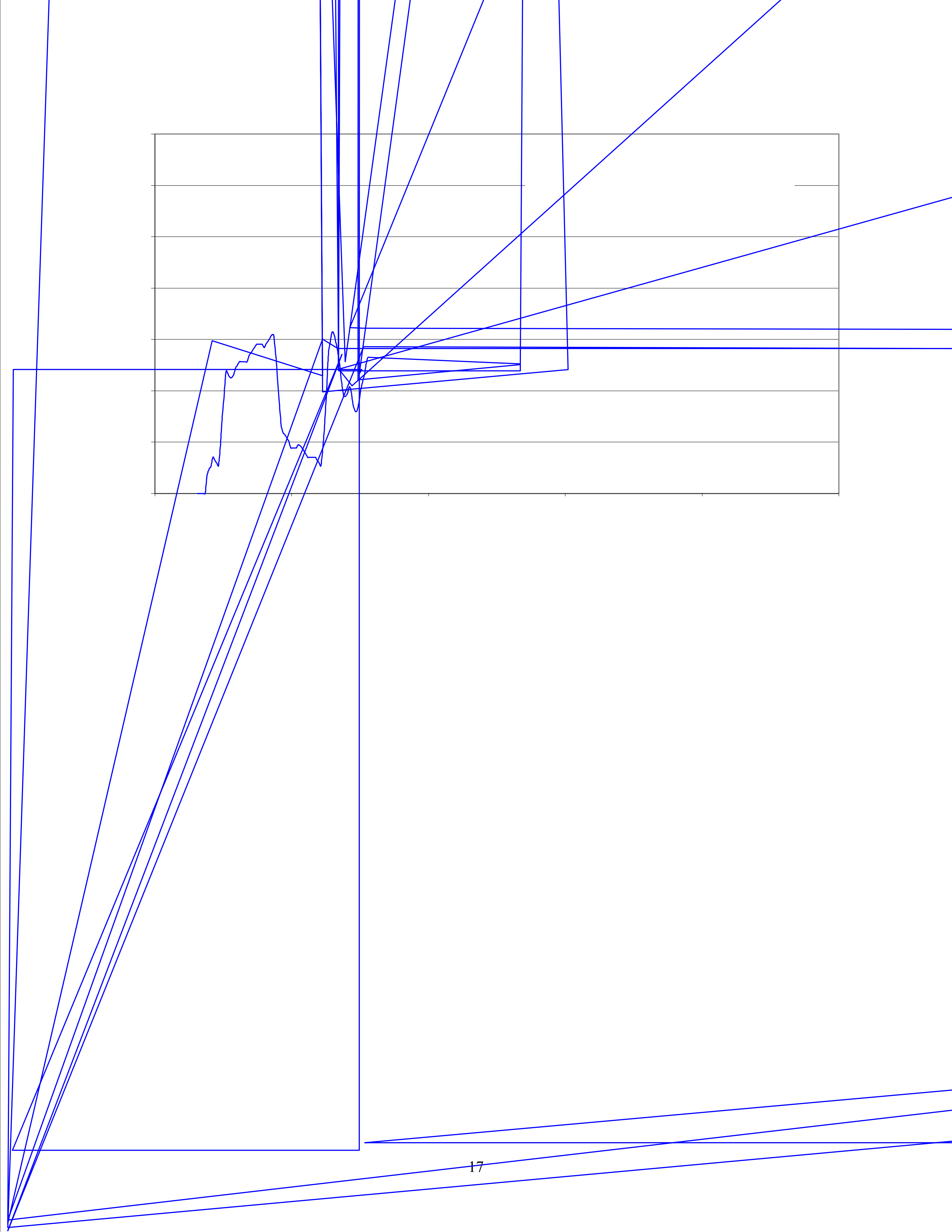


FIGURE 6. SCHEMATIC OF THE FLOOR PLAN FOR THE KITCHEN

TABLE 9. SCRIPTED ACTIVITIES DURING THE SACRAMENTO FIELD TEST

Date/Time	Activity
2/19/2003	**Day 1**
18:30	Start test with 4 burners on high
19:00	Turn off 4 burners
19:23	Turn on oven on to 375^{o}
19:45	Turn 3 burners on high: 2 back, 1 left front
20:00	Turn off 3 burners
20:25	Turn off oven
2/20/2003	**Day 2**
8:30	Turn 4 burners on high
9:02	Turn off 4 burners
9:20	Turn on oven to 375 F
9:45	Turn 3 burners on high: 2 back, 1 right front
10:05	Turn burners off
10:31	Turn oven off



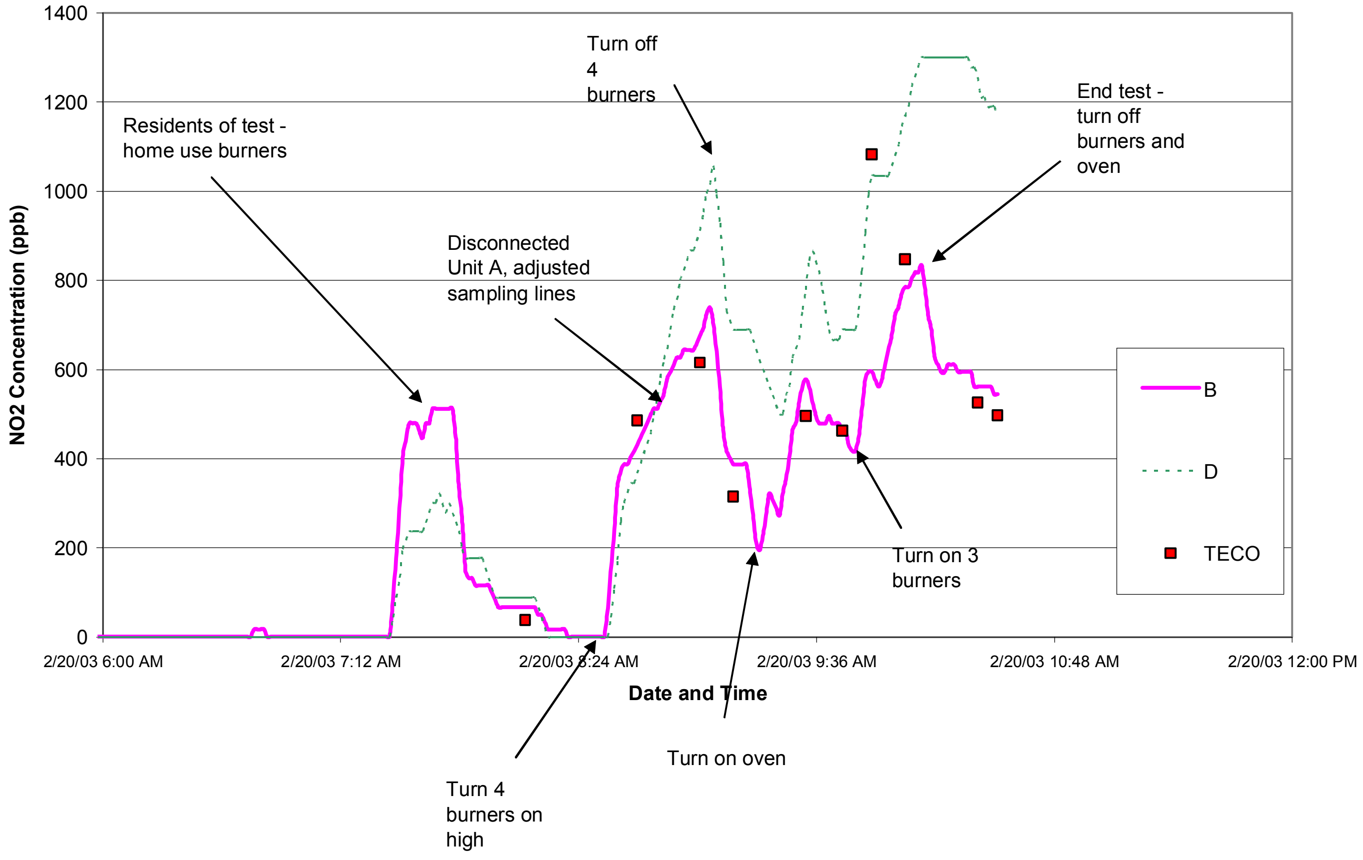


FIGURE 8. RESPONSE OF NO_2 MONITORS DURING SACRAMENTO FIELD TEST – DAY 2

It can be seen from these results that the monitors clearly respond to the activities of turning on the oven and burners. In addition, the three monitors and the TECO all respond at approximately the same levels. There is some disagreement in concentration among the four instruments however, although no instrument consistently reports a higher or lower measured concentration. For example, between 6:00 PM and 7:15 PM on February 19, 2003 Unit D records a higher concentration than Units A and B. However between 7:15 PM and 8:00 PM and again later at 9:00 PM this difference is not seen. Furthermore, on the following day, between 7:15 AM and 8:30 AM, Unit B records higher concentrations than Unit D. Unit D begins recording higher concentrations than Unit B again at 8:44 AM, after the inlet tubing is moved. This behavior suggests that the variations in recorded concentrations are real and not an artifact of monitor inaccuracies. These variations could be a result of each monitor having its own inlet tube, therefore sampling at slightly differing spatial locations.

5.0 MONITOR ACCEPTANCE TEST

At CARB's request, a set of guidelines were established that allow the monitor's operator to determine if the monitors are operating properly. Typical monitor performance had been characterized in previous routine operation in field locations. While extensive testing has been done to determine certain features of the monitors' behavior, such as sensitivity, calibration, and cross sensitivity in the presence of potential interferants, no strict set of criteria had been established that determine whether or not the monitor is working. Typically, failure had been characterized as the inability to properly calibrate the monitor in the laboratory. Monitor characteristics vary from unit to unit, depending upon the electrochemical cell located within it. The electrochemical cell sensitivities vary from piece to piece, and in general, decrease over time. Therefore characteristics such as minimum detection limit and linear range are not constant from monitor to monitor. The values listed here are expected behaviors of a monitor with a new sensor cell.

Voltage – the monitor requires 110VAC

Bias Voltage – the bias voltage on the sensor cell must be a constant -100mV. This voltage is set by the PCB in each monitor, and can be monitored from an analog output on the rear of the instrument.

Minimum detection limit – the typical noise from the monitor is on the order of +- 10mV. This corresponds to roughly 2 ppbv NO_2 on the high gain setting and 10 ppbv NO_2 on the low gain setting.

Sensitivity – when new, the monitors typically have sensitivity between 1.0 and 2.5 mV/ppbv NO_2 on the low gain setting and between 2.5 and 4.0 mV/ppbv NO_2 on the high gain setting. It is recommended that the sensor cell be replaced when the sensitivity of the monitor falls below approximately 0.2 mV/ppbv NO_2.

Flow rate – the monitors are sensitive to changes in flow. A flow of 800 to 1000 cc/min is recommended.

Pressure – the sensor cells within the monitors should not be pressurized or evacuated.

Range – the monitors respond linearly over a range of 0 to 1500 ppbv. An abbreviated linear range may require replacement of the sensor cell.

Temperature – recommended operating range is between 10 and 40 deg. C

RH - recommended operating range is between 15% and 85% RH.

Response time – typical response time is 20 sec to 90% full scale.

A complete user manual is attached as Appendix A.

6.0 RECOMMENDATIONS AND FUTURE WORK

Delivery of the monitors to CARB staff concludes Battelle's involvement in this program. To achieve maximum benefit from the delivered monitors, it is recommended that CARB continue to operate and use these monitors in indoor air quality tests and studies. These monitors have been evaluated and used to a limited degree in field tests, by both Battelle and CARB personnel. Further evaluations by a contractor other than CARB or Battelle are recommended as these evaluations would provide additional information about the robustness of the monitors.

7.0 CONCLUSIONS

The monitor refinements performed on this project were successfully implemented. The printed circuit board redesign eliminated electronic noise, provided an extra signal to record valve position, and allowed the operator to boost the output by a factor of three by selecting the high gain setting. A tamper proof cover was put on the front of the monitors to prevent accidental manipulation of the monitor controls. The monitors were made to operate within the recommended decibel level, and one additional monitor was built. Finally, additional data analysis software was developed that allows users to easily convert recorded output volts to concentration units.

The monitors were successfully evaluated by CARB staff and field demonstrated by Battelle staff in a Sacramento, CA home. CARB staff determined that in general the monitors were easy to use and that the response from the monitors was reproducible and linear over the range tested. The monitors were able to detect as little as 15 ppbv NO_2 in indoor air and exhibited very little drift. Battelle staff demonstrated that the NO_2 concentration produced by a natural gas oven and burners was measurable in real time and each of the four monitors taken into the field showed comparable results. In addition, the monitors showed similar calibration factors as those recorded by CARB staff during the previous evaluation, demonstrating the monitors' ability to maintain their calibration.

8.0 REFERENCES

Kelly, T.J, and Myers J.D., "Development of a Short-Averaging-Time Indoor Nitrogen Dioxide Monitor", Final Report to the California Air Resources Board, Contract No. 96-312, Battelle, Columbus, Ohio December 1999

APPENDIX A

OPERATING MANUAL FOR THE

BATTELLE/NO_2/HONO MONITOR

OPERATING MANUAL

FOR THE BATTELLE NO_2/HONO MONITOR

Last updated March 17, 2003

PLEASE READ ENTIRE MANUAL CAREFULLY BEFORE OPERATING THE MONITOR

Introduction

This document is the operator's manual for the instrument that Battelle has developed to continuously monitor nitrogen dioxide (NO_2) and nitrous acid (HONO). This document describes the purpose, design, and operation of the monitor, and includes instructions for starting up and shutting down the monitor, initiating data collection, transferring data to a personal computer, and converting data to Excel or Lotus spreadsheets.

The NO_2/HONO monitor was developed for the California Air Resources Board, under contract 99-327, for the purpose of conducting screening measurements of NO_2 levels in California homes. A one-hour average NO_2 standard of 250 ppbv exists in California to protect the health of residents. Previous indoor NO_2 measurements, typically averaged over periods of 48 to 168 hours, have suggested that one-hour average NO_2 levels are very likely to exceed that 250 ppbv standard in homes with unvented combustion appliances used for cooking or heating. The development of the NO_2/HONO monitor thus was motivated by the need for a rapid, portable, and inexpensive means of determining NO_2 in homes. Capability for HONO monitoring, while not the primary goal of the development effort, was included because of the greater toxicity of HONO relative to NO_2, and the known production of HONO from NO_2 indoors.

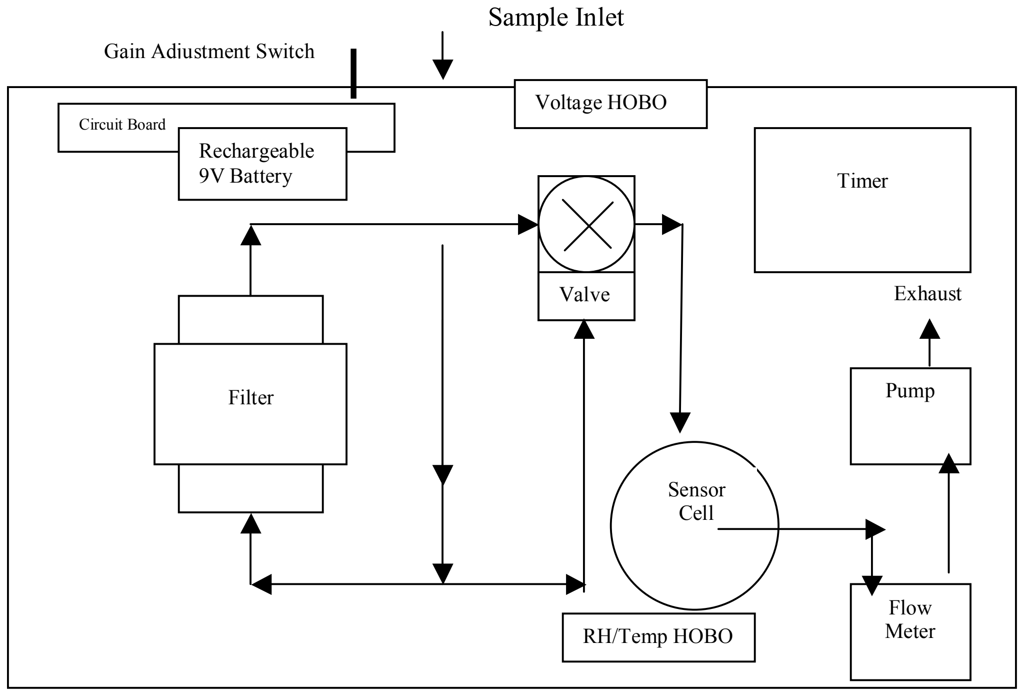
This Operator's Manual describes a second generation of the NO2/HONO monitor. The first generation was tested in the laboratory and in a research house. The second generation instrument was then developed to address shortcomings of the first instrument.

Detection Principle

The NO_2/HONO monitor is based upon a sensitive commercial electrochemical sensor (NO2-SNL, TSI, Inc., St. Paul, Minn.). The sensor includes a proprietary electrode design that produces very low background current, allowing detection of NO_2 at levels below 10 ppbv. In addition, the sensor responds to HONO with a sensitivity several times that to NO_2. As a result, HONO can readily be detected by difference in the presence of an excess of NO_2, using a chemically treated filter to selectively remove HONO from air containing NO_2. In practice, the monitor functions as an automatic two-channel analyzer, using a three-way valve to switch the sample air flow alternately around or through the treated filter. These two modes of operation thus measure (NO_2 + HONO) and NO_2, respectively. Accounting for the different sensitivities to NO_2 and HONO allows both species to be determined from the alternating operating modes. The sensor current is converted and amplified to a 0 – 2 V DC output, which is directed to rear panel analog terminals and recorded by an internal data logger. Only one of the two alternating measurement modes provides signal at any time, the other going to zero.

Instrument Schematic

The NO_2/HONO monitor consists of a single chassis about 8 in. by 12 in. by 10 in. The lower part of the chassis encloses the power supply, and the upper part encloses the monitor itself, consisting of the air pump, rotameter, valve, filter holder, sensor housing, valve timer and relay, and associated electronics and plumbing. The monitor requires 110 VAC power, however all electrical connections within the upper part of the chassis are of low voltage (12 V DC maximum) for safety. Sample air is drawn through a port on the rear panel of the instrument by an internal pump, and is expelled inside the chassis. Data acquisition is accomplished by two miniature dataloggers inside the instrument, connected to plug-in jacks for data startup and downloading on the back panel. Analog outputs for the two measurement modes are also mounted on the back panel. A schematic of the components in the upper chassis of the monitor is shown in Figure 1.



Schematic of monitor's top section.

Things Not to Do

Before describing the controls and displays, and presenting step-by-step procedures for start-up, operation, data acquisition, and shutdown, a few cautionary comments are in order:

1. Do not plug the air inlet on the back of the analyzer, with a finger or any other object; the sensor does not like being under vacuum.
2. Do not pressurize the air inlet, e.g., by connecting it to a pressurized gas supply; the sensor also doesn't like being under elevated pressure.
3. Do not operate the analyzer for long periods on excessively dry (< 15 % RH), wet (>85% RH) or hot (> 90 ^{o}F) air.

Front Panel Features

The following are the features on the front panel of the monitor, listed as they are labeled on the monitor:

12 V Power – this switch supplies DC power to the upper chassis components, such as the air pump, timer, valve, relay, and electronics. The light is lit when this switch is in the ON position. (See also **110V**, under Back Panel Features, below).

Pump – this switch turns the air pump on and off. The light is lit when this switch is in the ON position, and the sound of the pump may also be heard.

Timer Manual/Auto – this switch selects between Automatic operation, in which the monitor cycles regularly between the two measurement modes, and Manual operation, in which the monitor remains in one mode until advanced to the other mode by activation of the **NO2/NO2+HONO** switch (see below). In Automatic operation, the monitor switches between modes at intervals of about three minutes.

NO2/NO2+HONO – this switch only works when the Timer switch is in the manual position. This switch allows the operator to manually control the air flow path within the monitor, either going around or going through the carbonate filter. The light may be lit in either Automatic or Manual operation, indicating that the monitor is operating with the filter in-line.

Carbonate filter preparation;

Coat a Whatman 47mm glass fiber filter with a solution of 10 ML of 1% (w/v) Na_2CO_3/1% (v/v) glycerol in 1:1 methanol/water solution. After coating the filter, allow the filters to dry in an environment of clean, dry air.

Digital Display (ppb) – this display shows the approximate sample NO_2 level in ppbv. This display is based on the assumptions that the sensor response is due entirely to NO_2, with no HONO present, and that the monitor reads exactly zero when sampling clean air. This display is intended solely as a visual qualitative indicator of sampling conditions, and not as a quantitative readout.

Flow Rate – this front panel rotameter will show the air flow when the pump is operating (the rotameter ball should be at about 0.8 to 1.0 L/min.)

Back Panel Features

The following are the features on the back panel of the NO_2/HONO monitor, listed as they are labeled on the monitor:

110V – this switch controls the supply of 110 VAC power to the monitor. Whenever this switch is ON, the battery and circuit that provide the 100 mV bias voltage to the electrochemical sensor are continuously recharged. When this switch is off, the battery will maintain bias voltage on the sensor, thereby assuring sensor stability. However, after 8 hours the battery will discharge, and a sensor re-stabilization period will be needed when power is restored and the rechargeable battery may need to be replaced.

Sample Inlet – this port is the intake for sample air. Do not obstruct or pressurize!

NO2/NO2+HONO – these two sets of analog terminals carry the 0 to 2 V analog signal from the monitor. Only one set of terminals will have a positive analog signal at any time, the other being zero. In Automatic operation the analog output will switch from one set of terminals to the other approximately every three minutes. The Filter Out mode provides measurement of (NO_2 + HONO), and the Filter In mode provides measurement of NO_2 only.

Voltage and Temp/Humidity – these two female stereo jacks are each connected to a HOBO® datalogger located inside the monitor, which collect temperature/relative humidity data, and sensor output voltages, respectively. These jacks are used for launching the dataloggers and for downloading the collected data, using the HOBO Shuttle (see section entitled Data Acquisition for instructions regarding these components).

Bias – this analog terminal allows the operator to measure the bias voltage on the sensor. This value should be -100 mV for proper operation.

Zero Adj – this hole in the rear panel allows access to the zero potentiometer on the electronic printed circuit board (PCB). A miniature screwdriver can be inserted through the hole to adjust the sensor's output to near zero when sampling clean air.

Bias Adj – this hole in the rear panel allows access to the bias potentiometer on electronic PCB. A miniature screwdriver can be inserted through the hole to adjust the sensor's bias to -100mV before sampling.

Front Panel Adj – this hole in the rear panel allows access to the front panel potentiometer on the electronic PCB. During calibration, a miniature screwdriver can be inserted through the hole to adjust the front panel display to approximate the ppbv concentration of NO_2.

Internal Features

The following features can be located within the instrument. Figure 1 shows a schematic of the monitor and displays the internal features that require periodic attention.
Gain Adjustment Switch – this switch, located on the PCB, allows the operator to adjust the output gain by a factor of 3. In the 'up' or 10M position the instrument output voltage is approximately 3 that when the switch is in the 'down' or 3.3M position. The best position of this switch, during monitor use, depends upon the expected concentration of NO_2 and the age (i.e., sensitivity) of the sensor cell.

Filter – this carbonate-coated filter removes the HONO from the sampled air before reaching the sensor cell.

Timer – the timer allows the operator to control the length of time (in seconds) that the monitor spends in each measurement mode before switching to the other mode.

Rechargeable Battery – this battery keeps a bias voltage on the sensor cell, eliminating the need for the 24 hr warm up period. It is recommended that the battery remain uncharged for no longer than 8 hrs. The battery is charged as long as the monitor is plugged into an 110V source and the 110V switch on the rear panel is 'on'.

Temp/Humidity HOBO – this item records the temperature and relative humidity data. The lithium battery requires periodic replacement. The battery life can be monitored using the HOBO software.

Voltage HOBO – this item records the output of the NO_2/HONO monitor. The lithium battery requires periodic replacement. The battery life can be monitored using the HOBO software.

Instrument Start-Up

1. Plug in the AC power cord. If the front panel Digital Display shows nothing, turn on the 110 V main power switch on the rear panel, and allow the instrument to stabilize overnight before proceeding to step 2. If the front panel display is active, turn on the 110 V main power switch and proceed to step 2.

2. Switch on the front panel 12 V Power switch.

3. Check that the Sample Inlet on the rear panel is unobstructed. If the port is open, switch on the Pump switch on the front panel. Check that proper air flow (0.8 to 1.0 L/min) is indicated on the front panel rotameter.

4. Check that the monitor is in Automatic operation, and allow the monitor to sample clean air, either by providing purified air to the inlet (with overflow venting through a "tee" fitting to avoid pressurization), or by connecting a charcoal trap to the Air Inlet.

5. After sampling clean air for at least 20 minutes, adjust the Zero Adj. potentiometer on the back panel of the analyzer until the front panel display reads approximately 10 to 20 ppbv.

6. Remove the source of clean air, and commence sampling of the room air. Initiate data collection using the procedures outlined below under Data Acquisition.

Data Acquisition

Data acquisition can be accomplished with an external chart recorder, voltmeter, or computer-based data acquisition system, using the analog outputs at the back of the monitor labeled ‘Filter In’ and ‘Filter Out’, (corresponding to measurement modes for NO_2, and (NO_2+HONO) respectively). However, for its intended use as a portable screening tool the monitor has been equipped to acquire and store its own data using two internal HOBO dataloggers. One of those loggers records the temperature and relative humidity of the sampled room air, and the other records the sensor output voltage in the two measurement modes. The complete set of materials needed to perform data collection with the HOBO loggers includes the HOBOs themselves, the handheld HOBO Shuttle® data transfer device, and the Boxcar® computer software to start data collection and transfer data files after collection. The two HOBOs are located inside the monitor, and the Shuttle and software are provided with the monitor.

When the HOBOs have been set up to collect data once per minute, they have a capacity of about 11 days of data collection at that rate with two channels of data collected. Each HOBO is powered by its own battery, and has its own internal clock. Whenever the Shuttle is used to start data acquisition or download data, the HOBO’s clock is reset to match the clock in the PC running the Boxcar software. Instructions and illustrations provided by the manufacturer of the HOBO dataloggers accompany this document, and should be consulted for the details of use of the HOBOs. The following is a general stepwise procedure:

1. With the Boxcar software running on the PC, connect the Shuttle to the PC using the stereo cable provided. Select “Download Shuttle” from the main menu, and download any data files from the shuttle. This resets the Shuttle clock to match the PC clock. If no Shuttle is available skip to step 4.

2. Disconnect the Shuttle from the PC, connect it to the Voltage jack on the rear of the monitor, and press the button on the end of the Shuttle. Data from the HOBO will be downloaded and the HOBO clock reset. While downloading, the orange “relaunching” light indicates that the HOBO is working properly. When finished, the orange “relaunching” light will flash briefly and then the green “successful” light flashes. Finally push the button on the end of the shuttle to turn off the green “successful” light and complete the operation. Then plug the stereo cable into the Temp/Humidity jack and press the button to download the Temp/Humidity data.

3. To transfer the collected data from the Shuttle to the PC, connect the Shuttle to the PC using the stereo jack/serial cable provided, choose “Logger” from the menu, and then “HOBO Shuttle Readout” from the dropdown menu that appears. This selection will initiate the transfer from the Shuttle to the PC. When the transfer is complete, the program will prompt the user to input the file name under which the information will be stored. Files are stored in ASCII format for later introduction into Excel or Lotus Spreadsheets.

4. To transfer the collected data from the HOBO to the PC, connect the HOBO to the PC using the stereo jack/serial cable provided, choose “Logger” from the menu, and then “HOBO Offload” from the dropdown menu that appears. This selection will initiate the transfer from the HOBO to the PC. When the transfer is complete, the program will prompt the user to input the file name under which the information will be stored. Files are stored in ASCII format for later introduction into Excel or Lotus Spreadsheets.

Data Analysis

The software used to enhance the data analysis procedure is a self installing executable. This java based software will allow the user to select the raw data files to be analyzed,and then prompt the user to input calibration factors. Finally it calculates the final concentrations of NO2 and HONO in ppb and saves the data. Before using the software the user should know the name of the output file that will be created, the name and location of the temperature and RH HOBO data, and the name and location of the concentration HOBO data. The following steps are to be followed when using the software:

1. Enter the filename that the data will be saved to, and specify the monitor that is being used.

2. Select the method for entering the calibration factor for NO2, choices are: compute manually, manually input (assuming user has computed factors previously), and use previous calibration factors (from earlier data processing efforts).

3. Select the method for entering the calibration factor for HONO, choices are: compute manually, manually input (assuming user has computed factors previously), and use previous calibration factors (from earlier data processing efforts).

4. Select the file that contains the raw data for valve position, NO2 and NO2+HONO. Data from the HOBO must have previously been downloaded by the user.

5. Select the file that contains the raw data for temperature and RH. Data from the HOBO must have previously been downloaded by the user.

6. The raw data is then displayed.

7. User is prompted for Temperature and RH corrections to be applied to NO2 then to HONO, choices are: use calibration factor from date, use average calibration factors from two dates (selected if user wants to use an average from a pre- and post-test calibration), and weighted average between two dates (selected if user

wants to allow the software to linearly interpolate between two sets of calibration data)

8. Final window displays raw data and final data. Across the top, tabs exist for viewing the calibration factors applied and the input and output filenames. Selecting the "finish" button here stores the data to the location previously selected. These data are then available to be used in any data graphing software such as Microsoft Excel.

APPENDIX B

ARB Laboratory Evaluation of the Battelle Indoor NO_2 Monitor

ARB Laboratory Evaluation of the Battelle Indoor NO_2 Monitor

February 2003

Summary

This document describes procedures staff of the California Air Resources Board (ARB) used to evaluate the performance of an indoor nitrogen dioxide (NO_2) monitor in a laboratory setting under controlled environmental conditions (constant temperature, controlled relative humidity, and limited interference from gases other than NO_2). The indoor NO_2 monitor has been recently developed by Battelle under contract to the ARB. Limited testing of the indoor NO_2 monitor in field situations has been previously undertaken by Battelle. The purpose of the current procedures was for an independent party (i.e., ARB) to verify the performance characteristics of the indoor NO_2 monitors in a laboratory setting. This evaluation confirms the performance characteristics of the indoor NO_2 monitors while also identifying areas in need of further development in the future.

The procedures for the laboratory evaluation were designed to determine overall monitor performance as well as ease of use in the field. The results provide information on the reproducibility, accuracy, bias, precision, linearity, ease of use, sensitivity, and drift of the sensors in the indoor NO_2 monitors. The procedures were carried out by staff of the Research Division (RD) at ARB with staff of the Monitoring and Laboratory Division (MLD) providing lab space for the calibration of the monitors, equipment and supplies such as a reference NO_x monitor, reference ozone monitor, and calibration gas, and technical advise.

The testing was conducted in several discreet periods in the following order:

- Initial calibration of Units A and B
- Initial calibration of Units C and D
- Evaluation of the effects of varying RH on Units C and D
- Evaluation of the effects of varying RH on Units A and B
- Performance evaluation one
- Performance evaluation two
- Performance evaluation three
- Final calibration of all four indoor NO_2 monitors.

For practical reasons, an extensive investigation into the effect of varying temperatures on the output of the sensors in the indoor NO_2 monitors was beyond the scope of these procedures. All tests were conducted at fixed temperature, consistent with conditions during the calibration of the indoor NO_2 monitors. However, the effect of varying the relative

humidity (RH) in the calibration gas supplied to the indoor NO_2 monitors was evaluated, though corrections for changes in relative humidity were unnecessary as all of the performance evaluations were conducted with a constant nominal RH of 40% in the calibration gas. The total flow of calibration gas commanded from the calibrator was 4.250 liters per minute for all tests.

The objectives of the field evaluation of the indoor NO_2 monitors were as follows:

1. To evaluate the performance of a newly purchased modified Environics 6100 calibrator.
2. To calibrate the indoor NO_2 monitors to known concentrations of NO_2.
3. To evaluate the laboratory performance of the indoor NO_2 monitors in comparison to measurements from a standard reference method for NO_2 concentration in ambient air.

Completion of the first objective confirmed that the Environics 6100 calibrator was working correctly and allowed evaluation of the accuracy and precision of the dilution concentrations. The performance of the calibrator was acceptable for use during this evaluation, exhibiting good accuracy and precision. The NO_2 concentrations delivered by the modified Environics 6100 calibrator as measured by the reference NO_x monitor were about 96% of the set point on average, while the precision of the concentration delivered by the calibrator was about 4%.

Completion of the second objective facilitated the development of calibration functions for each indoor NO_2 monitor at specified temperature and RH. The final calibrations of the indoor NO_2 monitors showed a slight decrease in sensitivity to NO_2 over the five days over which the testing was conducted versus the initial calibration, but the calibration functions were generally similar for each monitor. Also, for all three indoor NO_2 monitors except Unit C, the response during calibration was highly linear and thus linear models were considered appropriate for use as calibration functions. The response from Unit C deviated from the linear model, so a polynomial function was used and also provided a good model fit.

Completion of the third objective facilitated evaluation of the reproducibility, accuracy, precision, bias, linearity, ease of use, sensitivity, and drift of the indoor NO_2 monitors. The reproducibility of the indoor NO_2 monitors was generally very good, with absolute differences generally less than 10 ppbv NO_2, though the reproducibility of the response of the indoor NO_2 monitors was shown to be higher (i.e., better) at concentrations above 50 ppbv NO_2. The accuracy of each indoor NO_2 monitor was generally good, measuring on average between 80.2% and 91.8% of the concentration measured by the reference NO_x monitor. However, all accuracy estimates (mean ratio) for the indoor NO_2 monitors were lower than 100%, indicating a slight negative bias in the response of the indoor NO_2 monitors. The precision of the indoor NO_2 monitors was high, with within and between instrument differences representing less than 6% of the measured concentrations on average. The response of each indoor NO_2 monitor was highly linear across the range from zero to

699 ppbv NO_2, with values for the coefficient of determination (R^2) greater than 0.99 for each monitor.

In general, the indoor NO_2 monitors were easy to operate during the testing. The most cumbersome aspect of using the monitors was the data reduction process. As part of this process, calibration functions were developed and adjusted for changes in calibration over the testing period. Corrections for temperature and relative humidity were not applied during these procedures, but would add an additional level of complexity to the data reduction process. A software package that would convert the output from the data loggers into concentration values would be a valuable tool in saving time and effort during data reduction. The sensitivity of the indoor NO_2 monitors was found to be very high, with a level of 15 ppbv NO_2 being clearly detectable. The lowest detectable concentration is specific to each monitor and its age, though, as the characteristics of the sensors in the indoor NO_2 monitors change over their lifetime. The indoor NO_2 monitors also exhibited very little drift over the testing period, staying within 1 ppbv NO_2 of the initial value on average when supplied with zero air.

In summary, the performance of the indoor NO_2 monitors was high; the response from the monitors was reproducible, precise, and linear, with only a small bias. The indoor NO_2 monitors were easy to use, showed high sensitivity (i.e., 15 ppbv NO_2 was easily detectable), and very little drift of the zero point. Additional evaluations of monitor performance are warranted to further characterize monitor performance under the more realistic and less controlled conditions present during field use.

Testing apparatus

Gas dilution systems	Modified Environics 6100 with humidification capabilities; ARB MLD certified Environics 9100
Balance gas	Advanced Pollution Instrumentation (API) 701H zero air generator
Nitric oxide (NO)/NO_2 (NO_x) reference instrument	Thermo Environmental Company (TECO) Model 42 Oxides of Nitrogen analyzer with potassium carbonate-coated filter on inlet
Gas standard for NO_2	15 ppm NO +/- 1% in balance nitrogen; titration of NO with ozone
Ozone reference analyzer	API 400 AMX Federal Equivalent Method Ozone Analyzer
Data recording	Environmental Systems Corporation (ESC) 8816 data logger and MLD standard Yokogawa strip chart recorder

Relative humidity and temperature measurements	TSI, Inc. Model 8554 Q-Trak Indoor Air Quality monitoring and data logging instrument
Electronic interface	Personal computer with Boxcar software and Microsoft Excel

Acceptance testing of the modified calibrator and calibration of the indoor NO_2 monitors

Test procedure

This task involved both evaluating the performance of a newly purchased modified Environics 6100 calibrator and calibrating the indoor NO_2 monitors relative to known concentrations of NO2. The calibrator delivered a series of concentrations of NO_2 to the indoor NO_2 monitors and to a reference NO_x monitor to determine indoor NO_2 monitor-specific response factors. The accuracy and precision of the dilution concentrations as well as programmed RH levels was evaluated by comparison of the calibrator settings to measurements made by a reference NO_x monitor and a reference RH measurement device, respectively. Prior to beginning this task, the reference NO_x monitor was calibrated by a certified Environics 9100 calibrator using standard MLD procedures. In summary, the linearity of the response of the indoor NO_2 monitors was evaluated by comparing the response of the sensors to measurements made by a reference NO_x monitor, and calibration functions were developed from these data at fixed temperature and RH for each of the four indoor NO_2 monitors to allow for conversion of the output of the sensor in millivolts (mV) to concentration units in parts per billion by volume (ppbv or ppb) NO_2.

The calibrator had previously undergone an acceptance test according to MLD procedures to the fullest extent possible, within the time constraints of the project. Results from this testing showed a dependence of the accuracy of the ozone generated on the total flow delivered by the calibrator. Thus, a total flow from the calibrator that minimized the error in the ozone concentration generated was used for all tests during the current evaluation; this total flow was found to be 4.250 liters per minute. The calibrator was plumbed to a standard MLD nine port sampling manifold connected to a reference NO_x monitor and, during the initial calibration periods, a reference O_3 monitor. As the focus of this performance evaluation was on NO_2 rather than nitrous acid (HONO), a potassium carbonate-coated filter was placed in the sampling stream of the reference NO_x analyzer, just before the inlet filter. The reference NOx and ozone monitors were connected to a ESC 8816 data logger to record data from these instruments.

The four indoor NO_2 monitors were also acceptance tested prior to beginning the performance evaluation, but did not undergo standard MLD acceptance test procedures due to the unique nature of their operation and their prototype stage in development. However, the indoor NO_2 monitors had received new sensors and had been calibrated at Battelle immediately prior to this evaluation. Thus the sensors were slightly less than one month old at the beginning of these tests. The manufacturer's instructions were carefully reviewed prior to operating the indoor NO_2 monitors, and the directions for use were followed prior to each period of use. These directions involved evaluating the flow though each indoor NO_2 monitor (set to 800 ml/min for all indoor NO_2 monitors for these tests) and evaluating the bias voltage and zero voltage of the sensors in the indoor NO_2 monitors. Bias voltages were set to within +/- 1 mV of the nominal set point of –100 mV, whereas acceptable zero point voltages were zero +/- two mV.

Upon confirmation that the indoor NO_2 monitors were working correctly, the sample inlets were plumbed to the sampling manifold connected to the reference NO_x and ozone monitors, as described above. The RH of the air in the sampling manifold was also measured by an RH probe inserted into an enclosure that was connected to the sampling manifold and pressurized by the output of the modified Environics 6100 calibrator.

The modified calibrator was then programmed to deliver five concentrations of NO_2 to the sampling manifold as the calibration sequence for the indoor NO_2 monitors. Because the modified calibrator uses gas-phase titration of NO with ozone to generate NO_2, the highest ozone concentration that the calibrator can deliver determines the highest concentration of NO_2 that the calibrator can deliver. The calibrator was calibrated by Environics to deliver at most 500 ppbv of ozone, and therefore cannot be programmed to deliver more than a set point of 699 ppbv, because the calibrator has not been calibrated in this range of ozone concentrations. It is possible to calibrate the calibrator at ozone concentrations up to 1000 ppbv (one part per million by volume) to achieve higher concentrations of NO_2, though the accuracy of the ozone delivered at concentrations lower than 500 ppbv may be slightly as a result. During calibration of the indoor NO_2 monitors, concentrations of NO_2 were presented for periods of approximately equal duration. These periods were usually about 25 minutes, though some were up to two hours in length.

The standard procedure used by the ARB MLD for calibrating the reference NO_x monitor was adopted for use in these procedures. This procedure involves delivering a gas from the calibrator for a period of 18 minutes, while using the average of the readings during the last five minutes of that period. All of the NO_2 concentration data points presented in these results represent the mean of five one-minute average measurements, except those used as part of the evaluation of interfering gases, where the one-minute averages themselves were used.

The NO_2 concentrations for calibration were 0, 699, 400, 200, and 50 ppbv. The calibrator was programmed to present about 40% RH in the calibration gas. The RH of the calibration gas is designated by turning two valves, referred to as V1 and V2, on the top of the modified Environics 6100 calibrator. One of these valves, V1, allows the calibration gas to flow through the humidifier while the other valve, V2, allows the calibration gas to bypass the humidifier. Both valves can be set from zero (closed) to 15 (fully open). To achieve the setting of about 40% RH, V1 and V2 were both open fully to 15. The position of V1 was found to affect the accuracy of the ozone delivery of the calibrator; thus V1 should remain in the full open position during future use of the modified Environics 6100 calibrator. If no humidity is desired in the calibration gas, a bypass line supplied by Environics can be attached. However, V1 should remain in the full open position at 15 even when this bypass line is attached or the accuracy of the ozone delivery may suffer. In practice, this limits the humidification delivery of the modified Environics 6100 calibrator to a range of about 40% to about 65% (see Table 4). Though humidity levels below this range can be achieved by closing V1, the effect of constricting flow through this valve on the accuracy of the ozone and therefore NO_2 concentrations delivered must be evaluated. It is recommended that during field use, a level of 40% RH is specified during calibration, such that both V1 and V2 remain in the full open positions.

In addition, the ability of the modified Environics calibrator to deliver humidified air was assessed by measuring the precision of the humidity of the air supplied by the calibrator. The calibrator was set to deliver zero and 400 ppbv NO_2 at varying RH while the actual RH value was measured by the humidity probe. The reference O_3 monitor was operated throughout the initial calibration period to evaluate the level of residual O_3 in the calibration gas, which was found to be near zero whenever excess NO was present.

Results

Accuracy of the NO_2 dilution concentrations delivered by the calibrator

Results from the above procedure were used to evaluate the ability of the modified Environics calibrator to deliver specified concentrations of NO_2. For this analysis, measurement error in the reference NO_x monitor measurements is assumed to be negligible. For each concentration level, relative accuracy was calculated by taking the ratio of the programmed concentration level and the reference NO_x monitor measurement, both in ppbv units. The ratios are therefore unitless and the nominal value of each is unity. Data from the initial and final calibration of the indoor NO_2 monitors at constant RH (about 40%) were used for this analysis, and data for which the programmed concentration was zero were omitted. Ratios are presented as the percent (%) accuracy by multiplying by 100%, as:

$$\%\ \text{Accuracy}_k = \left(\frac{Y_k}{X_k} \right) \times 100\%$$

where Y_k is the value of the programmed concentration level in ppbv, X_k is the reference NO_x monitor measurement in ppbv, and k is the concentration level. The mean of the individual percent accuracy estimates was then calculated to estimate the overall relative accuracy of the dilution concentrations delivered by the calibrator. The results are presented in Table 1.

Table 1. Accuracy of the NO_2 dilution concentrations delivered by the modified Environics 6100 calibrator.

NO_2 set point (ppb)	TECO 42 NO_2 (ppb)	Ratio (% Accuracy)
699	679.7	97.2%
400	389.2	97.3%
200	192.0	96.0%
50	47.8	95.5%
699	669.2	95.7%
400	388.1	97.0%
200	194.2	97.1%
50	47.3	94.5%
699	679.2	97.2%
699	652.9	93.4%
400	379.1	94.8%
200	192.0	96.0%
50	47.5	95.1%
	Mean-	95.9%
	Standard deviation-	1.2%

In general, the modified Environics calibrator delivered concentrations of NO_2 that were very near the set point value, as measured by the reference NO_x monitor. Again, the reference NO_x monitor was calibrated using standard MLD procedures with an MLD certified Environics 9100 calibrator immediately prior to these tests. The accuracy of the modified Environics 6100 calibrator was shown to be less (i.e., worse) at higher concentrations of NO_2, but was generally acceptable throughout the range of NO_2 concentrations.

Precision of the NO_2 dilution concentrations delivered by the calibrator

Results from this task were used to estimate the precision of the NO_2 concentrations delivered by the calibrator by evaluating the variance in the differences between pairs of measured and programmed concentrations from the reference NO_x monitor and the calibrator, respectively. For this analysis, measurement error in the reference NO_x monitor measurements is assumed to be negligible. Data from the initial and final calibration of the indoor NO_2 monitors were used for this analysis. The precision of the concentrations delivered by the calibrator was estimated as:

$$P_C = \frac{\sqrt{\dfrac{\sum_{k=1}^{1\rightarrow k} d_k{}^2}{n-1}}}{\sqrt{2}}$$

where d_k is the difference between the measured NO_2 concentration from the reference NOx monitor and the programmed NO_2 concentration from the calibrator at concentration level

k while n is the number of measurement pairs ($n = 22$ in this case). The precision estimate is also expressed as relative precision in percent by dividing by the mean of the programmed concentrations and multiplying by 100%. The results are presented in Table 2.

Table 2. Precision of the NO_2 dilution concentrations delivered by the modified Environics 6100 calibrator.

NO_2 set point (ppb)	TECO 42 NO_2 (ppb)	Difference (ppb)
0	-1.5	-1.5
699	679.7	-19.3
0	-0.7	-0.7
400	389.2	-10.8
200	192.0	-8.0
50	47.8	-2.2
0	-0.7	-0.7
0	0.0	0.0
699	669.2	-29.8
0	0.1	0.1
400	388.1	-11.9
200	194.2	-5.8
50	47.3	-2.7
0	0.1	0.1
699	679.2	-19.8
0	0.1	0.1
699	652.9	-46.1
0	0.1	0.1
400	379.1	-20.9
200	192.0	-8.0
50	47.5	-2.5
0	0.1	0.1
	Mean (ppb)-	-8.7
	Standard deviation (ppb)-	12.0
	Precision (P_C, ppb)-	8.5
	Precision (P_C, %)-	3.9

The precision of the NO_2 concentrations delivered was also very high (3.9%), as evidenced by Table 2, as well as the low standard deviation (1.2%) of the percent accuracy estimates in Table 1. Both show that the modified calibrator is able to produce repeatable levels of NO_2, though the differences in Table 2 are inflated by the slight low systematic bias of the calibrator. Eliminating or reducing this bias by recalibrating the ozone generator or increasing the total flow delivered by the modified Environics 6100 calibrator should reduce these differences and therefore increase the precision as measured by this approach.

Precision of the RH levels delivered by the calibrator

Results from this task were used to estimate the precision of the RH levels delivered by the calibrator by evaluating the variance in the differences between the measured values from the RH probe and the mean of these measured values at each RH level. The modified Environics calibrator allows varying levels of RH to be specified by adjusting the position of two valves, as discussed above. It is possible to record the position of the valves and record the RH with a measurement device, but there is no specified RH value with which this measurement can be compared. As such, the user does not specify a specific RH level, and therefore assessing the accuracy of the RH delivered by the calibrator is not meaningful. For this analysis of precision, measurement error in the reference RH probe measurements is assumed to be negligible. The precision of the RH levels delivered by the calibrator was estimated as:

$$P_{RH} = \frac{\sqrt{\frac{\sum_{k=1}^{1\to k} d_k^{\,2}}{n-1}}}{\sqrt{2}}$$

where d_k is the difference between the measured RH from the reference RH probe and the mean of the measured RH at each setting k while n is the number of measurement pairs (n = 3,783 in this case). The results are summarized in Table 3, as many (3,783) data points were used in this analysis.

Table 3. Precision of the RH levels delivered by the 6100 calibrator

Precision (P_{RH}, % RH)-	0.7
Number of differences evaluated-	3783

The precision of the RH levels is very high (0.7%) indicating very stable delivery of the humidified calibration gas by the modified Environics 6100 calibrator during these procedures. The measured value of the RH of the calibration gas ranged from 24% to 68% RH during this analysis. The V1 and V2 settings that led to these RH levels are presented in Table 4.

Table 4. V1 and V2 settings and measured RH

V1	V2	RH by Q Trak (%)
7.5	15.0	25
15.0	15.0	39
15.0	7.50	53
15.0	0.0	65

Linearity

Data analysis for this task included application of ordinary least squares (OLS) linear regression to assess the linearity of the response of the indoor NO_2 monitors during calibration. The R^2 from OLS was used as an indicator of the linearity of the response. Slope and intercept parameter estimates from the OLS model were also used to generate calibration functions for the indoor NO_2 monitors. In addition, second-order polynomial models were explored to improve the fit of the calibration functions, again using the R^2 as an indicator of goodness-of-fit, when linear models deviated substantially from the observed measurements upon visual inspection. These polynomial models may be more appropriate than linear models due to the finite number of receptor sites on the surface of the electrochemical sensor, or for other reasons. Polynomial models were used only for Unit C, as the response of the sensor in Unit C deviated from a linear relationship at the higher NO_2 concentrations. Results from these data analyses were used to convert the sensor output from mV to concentration units (ppbv) of NO_2. The initial calibration data are shown in Figures 1 and 2, and the calibration factors corrected per day are shown in Table 5.

Figure 1. Initial calibration of Units A and B

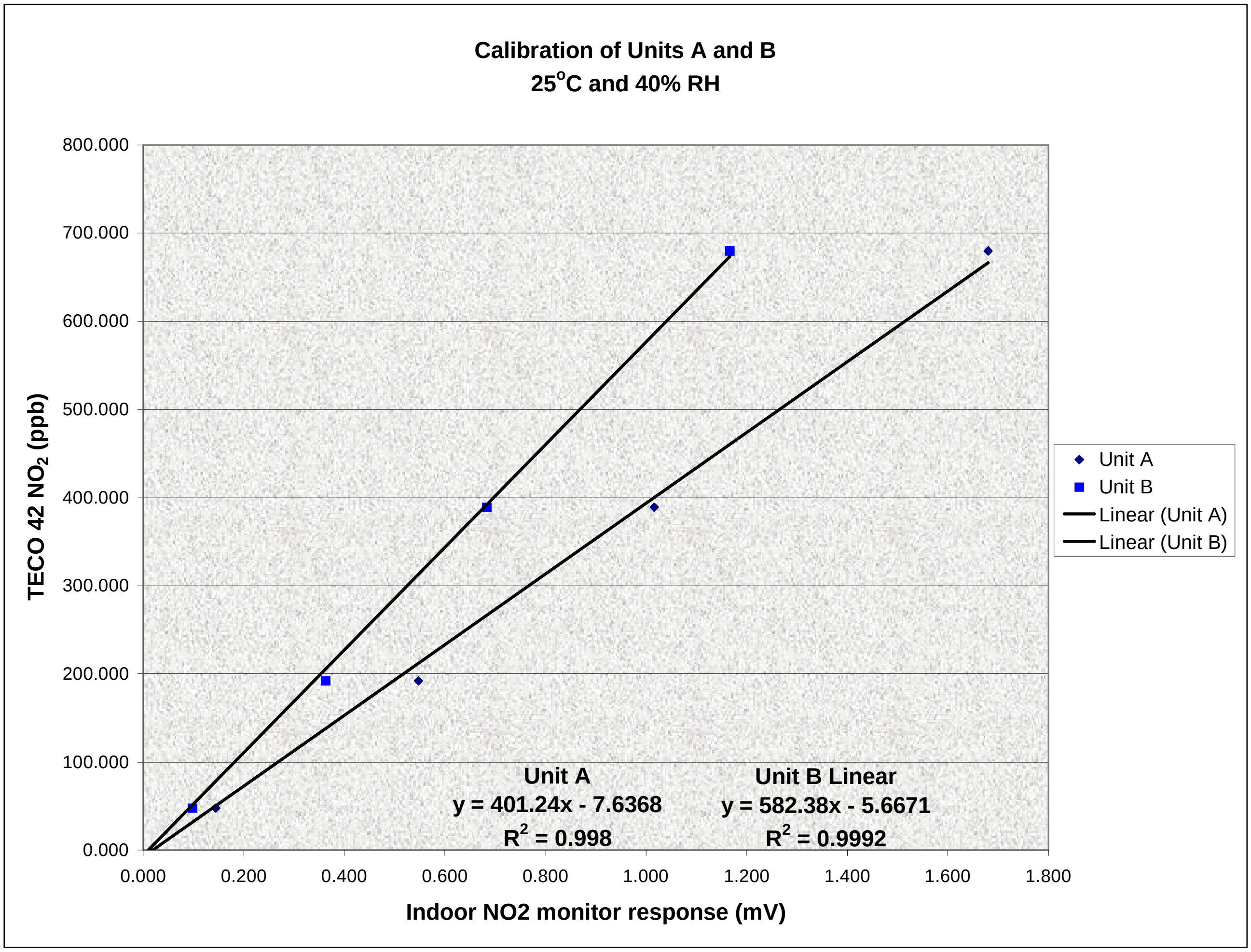


Figure 2. Initial calibration of Units C and D

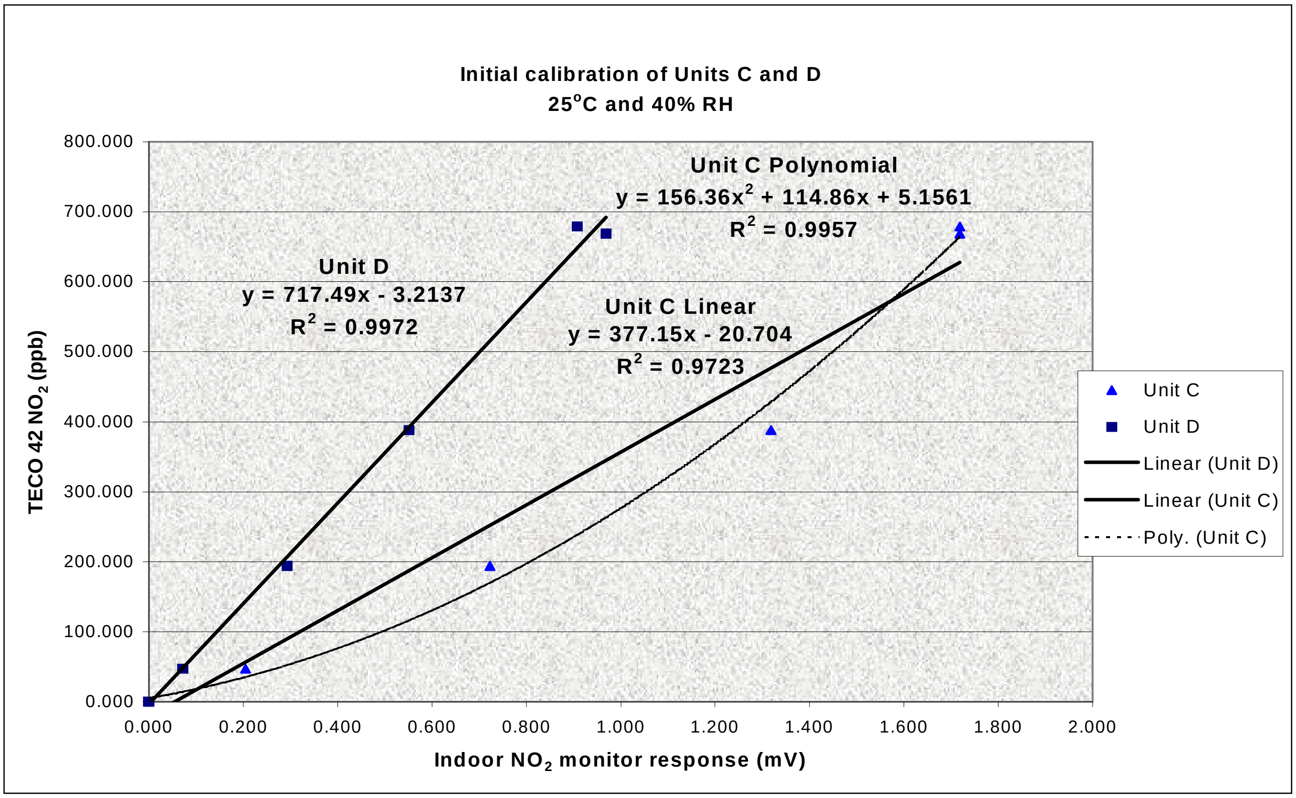


Figure 3. Final calibration of all four indoor NO_2 monitors

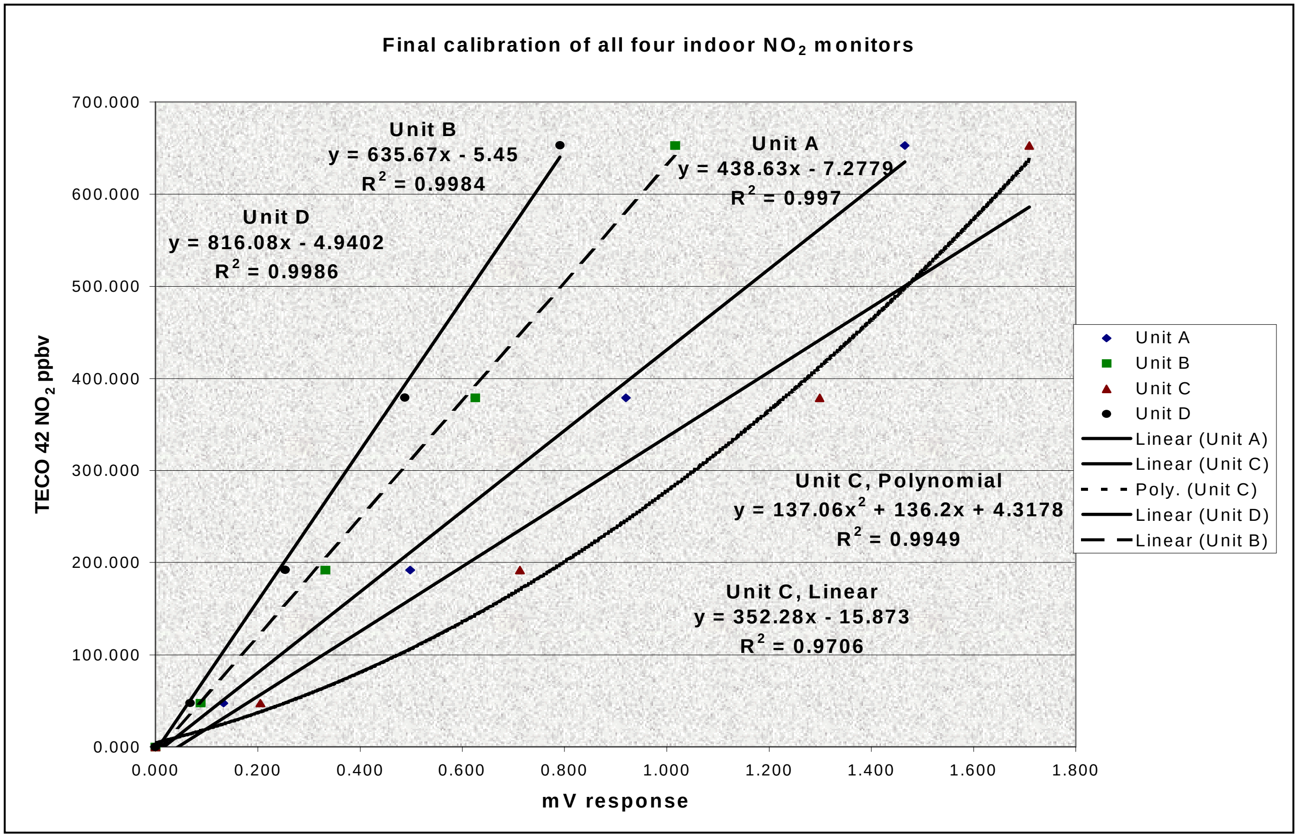


Table 5. Calibration factors used to convert mV signals from the indoor NO_2 monitors to ppbv NO_2

Date	Unit A		Unit B		Unit C (linear)*		Unit D		Unit C (polynomial)		
	Intercept	Slope	Intercept	Slope	Intercept	Slope	Intercept	Slope	Intercept	1st order	2nd order
01/13/03	-7.6	401.2	-5.7	582.4	-20.7	377.2	-3.2	717.5	5.2	114.9	156.4
01/14/03	-7.5	410.2	-5.6	595.3	-19.5	370.9	-3.6	741.7	4.9	120.2	151.5
01/15/03	-7.5	419.5	-5.6	608.6	-18.3	364.7	-4.1	766.3	4.7	125.5	146.7
01/16/03	-7.4	428.9	-5.5	621.9	-17.1	358.5	-4.5	791.0	4.5	130.9	141.9
01/17/03	-7.3	438.6	-5.5	635.7	-15.9	352.3	-4.9	816.1	4.3	136.2	137.1

*The polynomial model shown in the far right column was used instead of the linear model for Unit C.

Slopes shown are in units of ppbv NO_2/mV; intercepts are in units of ppbv NO_2.

Figures 1, 2, and 3 show the highly linear response of the indoor NO_2 monitors, except for Unit C, as well as the similarity in the calibration functions before and after testing. For all calibration functions that were used (linear models for Unit C were not used), the intercepts were less than +/- 10 ppbv NO_2 from the nominal value of zero. Therefore, intercepts were included in the calibration functions to maximize the accuracy of the predicted NO_2 concentrations at all concentration levels. However, an alternative approach would be to eliminate the intercept, and therefore 'force' the intercept through the origin. These methods may be explored in the future, and should be an option in a data reduction software package, but were not employed here as intercepts within +/- 10 ppbv NO_2 were considered acceptable.

The response from Unit C was observed to flatten at 1,714 mV and therefore a linear model did not fit the highest concentration well. Provided that it is determined that this maximization of the sensor output is indicative of a malfunction within the unit, repair of this problem should result in a linear model being appropriate for use for this monitor. Unit C also had the highest sensitivity to NO_2, and as the sensor ages and its sensitivity is decreased, the response at higher concentrations may become more linear. All calibration functions used (again, linear models were not used for Unit C) were judged to have good model fit because all R^2 values were greater than 0.99.

Determination of the reproducibility, accuracy, bias, precision, linearity, ease of use, sensitivity, and drift of the indoor NO_2 monitors

Test procedure

The objective of this task was to evaluate the reproducibility, accuracy, bias, precision, linearity, ease of use, sensitivity, and drift of the indoor NO_2 monitors compared to a calibrated reference NO_x monitor. The modified Environics 6100 calibrator was programmed to present both the indoor NO_2 monitors and the calibrated reference NO_x monitor with the concentrations shown in Table 6 during each of three evaluation periods.

Table 6. Concentrations presented during the performance evaluation

Calibration gas	NO_2 concentration	Duration
Zero air	100%	18 minutes
NO in air	889 ppbv	24 minutes
NO_2 in air	699 ppbv	24 minutes
NO_2 in air	400 ppbv	24 minutes
NO_2 in air	200 ppbv	24 minutes
NO_2 in air	50 ppbv	24 minutes
NO_2 in air	15 ppbv	24 minutes

The first evaluation period began at 4:20 PM January 15, 2003 and had an elapsed time of four hours 33 minutes, the second evaluation period began at 9:24 AM January 16, 2003 and had an elapsed time of four hours 26 minutes, and the third evaluation period began at 5:15 PM on January 16, 2003 and had an elapsed time of 16 hours 49 minutes, due to having zero air delivered overnight. The temperature of the sampling environment as well as of the calibration gas remained as constant as possible throughout these tests (including the calibration of the indoor NO_2 monitors). Throughout the three evaluation periods, the calibrator was set to deliver calibration gas at about 40% RH (V1 set to 15 and V2 set to 15). The NO_2 concentrations listed in Table 6 were obtained using the gas-phase titration feature of the modified Environics 6100 calibrator. At each concentration level, the ozone concentration was programmed to the desired NO_2 concentration, and an excess of approximately 100 ppbv of NO was maintained at each concentration level to minimize residual ozone in the calibration gas. Note that the test sequence above includes interference testing for NO in the second step. Other gases were not tested for interference with the response of the sensors in the indoor NO_2 monitors as part of these procedures.

Results

For these analyses, losses in sensitivity of the sensors in the indoor NO_2 monitors are assumed to be negligible within one day of testing, and the calibration factors were adjusted each day for the change between initial and final calibration. Therefore, these data are expected to be representative of the inherent measurement error in the indoor NO_2 monitors. The validity of this assumption was evaluated with respect to the drift in the response of the sensors across the testing period, as described below.

Reproducibility

Results from this task were used to evaluate the reproducibility of the response of the individual indoor NO_2 monitors by comparing the daily mean levels at each concentration from each indoor NO_2 monitor across the three evaluation periods. Reproducibility as used here is analogous to the drift in the indoor NO_2 monitors response at a non-zero NO_2 concentration. The percent difference in the largest and smallest mean levels across the three evaluation periods was used to determine the reproducibility of the individual indoor NO_2 monitors at specified concentrations. The mean of these percent differences across the four monitors was taken to represent the reproducibility of the indoor NO_2 sampling method at each specified concentration. Determination of the reproducibility of the response of the indoor NO_2 monitors across the range of concentrations presented is addressed as part of the evaluation of the within-instrument precision of the indoor NO_2 monitors, as described below.

Table 7. Reproducibility of the indoor NO_2 monitors across evaluation periods by concentration

NO_2 set point	A		B		C		D		Mean %
	Absolute (ppbv)	Relative (%)	Absolute (ppbv)	Relative (%)	Absolute (ppbv)	Relative (%)	Absolute (ppbv)	Relative (%)	
0	-0.5	7.0%	-1.2	24.0%	1.1	21.4%	NA	NA	17.5%
15	19.0	60.3%	28.4	42.7%	10.4	32.0%	NA	NA	45.0%
50	8.1	19.3%	11.8	33.7%	21.4	23.3%	NA	NA	25.4%
200	0.6	0.3%	1.7	0.9%	8.2	4.9%	NA	NA	2.0%
400	8.6	2.1%	14.9	3.0%	8.3	5.0%	NA	NA	3.4%
699	8.8	3.0%	6.8	4.4%	5.8	1.6%	NA	NA	3.0%

The reproducibility of the indoor NO_2 monitors at concentrations above 50 ppbv NO_2 was shown to be excellent, with the largest variation from day to day representing less than 3.4% of the measured concentration. However, the reproducibility of the indoor NO_2 monitors was markedly decreased at concentrations of 50 ppbv NO_2 and below as measured using a relative indicator, though the absolute differences were only slightly elevated.

Accuracy and bias

Results from this task were used to evaluate the accuracy and bias of the indoor NO_2 monitors relative to the reference NO_x monitor. The mean response from each indoor NO_2 monitor at each concentration ($\overline{Y}_{jk}$) was calculated across three evaluation periods as:

$$\overline{Y}_{jk} = \frac{\sum_{i=1}^{1\to n} Y_{ijk}}{n}$$

where Y_{ijk} is the mean of the concentration from the indoor NO_2 monitors at each concentration level k on each day i for each indoor NO_2 monitor j, and n is the number of evaluation periods (three). Similarly, the mean of the reference NO_x monitor concentrations ($\overline{X}_k$) at each concentration was calculated across three evaluation periods as:

$$\overline{X}_k = \frac{\sum_{i=1}^{1\to n} X_{ik}}{n}$$

where X_{ik} is the mean of the concentration from the reference NO_x monitor at each concentration level k on each day i, and n is the number of evaluation periods (three).

The accuracy of the indoor NO_2 monitors was then assessed by two methods, both using the above calculated mean concentrations. The first determines the absolute accuracy in concentration (ppbv) units by taking the difference between the mean concentrations measured by the indoor NO_2 monitors and the reference NO_x monitor at each concentration level. The nominal value for each of these differences is zero. Differences between measured concentrations from the indoor NO_2 monitors and the reference NO_x monitor at each concentration level (D_{jk}) were then evaluated for consistency throughout the range of concentrations presented to the monitors, as:

$$D_{jk} = \overline{X}_k - \overline{Y}_{jk}$$

where $\overline{X}_k$ and $\overline{Y}_{jk}$ are as above, k is the NO_2 concentration level, and j is the indoor NO_2 monitor. The mean of these differences across concentration levels ($\overline{D}_j$) was then taken for each monitor as an indicator of the accuracy of the indoor NO_2 monitors across the range of concentrations presented, as:

$$\overline{D}_j = \frac{\sum_{k=1}^{1\to n} (\overline{X}_k - \overline{Y}_{jk})}{n}$$

where $\overline{X}_k$ and $\overline{Y}_{jk}$ are as above, k is the NO_2 concentration level, j is the indoor NO_2 monitor, and n is the number of NO_2 concentration levels (six). The results of these analyses are presented in Tables 8 and 9.

Table 8. Accuracy and precision of the indoor NO_2 monitors as compared to the reference NO_x monitor.

Evaluation period	NO_2 set point	A-TECO	B-TECO	C-TECO	D-TECO	A-TECO (average)	B-TECO (average)	C-TECO (average)	D-TECO (average)
1	0	-6.8	-4.3	5.5	NA	-7.3	-5.2	4.7	-4.9
2	0	-7.5	-5.6	4.4	NA				
3	0	-7.5	-5.6	4.3	-4.9				
1	699	-36.2	-18.8	-32.4	NA	-26.0	-18.0	-28.0	-6.9
2	699	-24.7	-16.6	-36.5	NA				
3	699	-17.1	-18.4	-15.0	-6.9				
1	400	1.9	2.5	46.6	NA	7.8	3.0	37.1	1.5
2	400	13.3	9.6	37.0	NA				
3	400	8.1	-3.1	27.6	1.5				
1	200	12.3	6.8	-21.2	NA	12.8	7.3	-24.8	0.9
2	200	13.5	9.2	-27.8	NA				
3	200	12.6	5.9	-25.5	0.9				
1	50	-7.3	-10.8	-16.0	NA	-3.1	-3.7	-12.3	-20.4
2	50	1.3	4.2	-7.6	NA				
3	50	-3.3	-4.5	-13.5	-20.4				
1	15	-9.4	-10.0	-6.4	NA	-9.2	-8.5	-5.8	-13.2
2	15	-13.5	-11.2	-8.4	NA				
3	15	-4.7	-4.4	-2.6	-13.2				
		Mean difference-				-4.2	-4.2	-4.9	-7.2
		Stdev of differences-				13.737	8.863	23.836	8.450
		Between-sampler precision (P_B)-				9.968			
		Between-sampler precision (P_B)-				4.5%			

All units are ppbv unless otherwise noted. 'Stdev' is standard deviation.

The second method of determining accuracy examines the relative accuracy of the indoor NO_2 monitors by evaluating the ratio between the mean concentrations measured by the indoor NO_2 monitors and the reference NO_x monitor, both in ppbv units. The ratios are therefore unitless and the nominal value of each is unity. Ratios are presented as the percent accuracy by multiplying by 100%, as:

$$\%\ \text{Accuracy}_j = \left(\frac{\overline{Y}_{jk}}{\overline{X}_k}\right)\times 100\%$$

where $\overline{Y}_{jk}$ and $\overline{X}_k$ are as above and j is the indoor NO_2 monitor. The mean of the individual indoor NO_2 monitor percent accuracy estimates was then calculated to estimate the overall relative accuracy of the indoor NO_2 monitor sampling method.

Table 9. Accuracy of the indoor NO_2 monitors across days

Evaluation period	NO_2 set point	A: TECO ratio	B: TECO ratio	C: TECO ratio	D: TECO ratio	A (average)	B (average)	C (average)	D (average)
1	0	325.173	204.686	-259.442	NA	6628.4%	3675.4%	-6080.5%	-3649.3%
2	0	-69.759	-52.116	42.866	NA				
3	0	-56.564	-42.308	34.162	-36.493				
1	699	0.947	0.972	0.952	NA	96.1%	97.3%	95.9%	98.9%
2	699	0.964	0.975	0.946	NA				
3	699	0.974	0.972	0.977	0.989				
1	400	1.005	1.006	1.120	NA	102.0%	100.8%	109.6%	100.4%
2	400	1.035	1.025	1.096	NA				
3	400	1.021	0.992	1.071	1.004				
1	200	1.064	1.035	0.891	NA	106.6%	103.8%	87.1%	100.4%
2	200	1.071	1.048	0.855	NA				
3	200	1.065	1.031	0.868	1.004				
1	50	0.846	0.773	0.664	NA	93.5%	92.3%	74.0%	56.8%
2	50	1.028	1.089	0.840	NA				
3	50	0.930	0.906	0.716	0.568				
1	15	0.595	0.571	0.726	NA	60.9%	63.8%	75.4%	44.5%
2	15	0.431	0.528	0.645	NA				
3	15	0.802	0.814	0.889	0.445				
			Mean ratio (without zero points)-			91.8%	91.6%	88.4%	80.2%

The accuracy of the indoor NO_2 monitors is directly related to the calibration functions used to convert the response of the sensors in the indoor NO_2 monitors to concentration units. Using the calibration functions displayed in Table 5 (except for the linear model for Unit C), the concentrations obtained from the indoor NO_2 monitors were shown to be very accurate across the three evaluation periods, with generally higher (i.e., better) accuracy at concentrations less than 699 ppbv NO_2.

It is unclear why Unit D showed a response lower than the other units at 50 and 15 ppbv NO_2, but it is interesting to note that Unit D had the highest calibration slope, indicating that the sensor in this unit was the least sensitive to NO_2. Also, Unit D showed the largest difference in initial and final calibration slopes, suggesting the sensor may be aging more quickly than the other sensors. Though the calibration factors were adjusted for each day of testing, changes in the sensors occurring more quickly than daily may account for some of the observed loss of response to the lower concentrations (50 and 15 ppbv NO_2) for Unit D.

Precision

Results from this task were used to evaluate the precision of the indoor NO_2 monitors by evaluating the variance in the differences between pairs of measured concentrations from the indoor NO_2 monitors as well as in the differences between pairs of measured concentrations from each of the indoor NO_2 monitors and the reference NO_x monitor.

The precision of the measurements among the indoor NO_2 monitors, or within-instrument precision, was estimated by using pairwise differences in the concentration measurements from the indoor NO_2 monitors at each concentration on each day, as:

$$P_W = \frac{\sqrt{\dfrac{\sum_{i=1}^{1\to i}\sum_{k=1}^{1\to k} d_{ik}^{\;2}}{n-1}}}{\sqrt{2}}$$

where d_{ik} is the pairwise difference among the measured concentrations from one half of the non-identical pairs of indoor NO_2 monitors j on day i at concentration level k, and n is the number of measurement pairs (n = 74 in this case). The precision estimate is also expressed as relative precision in percent by dividing by the mean reference method concentration and multiplying by 100%. The results of this analysis are presented in Table 10.

Table 10. Within-sampler precision of the indoor NO_2 monitor.

NO_2 set point	A-B	A-C	A-D	B-C	B-D	C-D
0	-2.5	-12.3	-6.9	-9.8		
0	-1.9	-11.9	-7.4	-10.0		
0	-1.8	-11.7	-2.6	-9.9	-0.8	9.1
699	-17.3	-3.7		13.6		
699	-8.1	11.8		19.9		
699	1.3	-2.1	-10.2	-3.4	-11.4	-8.1
400	-0.6	-44.7		-44.1		
400	3.7	-23.7		-27.5		
400	11.3	-19.5	6.7	-30.7	-4.6	26.1
200	5.5	33.5		28.0		
200	4.4	41.3		37.0		
200	6.7	38.1	11.7	31.4	5.1	-26.4
50	3.4	8.6		5.2		
50	-2.9	8.9		11.8		
50	1.2	10.2	17.2	9.0	16.0	7.0
15	0.5	-3.1		-3.6		
15	-2.3	-5.1		-2.8		
15	-0.3	-2.1	8.5	-1.8	8.8	10.6
	Mean of within sampler differences-				1.0	ppb
	Standard deviation of within sampler differences-				16.371	ppb
	Within-sampler precision (P_w)-				11.576	ppb
	Within-sampler precision (P_w)-				5.3%	

Blank cells represent missing values due to a download malfunction for Unit D.

Similarly, the precision of the indoor NO_2 monitors versus the reference NO_x monitor, or between-sampler precision, was estimated as:

$$P_B = \frac{\sqrt{\dfrac{\sum_{i=1}^{1\to i}\sum_{k=1}^{1\to k} d_{ik}^{\;2}}{n-1}}}{\sqrt{2}}$$

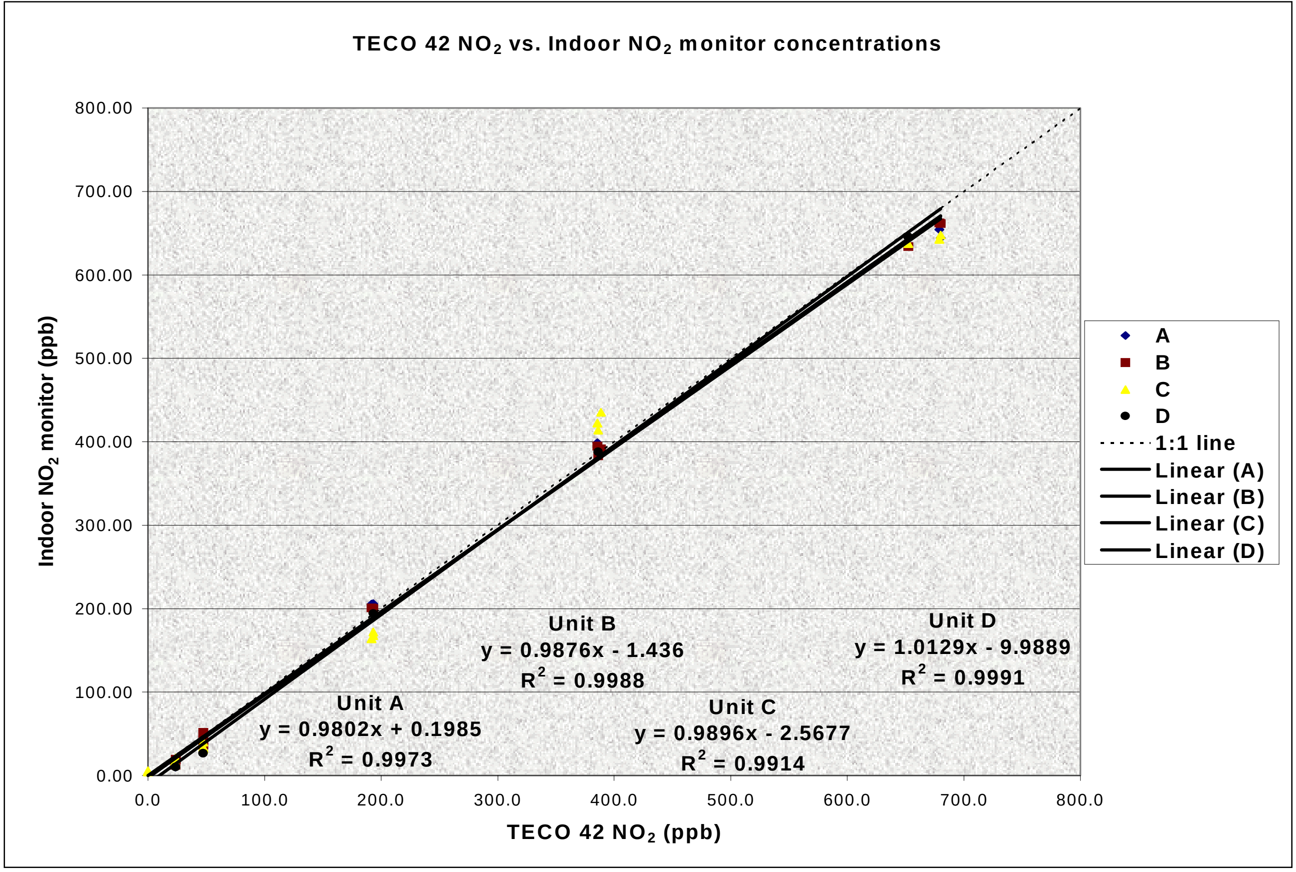
where d_{ik} is the pairwise difference among the measured concentrations from the one of the four indoor NO_2 monitors j and from the reference NO_x monitor on day i at concentration level k, and n is the number of measurement pairs ($n = 24$ in this case). The precision estimate is also expressed as relative precision in percent by dividing by the mean reference method concentration and multiplying by 100%. The data used to calculated the between-sampler precision are also those used in the calculation of the accuracy of the indoor NO_2 monitors. As such, the results of this analysis are presented in Table 8.

Both the within- and between-instrument precision of the indoor NO_2 monitors was shown to be high (less than 5.3%). Unit C exhibited the lowest (i.e., worst) precision, partly due to the poor fit of the polynomial model at the 400 ppbv NO_2 concentration level. As observed for the modified Environics 6100 calibrator, improvements in the accuracy of the indoor NO_2 monitors would also increase their precision as evaluated by this approach.

Linearity

Results from this task were used to evaluate the linearity of the response of the indoor NO_2 monitors relative to the reference NO_x monitor, as described above for the calibration of the indoor NO_2 monitors. The R^2 from OLS was used as an indicator of linearity and is shown for each indoor NO_2 monitor in Figure 3. The slope and intercept estimates for the OLS regression of the indoor NO_2 monitor concentrations on the reference NOx monitor concentration measurements are also shown.

Figure 3. Comparison of reference NO_x monitor and indoor NO_2 monitor concentrations



The linearity of the NO_2 concentrations measured by the indoor NO_2 monitors was excellent, with R^2 values greater than 0.99 for each monitor when compared to the reference NO_x monitor.

Response to interfering gases

The response of the indoor NO_2 monitors was evaluated while two potentially interfering gases (ozone and NO) were supplied to the sampling manifold. The measurements of the response of the indoor NO_2 monitors were taken as one-minute averages at the beginning and at the end of the periods where the interfering gases were supplied to the manifold. The results are presented in Table 11.

Table 11. Indoor NO_2 monitor responses to interfering gases

Interfering gas	Stage of measurement	Response in concentration units (ppb)			
		Unit A	Unit B	Unit C	Unit D
Ozone	Initial	-1.6	-2.8	4.9	-3.6
	Final	386.0	378.1	659.3	464.0
NO	Initial	631.1	638.1	659.3	716.2
	Final	7.2	10.1	10.4	3.8

The results in Table 11 show an artifact of the order in which the gases were introduced. The high initial response to NO is a result of following the high (699 ppbv) ozone concentration. When presented with only 889 ppbv of NO in zero air, the indoor NO_2 monitors quickly returned to a stable level, though as can be seen from the final values for NO, they did not return to zero. It appears from the above data that ozone interfered with the response of the sensors by slowly but continuously increasing the signal from the sensors. At the end of the ozone concentration period the response of the indoor NO_2 monitors had not leveled off but instead continued to rise incrementally. In contrast, the response to NO appeared to be constant and small during the testing period, once the ozone was purged from the sample stream.

Ease of use

The indoor NO_2 monitors were relatively easy to use during the testing, though several problems did occur. Twice during the testing the flow rates of the pumps on the indoor NO_2 monitors were observed to drop substantially. The monitors were turned off and the pump diaphragm cleaned and lubricated. This cleaning and lubrication procedure appeared to solve the problems with the pumps as both pumps were then able to maintain the required flow rate of about 800 ml/min.. Upon inspection of the fittings on the pumps, though, the fittings were observed to be loose and easily disconnected. The fittings on the two pumps that were repaired were secured with cable ties to address this problem. It is recommended that the other two pumps (on Units A and C) undergo a similar procedure. There were also difficulties with accessing the zero point potentiometer to adjust the zero point of the sensors. A knob on this potentiometer or larger hole in the back panel of the indoor NO_2 monitors may alleviate this difficulty. As shown below, the indoor NO_2 monitors were observed to respond positively to ozone when presented at a concentration of 699 ppbv.

Thus it is recommended that an ozone scrubber be attached upstream of the sensor on the indoor NO_2 monitors. Finally, the apparent deviation from a linear response for Unit C indicated that a polynomial model may be more appropriate for predicting NO_2 concentration from the mV response of the sensor in this unit. The data reduction process was somewhat complicated by this, as well as the need to adjust the calibration factors for trends in the sensitivity of the sensors between calibrations. A software package that can accomplish these features as well as adjust for temperature and RH effects during sampling would be very valuable in the data reduction procedure, as discussed above.

Sensitivity

Results from this task were also used to evaluate the sensitivity of the indoor NO_2 monitors relative to the 15 ppbv NO_2 concentration. Sensitivity was assessed by using a ratio of the signal to noise at the 15 ppbv concentration, where signal was defined as the mean of the sensor voltage when presented with 15 ppbv NO_2 (the lowest available concentration from the calibrator for a 15 ppm NO initial concentration) while noise was defined as the mean of the baseline voltage when the indoor NO_2 monitors are presented with zero air. A reference NO_x monitor was used to verify that NO_2 concentrations were very near zero when the manifold was supplied with zero air.

Table 12. Sensitivity of the indoor NO_2 monitors relative to 15 ppbv of NO_2

Mean (+/- Stdev) mV response	
Zero	15 ppb NO_2
1.2 +/- 3.4	54.2 +/- 4.8

'Stdev' is standard deviation.

The indoor NO_2 monitors clearly exhibited a detectable response to the 15 ppbv NO_2 concentration level, as the average response to this level was many times the average response to zero air, though the variability at the two levels was similar.

The sensitivity of the sensors in the indoor NO_2 monitors throughout the range of NO_2 concentrations was also assessed by determining the sensor output per unit NO_2 concentration for comparison with the 0.2 mV/ppbv threshold for sensor validity provided by the manufacturer.

Table 13. Indoor NO_2 monitor sensitivity relative to the 0.2 mV/ppbv threshold

Indoor NO_2 monitor	Unit A	Unit B	Unit C	Unit D
Sensitivity (mv/ppb)	2.3	1.6	2.8	1.2
Ratio to 0.2 mV/ppb	12	8	14	6

The sensitivities of the indoor NO_2 monitors were well above the recommended threshold for all monitors, indicating the low age of the sensors. Unit C exhibited the highest sensitivity to NO_2 while Unit D exhibited the lowest.

Drift

Results from this task were used to evaluate baseline drift using the difference between initial and final response to the baseline (zero) concentration for each indoor NO_2 monitor when presented with zero air. This difference ($d_{0,ij}$) was planned to be calculated as:

$$d_{0,ij} = Y_{initial,ij} - Y_{final,ij}$$

where $Y_{initial,ij}$ is the response of indoor NO_2 monitor j when initially presented with zero air, $Y_{final,ij}$ is the response of the indoor NO_2 monitor j when finally presented with zero air, and i is the day. However, a simpler approach was used that involved taking the mean response from the indoor NO_2 monitors whenever zero air was presented. Differences by evaluation period were then calculated, and the differences across monitors and across evaluation periods as:

$$\overline{d}_0 = \frac{\sum_{i=1}^{1\to n} \sum_{j=1}^{1\to n} d_{0,ij}}{n}$$

where $\overline{d}_0$ is the mean drift of all monitors across all evaluation periods, $d_{0,ij}$ is as above, j is the indoor NO_2 monitor, and n is the number of measurement pairs ($n = 4$ in this case). The results are presented in Table 14.

Table 14. Drift of the indoor NO_2 monitors across the three evaluation periods.

Evaluation period	NO_2 set point	Unit A (ppb)	Unit B (ppb)	Unit C (ppb)	Unit D (ppb)
1	0	-6.9	-4.3	5.5	NA
2	0	-7.4	-5.5	4.5	NA
3	0	-7.3	-5.5	4.4	-4.7
Difference between initial and final (d_{0ij})-		-0.5	-1.2	-1.1	NA
			Mean difference (d_{bar0})-	-0.9	ppb

Each indoor NO_2 monitor was shown to have a very stable zero point and to drift very little over the three evaluation periods, indicating stability in the calibration functions developed before and after the testing.