CONTRACT NO. 96-312
FINAL REPORT
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Development of a Short-Averaging-Time Indoor Nitrogen Dioxide Monitor

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

DEVELOPMENT OF A SHORT-AVERAGING-TIME INDOOR NITROGEN DIOXIDE MONITOR

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ABSTRACT

A small, quiet, portable instrument was developed to measure nitrogen dioxide (NO_2) and nitrous acid (HONO) in indoor air. These toxic compounds are present in indoor air because of emissions from combustion sources, such as cooking appliances, portable heaters, and tobacco smoking. The instrument is a fully self-contained continuous monitor, based on a miniature commercial electrochemical cell that responds to both NO_2 and HONO. The monitor was tested in the laboratory, in test chambers, in a research house, and in three occupied homes and one business. The monitor has no chemical interferences from common indoor air pollutants, and its response is readily corrected for a small dependence on the indoor temperature and relative humidity. Ozone produces a positive response, though this interference was found only when NO_2 and other air pollutants were not present. The monitor provides simultaneous measurements of NO_2 and HONO with a time response of two minutes. The accuracy of the monitor with new electrochemical sensors, relative to a conventional measurement method, was 10 to 20 percent in a variety of studies. The main limitation of the monitor is a gradual loss of sensitivity of the sensor. This monitor will be used to assess the exposures people receive to NO_2 and HONO in their homes, as part of an effort to determine the causes of respiratory illnesses.

EXECUTIVE SUMMARY

Background

Nitrogen dioxide (NO_2) is a toxic gas emitted from combustion sources, including those present in homes, such as gas cooking appliances, portable heaters, and tobacco smoking. Indoor levels of NO_2 may often be higher than those outdoors, and because most people spend most of their time indoors, much of their exposure to NO_2 comes from indoor sources. NO_2 is a likely contributor to respiratory ailments, and as a result, measurements of NO_2 have been made indoors to assess human exposures to this pollutant. Unfortunately, those measurements have been made using techniques that provide only long-term average concentration data. The short-term peaks and changes in NO_2 levels that occur with use of combustion sources indoors cannot be followed by those techniques. A rapid, portable means of monitoring NO_2 indoors is needed to improve the understanding of indoor NO_2 exposures. In addition, nitrous acid (HONO) can be formed indoors by the reaction of NO_2 on surfaces, and contributes much of the total exposure an occupant receives to acidic air pollutants. Thus a method for indoor monitoring of HONO, as well as NO_2, is needed. The purpose of this study was to develop a small, portable, fast-responding monitor that can be used to determine indoor NO_2 and HONO levels.

Methods

A monitor was developed that determines NO_2 and HONO, based upon a commercial electrochemical sensor that responds to both NO_2 and HONO, but with different sensitivities. The components of the monitor supply sample air to the sensor, amplify the sensor's response, automatically alternate between two channels of measurement, and record the data automatically. NO_2 is determined directly from one channel, and HONO is determined from the difference between the two channels. The monitor samples air continuously, and is fully self-contained, needing no reagents, expendables, or external data acquisition device.

Three NO_2/HONO monitors were assembled and subjected to laboratory testing using controlled sources of NO_2, HONO, and potential chemical and environmental interferences. Tests were conducted with air of varying temperature and relative humidity, to assess the effect of these conditions on the response of the sensors. Test chambers were also used, to control the test environment, to expose the monitors to complex mixtures of potential interferent gases, and to conduct tests with small combustion sources. Initial field tests were then conducted to assess the performance of the monitors in more realistic conditions. Those tests were performed in conjunction with a study of unvented gas hearth products in a research house, and also included periods of operation of a gas rangetop and oven.

Based on the results of the initial laboratory and field tests, four second-generation monitors were assembled and subjected to further testing. Additional chamber tests focused on measurement of gas range emissions, and further laboratory testing evaluated the long-term stability of the sensors. Final field tests were then conducted in two occupied homes and one business in southern California, and in an occupied home in Columbus, Ohio.

Results

The electrochemical approach to NO_2/HONO monitoring was found to be successful. The monitors proved to be rugged and reliable in severe field testing conditions. The monitors provide linear response to NO_2 and HONO over the range of concentrations expected in indoor air, and have a time response of about two minutes, sufficient to follow the changes in concentration that result from emissions from indoor combustion sources. None of the other common indoor air pollutants tested is a significant interferent in the measurement of NO_2 and HONO. Ozone showed a positive response when tested alone in humidified air, but did not cause a positive response when present along with NO_2 and other common air pollutants. Temperature and relative humidity of the sample air do have a small effect on the response of the electrochemical sensors (response increases with increasing temperature and RH). These effects are accounted for by recording the temperature and RH using a miniature datalogger built into the monitor. In field sampling in homes, these corrections amounted to less than a 15 percent adjustment to the data. The accuracy of NO_2 and HONO determination, determined by comparison to a conventional monitoring approach, was 10 to 20 percent with relatively new sensors in the monitors.

One limitation of the monitors is a gradual loss of the NO_2 sensitivity of the electrochemical sensors, at the rate of 20 percent per month or more. This behavior requires relatively frequent calibration to achieve accurate NO_2 and HONO measurements. The sensors can be obtained from the manufacturer in sets closely matched in sensitivity, but all exhibit this characteristic loss of response. Also, the amplifier circuitry provided with the sensors is relatively noisy, and an improved design would be beneficial. In addition, the data reduction process to determine NO_2 is straightforward, whereas that to determine HONO by difference is relatively complex. The recording of internal diagnostic signals would be valuable as a means of simplifying the latter process.

Conclusions

This study was successful in developing a fast, portable real-time monitor for NO_2 and HONO indoor use. Overall, the NO_2/HONO monitors are fully capable of providing indoor data suitable for assessing human exposures in large field studies. Their sensitivity, rapid response, small size, freedom from interferences, and data acquisition capability make them attractive for such studies. The monitors do require calibration with NO_2 and HONO, and determination of the temperature and relative humidity dependence of sensor response. The observed long-term loss of sensitivity means that in operation over extended periods, attention must be paid to the calibration of the sensors. A weekly one-point calibration of NO_2 response is recommended. The response to HONO is more stable; HONO calibration once per month is recommended. Key recommendations for further study include identifying the cause of the gradual loss of sensitivity, improving the sensor amplification circuitry, and modifying the data acquisition procedure to simplify the data reduction process. Finally, further field testing is recommended, to verify that the monitors measure relatively high NO_2 levels as well in California environments as in the laboratory. Contrary to expectation, indoor NO_2 levels were generally low in the field locations used in this study, and did not provide an opportunity for monitoring of high levels.

1.0 INTRODUCTION

This is the Final Report on California Air Resources Board (CARB) Contract Number 96-312, "Development of a Short-Averaging-Time Indoor Nitrogen Dioxide Monitor". The primary purpose of this work was to develop a small, portable detector for nitrogen dioxide (NO_2), a toxic air pollutant produced by combustion. The detector had to be sensitive enough to accurately measure NO_2 in people's homes, and rapid enough in its response to follow the changes in indoor NO_2 concentrations that occur from activities like cooking, smoking, or use of heating appliances. An additional purpose was to also provide measurements of nitrous acid (HONO), another toxic air pollutant which is formed indoors by the reaction of NO_2 with moisture on surfaces. This section presents the background for this work, states the study objectives, and outlines the research program that was conducted to achieve those objectives.

1.1 Background

Nitrogen dioxide has long been recognized as a toxic air pollutant that is present in indoor air, as well as in outdoor air. NO_2 is regulated as a hazardous air pollutant in outdoor air, and the U.S. Environmental Protection Agency (EPA) has established Reference methods for NO_2 measurement, which are widely used in urban outdoor monitoring networks for nitrogen oxides. However, most Californians spend most of their time indoors,[1] and several studies[e.g., 2-4] have shown elevated indoor NO_2 levels resulting from indoor combustion sources, such as cooking and heating appliances and tobacco smoking. As a result, personal exposure to NO_2 indoors may often exceed the exposure that occurs outdoors. Unfortunately, only very few data are currently available with which to evaluate the exposure of California residents to indoor NO_2.

One limitation of the existing data on indoor NO_2 levels is that most of the data have been obtained as average values over time periods of one day to several days. The long-term average NO_2 levels resulting from such measurements provide little information on short-term exposures to NO_2 that may result from use of indoor combustion sources. To protect the health of California residents, the California one-hour NO_2 standard is set at 250 ppbv. However, the existing long-term NO_2 data suggest that this standard may be violated at some times in some homes. For example, in the California Residential Indoor Air Quality Study,[5] indoor NO_2 levels up to 177 ppbv were determined as 48-hour averages. The implication is that if NO_2 averaged

177 ppbv over 48 hours, it is very likely that the 250 ppbv one-hour standard was exceeded for at least some portion of that time period.

The cause of the poor time resolution in the existing indoor NO_2 data is the use of passive samplers for NO_2 determination. These samplers require long exposure times to achieve adequate sensitivity for NO_2 indoors. In addition, the uncertainty in NO_2 levels determined by passive samplers is relatively high because of the lack of knowledge of the air volume sampled. Furthermore, it has been demonstrated that passive samplers for NO_2 also collect nitrous acid (HONO),[6,7] and thus overestimate the NO_2 level present. In order to avoid these limitations, a sensitive and interference-free method of NO_2 measurement is needed that employs active air sampling, and that provides time response fast enough to document the short-term peak exposures to NO_2 that can occur indoors. A response time of less than one hour is needed for direct comparison of measurements to the California one-hour NO_2 standard. This response requirement rules out passive samplers and other time-integrated sampling techniques using denuders and filters. Spectroscopic methods for NO_2 might provide suitable sensitivity, specificity, and time response, but those devices are typically large, complex, and costly, and are thus unsuitable for routine in-home measurements.

It is important to note that nitrous acid is not merely an interferent in NO_2 detection, but also a significant indoor pollutant. Nitrous acid is emitted along with NO_2 by gas combustion sources[6-9] and also is formed indoors by surface reactions of NO_2.[10-13] That is, NO_2 reacts with trace amounts of water on the numerous surfaces indoors to produce HONO. As a consequence, indoor HONO can be present at levels that are significant relative to NO_2, and HONO has been identified as a large contributor to total personal exposures to acidic air pollutants.[14] As a result, measurement of HONO indoors, not merely elimination of its interference in NO_2 measurements, is important. In particular, separate determination of NO_2 and HONO is needed, to allow the connection of any observed health effects with the appropriate pollutant.

Because of the issues summarized above, sensitive, fast, portable, rugged, and interference-free monitoring methods for NO_2 and HONO are needed to characterize the indoor concentrations and resulting human exposures of these compounds. The goal of the study described here was to develop a single monitoring approach that determines both compounds simultaneously.

The approach used in this study to achieve this goal is based on detection of NO_2 (and HONO) by a miniature electrochemical sensor. Such a sensor is small, lightweight, requires minimal electric power, and has a time response of about one minute. Previous testing has shown that these sensors provide linear response to NO_2 over a wide concentration range.[6,15] In addition, this approach provides a unique feature not available from other monitors: sensitivity for HONO that substantially exceeds that for NO_2.[6,15] This unique feature permits accurate measurement of HONO concentrations, even in the presence of much larger NO_2 levels.

1.2 Study Objectives

The two objectives of this study were:

1. To develop, test, and deliver to CARB a small, quiet, rugged, and inexpensive instrument for continuously monitoring NO_2 in indoor air, based on the electrochemical sensor approach. The monitor must have a time response of substantially less than one hour, be essentially interference-free, and allow accurate and precise measurements over the full range of expected indoor NO_2 concentrations (i.e., 10 ppbv to 1 ppmv).

2. To incorporate into the same NO_2 monitor the capability for monitoring of HONO in indoor air.

1.3 Overview of Study Plan

The work reported here was based on a planned sequence of research steps, starting with basic evaluation of the electrochemical approach for NO_2, and ultimately proceeding to field testing of multiple units of the monitor developed from that approach. The planned sequence of steps was as follows:

Initial Assembly of Monitors: This step called for assembly of three identical prototype NO_2/HONO monitors, based on the electrochemical sensors noted above. Basic air flow control, sensor amplification, and signal readout were required.

Laboratory Testing: In this step the prototype monitors were to undergo testing for chemical interferences, sensitivity, linearity, stability of response over time, dependence on temperature and relative humidity, and other factors.

Preliminary Field Tests: Following completion of the laboratory tests, a brief field test of the three prototype monitors was planned. This step involved operating the monitors in a home with various combustion sources.

Evaluate Prototype Performance: In this step, the results of the laboratory and preliminary field tests were used to assess the strengths and limitations of the prototype monitors, and to define improvements to be made in a second generation monitor.

Modify Monitors: This step called for building four units of a second generation NO_2/HONO monitor, incorporating the improvements defined in the previous step.

Final Field Test: For this step a field test was planned of the second generation NO_2/HONO monitors in homes and businesses in California.

As will be apparent from later sections of this report, all of the steps outlined above were conducted, but not in the simple progression suggested here. For example, the preliminary field tests were conducted before the laboratory tests were fully completed, in order to take advantage of an ongoing field study as a platform for the field test. Study activities and findings were reported at key points during the study, in two Interim Reports, which are included in this report as Appendices A and B. Reference will be made to those Appendices as appropriate, and the Appendices are summarized in Sections 3.1 and 3.2. However, the reader is encouraged to read the Appendices for the full details of the work conducted. Section 2.1 puts those Appendices in the proper chronological context within this study.

2.0 MATERIALS AND METHODS

In this section the approaches used to build, test, and modify the NO_2/HONO monitors are described. Because much of the work has already been documented in the Interim reports included as Appendices A and B, a chronology of the study is first presented, to put those reports in proper sequence with this final report.

2.1 Chronology of the Study

The organization of this report is based upon the chronological sequence of research and reporting in this study. The study began in March of 1997. Initial effort involved brief testing of the electrochemical NO_2 sensors, to judge whether the previous results noted in Section 1.1 were borne out by the currently available sensors. Those previous results were confirmed, and assembly of three prototype monitors then took place. The three prototype monitors were subjected to a variety of laboratory testing until the fall of 1997. At that time, an opportunity arose to conduct initial field tests of the monitors in a research house in Chicago, in collaboration with another Battelle research program. The advantages of cost savings and access to a variety of data made this opportunity attractive, and as a result the laboratory testing was interrupted at that point. To document progress in the study, a First Interim Report was prepared describing the assembly of the monitors and the results of the laboratory testing that had been completed. That report is included as Appendix A, and covers the time period from March to November, 1997. Appendix A is summarized in Section 3.1, but the Appendix itself should be read for the full details of the early stages of this program.

The initial field tests of the three prototype NO_2/HONO monitors were conducted in the Chicago research house in mid-November of 1997. Following those field tests, the field data were evaluated, and laboratory testing resumed, focusing on chemical interferences and the effect of temperature and relative humidity on sensor response. These activities were completed in early 1998, and a Second Interim Report was prepared documenting those tests and stating recommendations for further development of the monitors. That report is included as Appendix B, and covers the period from November, 1997 to May, 1998. Appendix B is summarized in Section 3.2, but again the reader is directed to the Appendix itself for full details of the work.

Following the testing described in Appendix B, four new second-generation NO_2/HONO monitors were constructed in late 1998, incorporating improvements based upon the results of all testing up to that point. Those four monitors were subjected to selected laboratory tests, and in April 1999 were deployed in field testing in two homes and one business located in southern California. Additional field testing also took place in May 1999 in a home in Columbus, Ohio.

The body of this Final Report describes primarily the study activities between June, 1998 and June, 1999, i.e., subsequent to the period reported in Appendix B. The earlier study activities documented in Appendices A and B are summarized as necessary, but the reader is referred to those Appendices for the details of the previous stages of this work.

2.2 Materials Used

2.2.1 Electrochemical Sensor

The electrochemical NO_2 sensor used as the basis of the NO_2/HONO monitors in this study is the Model NO_2-SNL sensor made by TSI, Inc., of St. Paul, Minnesota. This sensor is the subsequent commercial version of the sensors previously made by Transducer Research, Inc., which were found in testing at Battelle to have a strong response to HONO.[6,15] The SNL sensor consists of an electrochemical cell containing an electrolyte solution, with three electrodes: reference, working, and counter, respectively. The reference electrode sets the baseline potential of the cell. The application of a bias potential between the working and counter electrodes results in a current proportional to the concentration of the analyte. The choice of electrode potential determines the mode of electrochemical detection of the analyte (i.e., oxidation or reduction) and affects the discrimination against interferences. For NO_2 detection, TSI recommends a bias voltage of -100mV, to minimize interferences from other gases, and that bias voltage was used throughout this study. The sensors have a proprietary electrode design that minimizes baseline current, and consequently allows detection of NO_2 concentrations as low as 5 parts-per-billion by volume (ppbv, $= 1 \times 10^{-9}$ v/v). These sensors are circular in shape, 3 cm in diameter and 1.5 cm thick, and have three pins each 4 mm long for connection to the electrodes. One face of the sensor is a porous barrier, through which the analyte gas diffuses into the electrochemical cell. A control circuit made by TSI provides the required bias potential to the sensor, and converts and amplifies the sensor current to a voltage in the mV to V range. The range of output sensitivity of the sensors is about 0.3 to 0.8 mV per ppbv of NO_2 in air.

New sensors were purchased in batches of four to six at intervals during the study. At the start of this program, the NO_2 sensors were a relatively new product for TSI, and improvements in sensor performance were found as the study progressed. Gradual decay of sensitivity was observed during use, as described elsewhere in this report, but improvement was observed in this area. The manufacturer indicates a typical sensor life in use of about one year, with a longer storage lifetime before use, provided the sensors are kept sealed in their original packaging. Upon request TSI selected the sensors in a batch to be closely matched in sensitivity for NO_2. Batches of matched sensors had initial sensitivity for NO_2 that was within ± 3 percent of the average sensitivity of the batch.

2.2.2 General Instrument Design

The basic design of the NO_2/HONO monitors was as a two-channel instrument. In one channel, sample air was drawn directly past the sensor, and the sum of NO_2 and HONO was detected. In the other channel, sample air passed through a carbonate-coated glass fiber filter before flowing past the sensor. This filter selectively removed the HONO from the air stream, resulting in a measurement of NO_2 only. NO_2 was determined directly from response in the second channel, and HONO was determined by difference between the two channels, taking into consideration the different sensitivities of response for NO_2 and HONO. Switching between channels was accomplished using a Teflon three-way solenoid valve to direct the sample air stream through or around the filter. A schematic of the prototype NO_2/HONO monitors is shown in Figure 1 of Appendix A; with minor changes in components, this schematic also reflects the final version of the monitors.

Selection of the measurement channel of the NO_2/HONO monitor can be done manually, by means of a stepper switch on the front panel, or automatically over a wide range of switching intervals by means of a miniature programmable electronic timer. That timer controls a relay, which accomplishes two functions: switching the three-way channel selection valve, and directing the analog output from the sensor amplifier to either of two sets of terminals on the back panel of the monitor. That is, the two operating channels of the monitor each have a separate analog output. In automatic operation, only one set of terminals is active at a time. Thus the two measurement channels are recorded as separate alternating signals, simplifying the data reduction process. In typical use, measurements are made for two to five minutes in one channel of operation, before switching to the other channel.

2.2.3 Laboratory Test Equipment

In testing for the effects of temperature, relative humidity, and chemical interferences, and in calibrating the monitors with both NO_2 and HONO, a variety of laboratory equipment was used. That equipment included compressed gas standards; conventional monitoring equipment such as a chemiluminescent nitrogen oxides monitor; a humidity generation and flow dilution system; a HONO generation system based upon chemical conversion of nitric acid (HNO_3) released from a permeation source; and chambers used for temperature and combustion source tests. The primary calibration source was a standard of nominally 50 ppm NO_2 in air, obtained from Scott Technical Gases. The actual concentration of that standard was established by comparison to a 49.7 ppm NO in nitrogen Standard Reference Material, obtained from the National Institute of Standards and Technology. The standards and equipment used are described in detail in Appendices A and B; Figure 2 of Appendix A shows the air humidification system used in laboratory testing.

In nearly all laboratory testing, all the NO_2/HONO monitors were subjected to the same test procedures simultaneously. They received all sample gases from a common manifold, or else were placed entirely inside a test chamber filled with the test atmosphere, to assure consistency of testing. This approach allowed judgments to be made about the unit-to-unit variability of the monitors. The only exception to this practice was in interference testing with HNO_3, where the limitations of the HNO_3 source required testing with one monitor at a time.

Two chambers were used in laboratory testing: a 0.4 m^3 portable steel and glass chamber, and a 17.3 m^3 walk-in smog chamber. The former was used for temperature and relative humidity tests, in which all the NO_2/HONO monitors were placed inside the chamber, and sampled gas supplied from outside the chamber. The internal temperature of the 0.4 m^3 chamber was controlled by means of electric heating elements. In this way the NO_2/HONO monitors could be entirely enclosed in an environment having temperatures up to more than 100°F.

The 17.3 m^3 smog chamber was used in testing for interference from multiple gases present simultaneously, and in tests with actual gas combustion sources. In these tests the monitors were operated side-by-side in the chamber while multiple interferent gases were injected one at a time into the chamber, or while gas combustion sources were operating in the chamber. Comparative measurements were made with conventional monitors located outside the chamber. The multi-component interference tests are described in detail in Section 4.2 of

Appendix B, and are summarized in Section 3.2 of this report. The chamber combustion source tests are reported in Section 3.3 of this report.

2.2.4 Data Acquisition

During the laboratory and field testing described in Appendices A and B, the analog outputs of the NO_2/HONO monitors were recorded on a personal computer (PC) data system, using LabTech Notebook software. Data from conventional monitors operated in those tests were also recorded on the same system. This approach required taking the PC data system into the field along with the NO_2/HONO monitors, whenever field testing was done, and was contradictory to the intent of this study to develop a small, portable monitoring device. As a result, a miniature self-contained data logger was added to each monitor, in the modifications that produced the second-generation instruments. That data logger is a battery-powered HOBO® (Onset Computer Corporation) with 10 mV data resolution and capacity for storage of over 32,000 data points, allocated among from one to four input channels. The HOBO is only 5.8 cm x 4.5 cm x 1.8 cm, and weighs 27 grams, so it is a minimal addition to the chassis of the NO_2/HONO monitor. The HOBO can operate for about one year without battery replacement. The HOBO is initialized and its data acquisition schedule is set by means of software installed on a PC. Thereafter, data transfer from the instrument in the field to a PC in the office or laboratory is accomplished with a hand-held HOBO Shuttle® download device. Data collection in the field is interrupted for at most a few minutes for the data transfer process.

In addition, because of the temperature and humidity dependence observed with the TSI electrochemical sensors, a second HOBO was added to each NO_2/HONO monitor. This HOBO incorporates both a temperature and a relative humidity sensor, and automatically records those parameters. The temperature and relative humidity data are downloaded along with the NO_2/HONO data, and used to correct the measured NO_2 and HONO results for the effects of temperature and relative humidity. Data shown in Section 3.3 of this report include temperature and humidity corrections made by this procedure.

2.3 Field Testing

2.3.1 Initial Field Tests

The initial field tests of three prototype NO_2/HONO monitors took place from November 14 to 18, 1997 in the Gas Research Institute (GRI) conventional research house, in Chicago, Illinois. A separate Battelle program, studying the emissions from unvented gas hearth products, took place in the research house during that month. The study for GRI offered an opportunity to perform initial field trials of the NO_2/HONO monitors in collaboration with a well instrumented series of emission tests on a variety of hearth products. In addition, in periods when no hearth product tests were carried out, the gas range in the research house was operated in simulated cooking activities, providing additional data for evaluation of the monitors. The schedule, equipment, and results of the initial field tests are detailed in Section 3 of Appendix B, and are summarized in Section 3.2 of this report. Appendix B includes a plan diagram of the research house, and photographs of the field testing setup.

2.3.2 Independent Assessment

As preparation for final field testing, an independent assessment was needed of the field readiness of the second-generation NO2/HONO monitors. Independent in this context meant putting the monitors in the hands of someone other than the Battelle staff who had built and tested them throughout the study. This assessment was conducted in January 1999, by sending one of the second-generation monitors to Valley Research Corporation. This assessment focused on the readiness, user-friendliness, and reliability of the monitor; direct comparisons to other monitoring data, as were performed in the laboratory and field tests, were not part of this assessment.

VRC staff reviewed an operating manual prepared for the monitor, as well as instructions on use of the HOBO dataloggers and HOBO Shuttle transfer device. They operated the monitor in a laboratory setting for familiarization, and then in two different residential kitchens for periods of 12 and 24 hours, respectively. Data collected with the HOBO dataloggers were downloaded and plotted. VRC staff then summarized their observations and recommendations, in a report which is included as Appendix C of this final report. Based on VRC's comments, the brief operating manual for the monitors was revised; the revised version is included as Appendix D of this report. The key findings of the VRC assessment are presented in Section 3.3.3 of this report.

2.3.3 Final Field Testing - California

Final field testing was conducted primarily in two occupied homes and one restaurant in southern California from April 5 to 16, 1999. In these field tests, data from the electrochemical NO_2/HONO monitors were compared to those from a conventional chemiluminescent nitrogen oxides monitor, equipped with its own HOBO datalogger to record NO and NO_x (= NO + NO_2) data. Field testing focused primarily on realistic operation of gas cooking and heating appliances, as indoor sources of NO_2 and HONO. In the testing in the restaurant, no change from normal business activities occurred as a result of the testing conducted.

For this field testing, Battelle directed Valley Research Corporation (VRC) of North Hills, California, to locate appropriate test sites. The specific requirements for these sites were:

- One residence and a public building were to be located in an area where outdoor NO_2 levels are high and may affect indoor NO_2 levels,
- Another residence was to be in an area where outdoor NO_2 levels are low.
- The residences and the public building were to have indoor combustion sources of common design in frequent use. For the residences this meant gas ranges used for cooking and/or unvented combustion heating appliances such as gas space heaters. For the public building, this requirement implied restaurants or shops using gas combustion for cooking, or the presence of other combustion sources.

The South Coast Air Quality Management District (SCAQMD) monitors the ambient air quality in 38 areas covering most of four major Southern California counties (Los Angeles, Orange, Riverside, San Bernardino). VRC obtained this monitoring data for the most recent year available (1997) in order to classify areas as having low, medium, or high outdoor NO_2 concentrations. Table 1 lists the reported NO_2 concentrations for the 21 areas where NO_2 was monitored, in order of decreasing NO_2 levels. Of these areas, "Central LA" reported the second highest Annual Arithmetic Mean (AAM) at 0.0430 ppm, and "N Coast Orange" reported the third lowest AAM at 0.0199 ppm. The SCAQMD reported AAM range is 0.0158-0.0433 with the federal standard set at 0.0534 ppm.

TABLE 1. ANNUAL ARITHMETIC MEAN (AAM) OF NO_2 IN SCAQMD MONITORING AREAS

SCAQMD Monitoring Area (Area Number)	NO_2 (ppm)
Pomona.Wln V 1 (10)	0.0433
Central LA (1)	0.0430
S Cent LA Co (12)	0.0428
E Sn Fernan V (6)	0.0424
Cent SB V 1 (20)	0.0365
S Sn Gabrl V (11)	0.0363
Cent SB V 2 (21)	0.0353
NW SB V (19)	0.0341
W Sn Gabrl V (7)	0.0341
E Sn Gabrl V1 (8)	0.0338
S Coast LA Co (4)	0.0333
Cent Orange Co (14)	0.0332
N Orange Co (13)	0.0329
E Sn Gabrl V2 (9)	0.0300
NW Coast LA Co (2)	0.0285
SW Coast LA Co (3)	0.0280
Metro Riv Co 1 (16)	0.0262
W Sn Fernan V (5)	0.0260
N Coast Orange (15)	0.0199
Lk Elsinore (17)	0.0165
Coachella V 1 (18)	0.0158

The "Central LA" and "N Coast Orange" monitoring areas were of interest because, to maximize the likelihood of acceptance of the testing, VRC focused on potentially "friendly" candidate sites. For residential sites, this meant identifying personal contacts of VRC staff, living in residences which matched the site requirements. For the public site, this meant identifying local businesses with long-standing reputations for involvement in the community, but also having locations which matched the site requirements. Family-run businesses were sought in the hope of obtaining a rapid decision on participation as a field test site. Identification of "friendly" sites enabled successful testing and provided convenience to the field testing crew (e.g., able to ship equipment directly to the first site rather than to VRC's office or other location).

Figure 1 shows the location of the three chosen field test sites with respect to SCAQMD monitoring areas. Provided below are specific descriptions of each site.

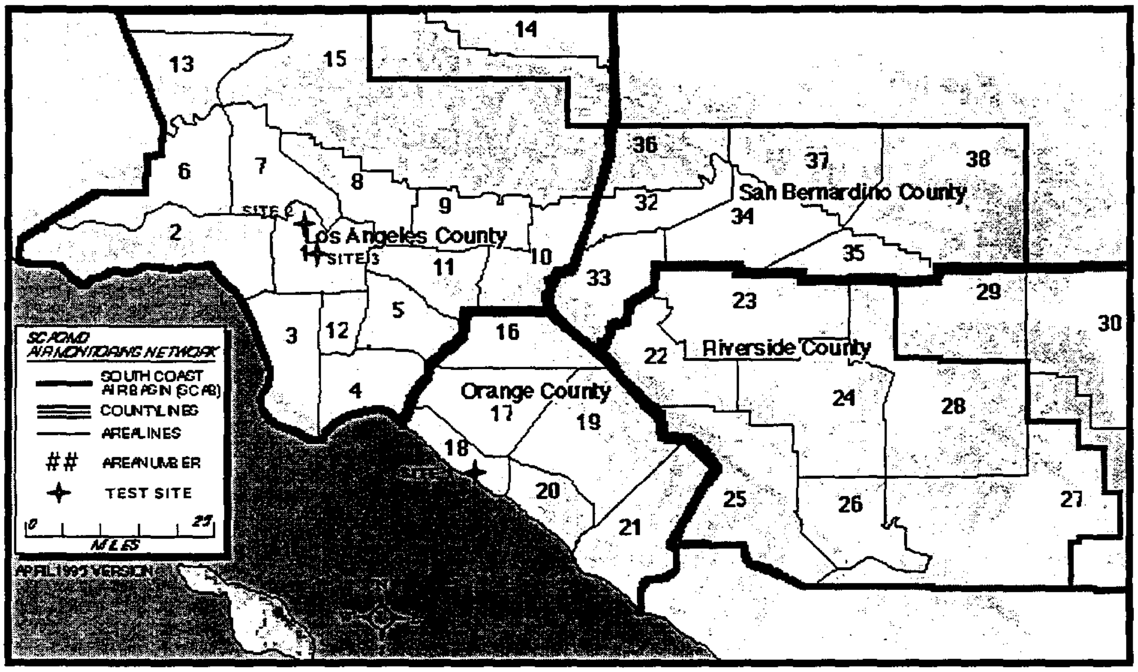


FIGURE 1. THREE FINAL TEST SITES AND SCAQMD MONITORING AREAS

Residence One (testing April 5-8, 1999)

Location:	Drake Ave., Costa Mesa, CA 92626. In a suburban coastal community about 30 miles south of Los Angeles. In SCAQMD's "N Coast Orange" monitoring area.
Description:	Single family residence with secured backyard. Gas oven, gas range, gas central heater, gas water heater.

Residence Two (testing April 9-12, 1999)

Location:	Glendale Blvd., Los Angeles, CA 90026. In an urban community about 1 mile northwest of downtown Los Angeles. In SCAQMD's "Central LA" monitoring area.

Description: One bedroom apartment in 4-unit multi-family complex with patio but no backyard. Gas oven, gas range, gas wall heater.

Public Location (testing April 12-15, 1999)

Location: Delicatessen,, Los Angeles, CA 90057. In an urban community about 1 mile west of downtown Los Angeles. In SCAQMD's "Central LA" monitoring area.

Description: Delicatessen restaurant with no outside area. Gas ovens and ranges throughout the kitchen area.

The sites identified above were used in the order listed for field testing of the NO_2/HONO monitors. The following are summaries of the characteristics and activities of each test. The house in Costa Mesa was a single family ranch located within a housing development. This home had an attached garage, a fenced-in back yard, and a combined kitchen and dining room. Figure 2 shows a layout of the house.

The sampling was performed at 1.5 m above the floor, near the range top, at the wall that divided the kitchen and living room. Figure 2 shows that the kitchen and the dining room were separated by only a countertop bar, and that the kitchen and dining room were connected to the living room by a five foot wide opening. The sampling point was positioned at the intersection of these three living areas. The sampling equipment consisted of three second generation NO_2/HONO monitors and a Monitor Labs 8840 conventional chemiluminescent nitrogen oxides analyzer. Figure 3 shows an overhead view of the manner in which the monitors were positioned at each site. The 8840 was placed on the floor, and the three Battelle electrochemical monitors were placed on top of it, so that the footprint would be as small and unobtrusive as possible. The vacuum pump, used with the 8840 was located next to that instrument. The three electrochemical monitors sampled from a common inlet line, that extended to the same point as the separate inlet line for the 8840.

The sampling procedure was similar at each site. First, each monitor was set up, allowed to stabilize, and a zero reading was obtained. Then, the monitors sampled and recorded data indoors for two days continuously. During these two days, the residents went about their normal daily activities, including cooking with the rangetop and oven. Periodically, all the monitors were zeroed and the recorded data were downloaded from the HOBO data loggers to a laptop PC. The data were immediately graphically displayed, to ensure that the monitors were functioning as expected. After approximately two days of indoor sampling, the instruments were relocated to

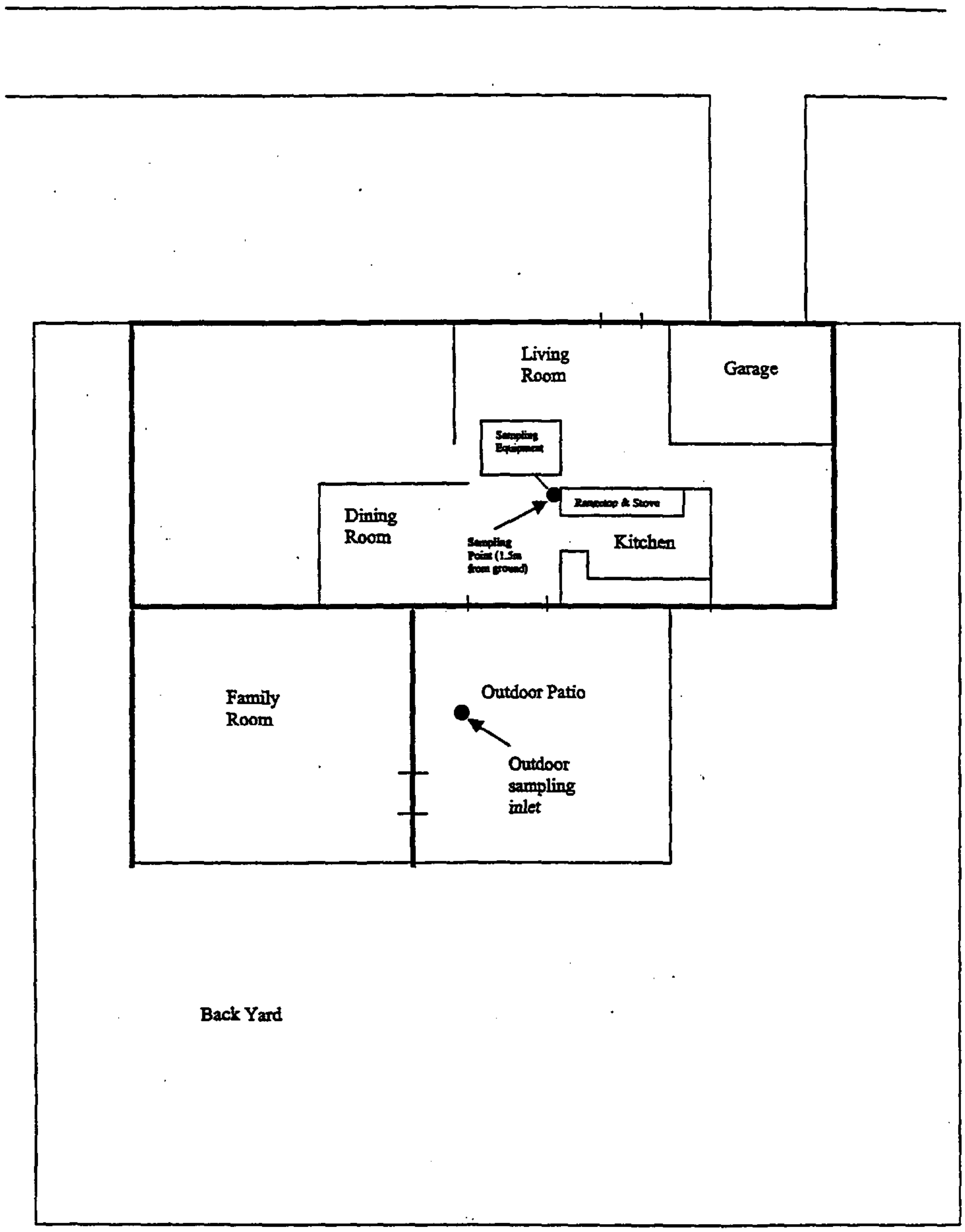


FIGURE 2. SCHEMATIC OF SAMPLING AREA AND LAYOUT OF SINGLE FAMILY HOME USED AS FIRST SITE FOR FINAL FIELD TESTING

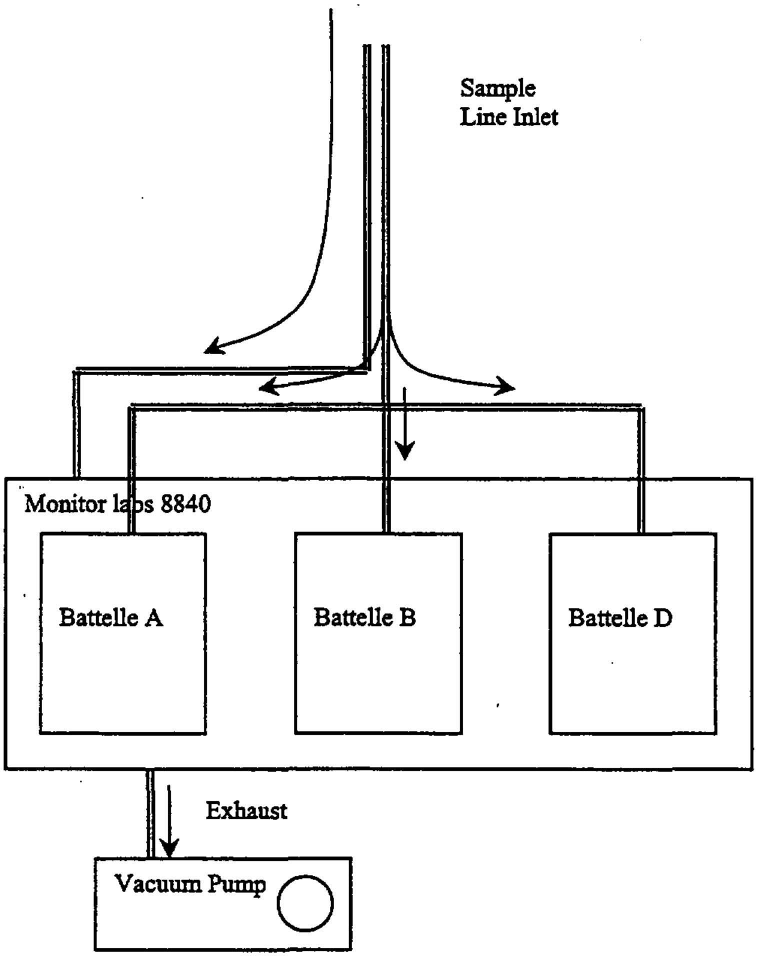


FIGURE 3. SCHEMATIC SHOWING SAMPLING EQUIPMENT AND SAMPLING MANIFOLD ARRANGEMENT USED IN FIELD TESTS

the covered patio and sampled outdoor air for one day, again near breathing height (1.5 m). Periodically, the monitors were zeroed and the data were downloaded to the laptop and displayed graphically. Table 2 lists the activities that may have affected the measured NO_2 concentrations, and their times of occurrence.

The Los Angeles apartment was located near the center of L.A. along a four lane road. The apartment was on the second floor. The layout of the apartment is shown in Figure 4. The monitors were placed on the floor within four feet of the sampling inlet. For the first day, the sampling inlet for the monitors was centered in the kitchen over the oven, and placed about 3 feet above the surface of the rangetop (sampling point #1 in Figure 4). The next day the sampling equipment was moved to the living room and the gas wall heater was turned on (sampling point #2 in Figure 4). Finally, the sampling inlet was moved outdoors, hung out of the second story window approximately one foot from the apartment's outer wall (sampling point #3 in Figure 4). Periodically during the sampling period, the instruments were zeroed and the data were downloaded and displayed to ensure the monitors were functioning properly. Normal daily activities, as noted in Table 2, were conducted.

The final sampling site was a delicatessen located on a busy street corner in downtown L.A. Sampling in the deli was conducted in the workers' area, between the grill and the dish washing area. The conventional analyzer and the electrochemical monitors were placed on a shelf, above the working area, and the sampling inlet was located at a height of 2 m above the floor. Figure 5 shows a layout of the restaurant and the sampling position. Again, periodically throughout the day, zero measurements were made, and the data were downloaded and checked. There was no outdoor sampling at this location.

2.3.4 Final Field Testing - Columbus, Ohio

In the California field testing described above, contrary to the test plans, a carbonate-coated filter was never inserted into the sampling line of the conventional nitrogen oxides monitor. Thus HONO was always present in the air sampled by the conventional monitor, and contributed to that monitor's indicated NO_2 levels. Consequently, it was not possible to directly compare NO_2 data from the conventional instrument to NO_2 data from the filtered channels of the three electrochemical monitors. Comparisons of data from the California field tests could only be made in terms of the NO_2 + HONO total determined by the different types of monitors. To

TABLE 2. SUMMARY OF TESTING ACTIVITIES IN THE CALIFORNIA FIELD TESTS

Location/Date	Local Time of Day	Cooking or Test Activity
Home		
April 5	3:30 PM	Began to install equipment in home, and readying for field test.
April 6	09:30 AM	All systems functioning. Took photos of setup.
	10:09 AM	Began data acquisition.
	10:25 AM to 10:35 AM	Zeroed NO2/HONO monitors using charcoal trap.
	10:35 AM to 10:45 AM	Zeroed 8840.
	10:4 5AM to11:03 AM	Heating water for tea, and cooking spaghetti sauce, using four rangetop burners.
	11:30 AM to 11:55 AM	Oven on.
	3:00 PM to 3:15 PM	Two burners operated.
	3:55 PM to 4:00 PM	One burner operated.
	4:40 PM to 4:45PM	One burner operated.
	5:25 PM to 6:00 PM	Two burners operated.
	5:45 PM to 6:00 PM	Oven on.
	8:18 PM to 8:25 PM	Used one burner.
April 7	6:40 AM to 6:50 AM	Used one burner.
	9:25 AM to 9:45 AM	Heating water for tea on three burners.
	3:25 PM to 3:30 PM	Ran three burners.
	5:35 PM	Moved all sampling equipment to outside sampling location.
April 8	09:13 AM	All units operating normally; ended data acquisition.
Apartment		
April 9	1:00 PM	Wall Heater is on.
	1:00 PM to 1:15PM	One burner to cook pasta. Turned on Oven.
	1:36PM to 1:41PM	Turned two burners on high.
April 10	9:40 AM to 10:00 AM	Oven on.
	9:45 AM to 955AM	One burner to cook eggs.
	5:55PM to 6:20PM.	Oven on cooking a pizza.
April 11	10:00AM to 10:10AM	One burner to cook tea.
	10:30AM to 10:37AM	Operated three burners.
	5:50 PM to 8:00 PM	Turned on wall heater to medium.
	5:52PM to 6:10PM	Turned on oven to cook pizza.
	8:00 PM	Moved testing equipment in position to sample outdoor air.
April 12	1:24 PM	Stopped sampling, ended data collection.
	1:30 PM	Packed up equipment for move to next location.
Delicatessen		
April 12	2:00 PM	Set up equipment at delicatessen.
	2:34 PM	Began data acquisition. Normal cooking activities.
April 13	All day	Normal cooking activities and outdoor traffic. Sampled and downloaded data.
April 14	All day	Normal cooking activities and outdoor traffic. Sampled and downloaded data.
April 15	3:05 PM	Stopped sampling, ended data collection.

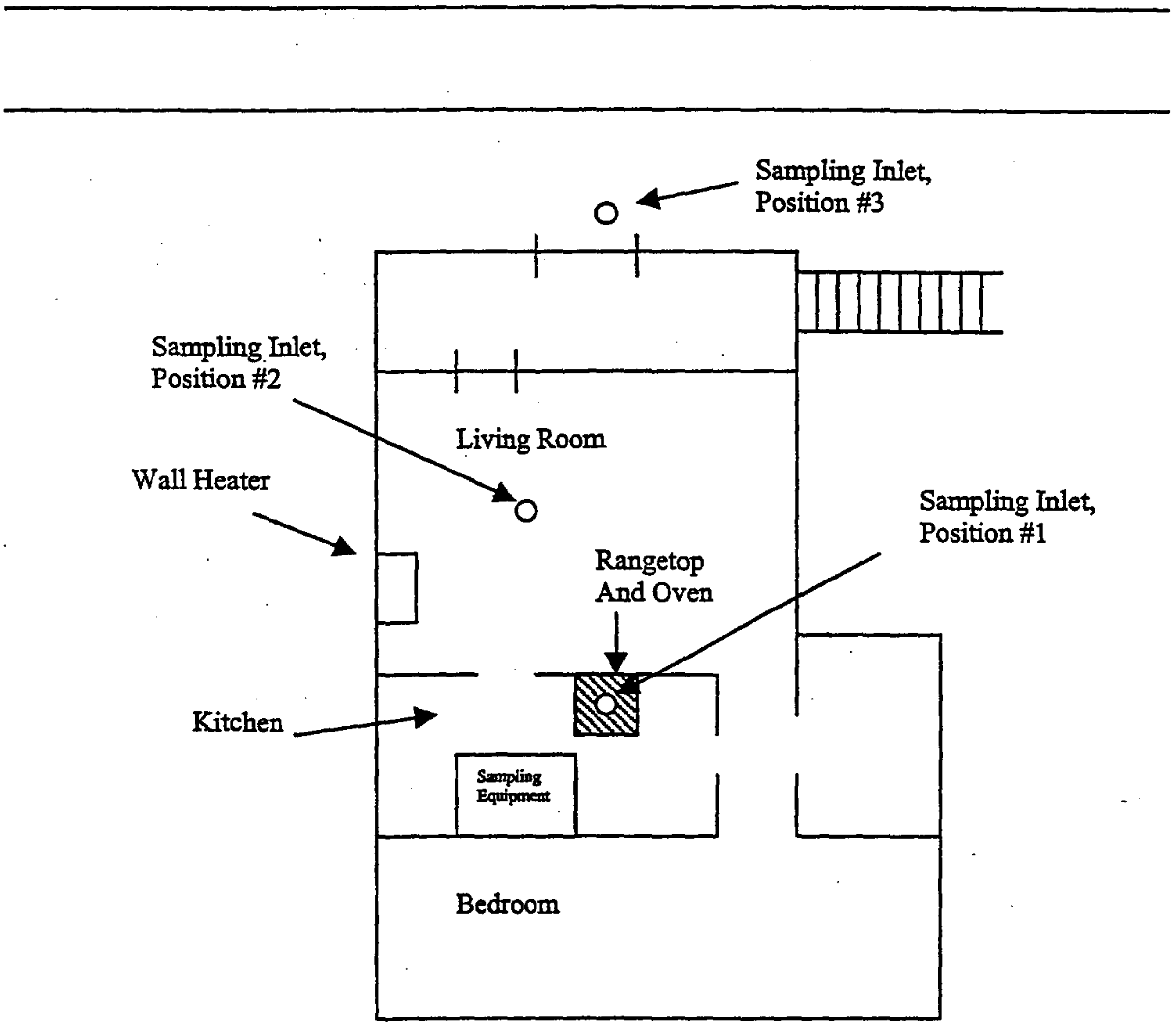


FIGURE 4. LAYOUT OF SECOND STORY APARTMENT USED AS SECOND SITE FOR FINAL FIELD TESTING

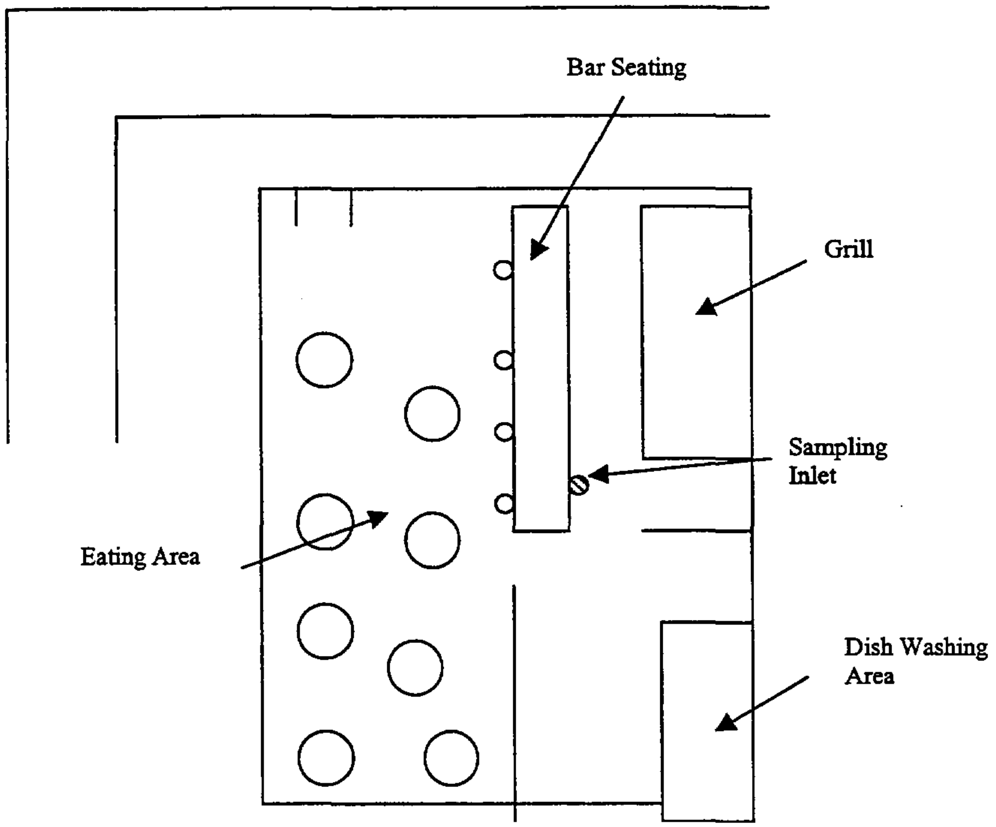


FIGURE 5. SCHEMATIC OF TEST LOCATION IN DELICATESSEN USED AS THIRD SITE IN FINAL FIELD TESTING

correct this shortcoming, two additional days of sampling were carried out in an occupied home at 4th Street and Neil Avenue in Columbus, Ohio, on May 30 and 31, 1999. Emissions from use of the gas range were sampled by the NO_2/HONO monitors and by the same conventional monitor used in the California field tests. However, a carbonate-coated filter was always present on the inlet of the conventional monitor. As a result, the data from this field test were used solely to compare NO_2 data from the two types of monitors. In this testing the monitors were located on the floor of the kitchen, with the Teflon inlet tubes for all monitors extending to a point about 1 m above the front edge of the gas rangetop. Normal cooking activities were carried out in this home, but no heating appliances were in use.

3.0 RESULTS

This section reports the results of the NO_2/HONO monitor development and testing. The assembly of the prototype monitors, and initial laboratory testing, are described in detail in the First Interim Report which comprises Appendix A; the results of those efforts are summarized in Section 3.1. Initial field testing, extensive further laboratory testing, and recommendations for additional development of the monitors, are detailed in the Second Interim Report which comprises Appendix B; those results are summarized in Section 3.2. The results of final laboratory tests and final field tests are described in Section 3.3.

3.1 Summary of Results from the First Interim Report

The foremost results of the work described in the First Interim Report (Appendix A) were the basic validity of the two-channel approach to NO_2/HONO measurement, and the consequent usefulness of the prototype monitors built upon that approach. The carbonate-coated filters were found to be completely effective in removing HONO from the sample air, allowing its separation from NO_2. The filters did, however, result in a somewhat lower response to NO_2 in the filtered channel of operation than in the unfiltered channel. This difference is not due to removal of NO_2 by the carbonate-coated filter, as tests with a chemiluminescent analyzer proved. Instead, this behavior is believed to result from the pressure drop induced by the filter when inserted into the sample flow path. This behavior requires calibrating the NO_2 response in both channels of the monitor, whereas the HONO response needs to be calibrated only in the unfiltered channel.

The three prototype monitors were tested for linearity of response to NO_2 over the range of 50 ppbv to 3 ppmv, and were found to provide linear response up to saturation of the output of their amplification circuits, near 1.8 V output. The detection limit for NO_2 was as low as 10 ppbv with a new sensor under ideal conditions, but a 20 ppbv detection limit is more typical of normal operating conditions. The TSI sensors used in the monitors were found to exhibit both consistent and individual behavior. For example, although all showed linear response to NO_2, the sensitivities in mV output per ppbv NO_2 input varied among the three monitors from about 0.4 to about 0.8. In turn, the maximum linear ranges of the three monitors (i.e., the maximum concentration measurable without saturation) ranged from about 2 ppmv to well over 3 ppmv. As was found in previous work,[6,15] the sensitivity to HONO was considerably larger than that to NO_2. HONO sensitivity was also found to be more uniform than the NO_2 sensitivity from one monitor to another, ranging from 1.48 to 2.05 mV/ppbv. The time response of the monitors to a step change in NO_2 or HONO was found to be less than two minutes, more than sufficient to meet the monitoring needs outlined in Section 1.1.

The monitors' response to a variety of individual potential interferents was tested, at interferent levels greatly exceeding those likely to be present in any indoor environment. No significant interference was found from carbon monoxide (CO), carbon dioxide (CO_2), formaldehyde (HCHO), sulfur dioxide (SO_2), or nitric acid (HNO_3). The response of the TSI sensors to NO was found to be at least 70 times lower than that to NO_2, indicating minimal interference even at an elevated indoor NO level of 1 ppmv. Response to peroxyacetyl nitrate (PAN) was unclear, but even in the worst case will not be a significant interference in indoor NO_2 or HONO measurements. Ozone (O_3) produced a response equivalent to that from an equal concentration of NO_2, but with a very slow time response. In many cases, interference from ozone will be unlikely because of the presence of indoor combustion sources of NO and NO_2. However, in some locations with high outdoor ozone levels, indoor O_3 could be significant when combustion sources are not operating.

An initial test of the dependence of NO_2 response on relative humidity was conducted, over an RH range of 5.5 to 38 percent at room temperature. A consistent increase of 11 to 12 percent in NO_2 sensitivity with increasing RH was found for all three monitors over this RH range.

The sensitivity of the monitors to NO_2 was found to decrease with time, at rates ranging from 20 to 40 percent loss per month. This decline in sensitivity was much greater than that stated by the manufacturer (i.e., 5 percent/month), and could not be attributed to the conditions of use, which were always well within the range of recommended conditions. Despite this decline in sensitivity, the overall performance of the NO_2/HONO monitors was judged sufficient to justify initial field testing.

3.2 Summary of Results from the Second Interim Report

The Second Interim Report (Appendix B) describes the initial field tests in the Chicago research house, and additional laboratory tests on the three prototype monitors. The laboratory tests included temperature, humidity, and interference checks, and further evaluation of the long-term stability of NO_2 response.

The initial field tests (see Section 3 of Appendix B) produced encouraging yet puzzling results. The monitors exhibited good ruggedness and reliability under difficult field conditions. The HONO results from the three prototype monitors were nearly identical over the entire field period, and furthermore showed very close agreement with HONO data obtained from a conventional chemiluminescent nitrogen oxides monitor. The excellent agreement obtained for HONO, which is determined by a difference measurement with the electrochemical monitors, should indicate good performance of those monitors. However, the NO_2 results from the three monitors did not show close quantitative agreement, either with one another or with the conventional monitor results. The NO_2 results from all three electrochemical monitors were highly correlated with the conventional monitor results throughout the field period (i.e., r^2 values approximately 0.97), but were consistently higher than the conventional monitor results by about 12 percent, 94 percent, and 48 percent, respectively. Despite a review of all calibration and field data, potential interference and temperature/humidity effects, and scrutiny of all test procedures, no explanation has been found for this result. The high correlations between the electrochemical and conventional monitor data suggest an error in data acquisition, rather than a problem with the monitors themselves, but no such error has been identified. The conclusion drawn from the initial field tests was that the performance of the NO_2/HONO monitors was encouraging, but that additional testing with combustion sources was needed.

Calibrations before and after the initial field study showed that the NO_2 sensitivities of the three monitors dropped by up to 50 percent after the field period, but the HONO sensitivities were much more stable, changing by only 10 to 20 percent. This observation indicated that the

HONO response is more stable over time, relative to the NO_2 response, as well as being more uniform from one sensor to another.

Laboratory tests (see Section 4.2 of Appendix B) showed that over the range of conditions likely to be encountered indoors, ambient relative humidity has a greater effect on response than does ambient temperature. For example, an increase in relative humidity from 24 to 84 percent at 21°C caused an increase in NO_2 response of 50 to 70 percent, whereas an increase in temperature from 20 to 30°C caused a 20 to 30 percent increase in response.

Two interference tests (also Section 4.2 of Appendix B) addressed the response of the NO_2/HONO monitors to complex mixtures of species, for comparison to the tests with individual species conducted previously (summarized in Section 3.1 above). These tests were conducted by operating the three prototype monitors in the 17.3 m^3 chamber, in an atmosphere of clean, humidified air. Potential interferent gases were then injected into the chamber one after another. The species tested were NO_2, HONO, NO, CO, CO_2, SO_2, HCHO, O_3, and ammonia (NH_3), at levels exceeding those likely to occur indoors. The results of these tests with complex mixtures were as expected based on the previous single component tests, except that no response was seen when ozone was added to the complex mixture. Ammonia, which had not been tested before, produced no response.

Two tests were also done of the long-term stability of electrochemical sensor response for NO_2. In the first (Section 4.1 of Appendix B), the stability test described in the First Interim Report was continued. This test showed that NO_2 sensitivity tended to stabilize at low values after three months of use. The second test evaluated the stability of NO_2 response for a set of new sensors obtained in March of 1998, and matched within 3 percent in initial sensitivity. Over 48 days of testing, these matched sensors exhibited loss of NO_2 response at rates of 19 percent, 20 percent, and 25 percent per month, respectively. These rates of decline are somewhat lower, and much more consistent, than those observed in previous testing with unmatched sensors (Section 3.1, above).

A test of humidity dependence was also conducted with these new sensors, and showed NO_2 response increasing by from 19 to 43 percent as RH increased from 19 to 74 percent at room temperature. These results indicate a smaller dependence of NO_2 response on humidity than was found with earlier, unmatched sensors (above, this section), but also confirm the observation of individual behavior from even matched sensors.

The tests reported in the Second Interim Report (Appendix B) established the advantages and disadvantages of the prototype NO_2/HONO monitors. Advantages included the small size, weight, and cost of the monitors; their fast and linear response; the near absence of interferences; and the high sensitivity to HONO. Disadvantages included the long-term decay of the NO_2 sensitivity; the unit-to-unit variability of the electrochemical sensors; their temperature and humidity dependence; the need for an external data system; and the complexities of processing the two-channel data to determine HONO by difference. Recommendations to improve the monitors included adding a miniature datalogger to the instrument; correcting for or controlling the humidity and temperature dependence; improving the physical assembly of the monitors; adopting single-channel operation for NO_2, with only occasional HONO measurements; and developing a zero trap and ozone scrubber. As will be discussed in the next section, most of these improvements were carried out, and other improvements were also developed. Further field testing was also required as part of the original research plan, in order to assess the real-world performance of the monitors.

3.3 Final Testing and Development of the NO_2/HONO Monitors

3.3.1 Assembly of Second-Generation Monitors

To address the recommendation from the Second Interim Report to improve the physical assembly of the NO_2/HONO monitors, four second-generation monitors were assembled. These followed the same basic design shown in Figure 1 of Appendix A, but used a larger and stronger chassis, 30 cm W x 20 cm H x 25 cm D, with a handle that made it easier to carry the monitor. The same locations of switches, indicator lights, and internal components were used, but the larger chassis allowed more room and better access for those components. The recommendation from the Second Interim Report (Appendix B) to adopt single-channel operation was not implemented, because the capability to monitor HONO was judged by CARB to be an important feature of the monitors. Thus the second-generation instruments had the same two-channel configuration as the prototype instruments, illustrated in Figure 1 of Appendix A. The weight of each second-generation monitor was 4.8 kg.

The recommendations to add on-board data acquisition, and to address the humidity and temperature dependence of the NO_2 sensors, were both addressed by incorporating HOBO dataloggers into each monitor. One HOBO was used to record the analog outputs of the two measurement channels of the monitor. The other was equipped with temperature and relative humidity sensors. Instead of attempting to control the temperature and relative humidity of the incoming sample air, this HOBO simply monitors the temperature and RH conditions under which the NO_2 sensor is operating, so that collected data can be corrected in data processing. In the field testing reported here, the temperature and RH corrections opposed one another and produced an overall correction of about 15 percent or less. This magnitude of correction is to be expected in the great majority of indoor measurements, and could be neglected if data accuracy is not critical.

In each monitor, both HOBOs were installed using Velcro fastening strips behind the front panel of the monitor. Two input jacks for the HOBO used to record the analog output data were connected to the two sets of analog output terminals on the back panel of the monitor. The HOBO used to record temperature and RH data was positioned next to the Teflon block containing the electrochemical sensor. In this position, the HOBO is at the same temperature as the sensor, and since the sensor is exposed to a flow of the same ambient air that surrounds the entire monitor, the HOBO also is exposed to the same relative humidity. Thus the HOBO measurements can be used to correct the sensor's response.

A summary of the components used to assemble the second-generation NO_2/HONO monitors is shown in Table 3. The total cost of the components is about $1,225. Construction of one monitor requires about 80 hours of labor; construction of multiple units simultaneously greatly reduces the labor effort per unit. In normal use, maintenance costs are essentially limited to occasional replacement of the electrochemical sensor to maintain adequate sensitivity.

The recommendation for a zero trap was readily implemented using a simple container of activated charcoal which can be attached directly to the inlet of the monitor. This trap efficiently removes both NO_2 and HONO from the sample air stream. This trap was used in the final field testing conducted in California and in Columbus. The recommendation to develop an ozone removal trap was not pursued, in part because of the difficulty of removing ozone from the sample air without also removing the NO_2 and HONO. In addition, such a trap was judged of low importance for indoor monitoring in the presence of combustion sources, because in that environment ozone is likely to be absent, due to its reaction with NO.

TABLE 3. COMPONENTS OF SECOND-GENERATION NO_2/HONO MONITORS

Component	Approximate Cost ($)
Chassis	80
Sensor	175
Amplifier Circuit	250
Relay	100
Solenoid Valve	50
Timer	100
HOBO Dataloggers	200
Power Supplies (12 V, 9V)	30
Air Pump	50
Rotameter	10
Filter Holder	50
Tubing and Fitting	60
Switches, LED's, etc.	70
TOTAL	1,225

The requirement for additional field testing was met by the California and Columbus field tests. This required activity was expanded to also include additional chamber testing with small combustion sources, with an emphasis on NO_2 determination. The reason for this addition was the unexplained disagreement found for NO_2 data in the initial field tests (Section 3.2). This issue was specifically addressed by two chamber tests, described in the next section.

Minor problems were also found during the assembly of the second-generation monitors. The Teflon three-way valves failed in two of the monitors, and the air pump in one of the monitors. These were replaced, but one of the replacement valves also failed. More rugged components were later identified, and should be used in any subsequent assembly of the monitors. The electronic amplifier circuits supplied by TSI were also found to be troublesome. These circuits perform a wide range amplification and conversion of the sensor current to a voltage output, and thus are prone to electronic noise. This problem was seen in the prototype units, but was minimized by selection of the quietest circuits from among several on hand. Discussion with electronics staff at Battelle indicated that a quieter circuit could be designed, but this effort was not feasible within the current project. Such an improvement would be valuable in any subsequent development. In the present effort, one of the amplifier circuits became so noisy that it was not possible to use the monitor in the final chamber or field testing described in subsequent sections. Nevertheless, testing with the other three second-generation monitors was sufficient to assess the performance of the units.

3.3.2 Final Chamber Testing

To assess the monitors' ability to determine NO_2 from combustion sources, and to attempt to explain the anomalies in NO_2 measurements found in the Chicago research house, two tests were conducted in December of 1998, using a commercial gas range in the 17.3 m^3 chamber. Three of the second-generation monitors were located inside the chamber, and their internal HOBO data loggers were used to record response data as well as temperature and relative humidity. A Monitor Labs 8840 chemiluminescent nitrogen oxides monitor located outside the chamber sampled from the same point in the chamber as the four monitors, and was used to obtain data for comparison. In the first test a single gas burner was operated on a Medium setting. An NO_x level of about 750 ppb was produced in the chamber after about 10 minutes of burner operation. The burner was then turned off, and levels decayed slowly during the next three hours as the chamber was purged. The second test then began, in which two burners were operated on a High setting, producing about 1,400 ppb of NO_x after five minutes of operation. That test also continued for three hours. Evaluation of the results of the chamber tests shows that the monitors functioned as expected, and the HOBOs recorded all data properly.

Data comparisons were done for units B and D (which had normal two-channel operation in the chamber tests) and unit A (which was fixed in the filtered, or NO_2, measurement mode because of a problem with the three-way valve). Table 4 shows the sensitivities of the active modes of these three monitors as calibrated for the chamber test, in mV of response per ppbv of NO_2. The chamber tests show good results, in that the monitors agree well among themselves and relative to the conventional monitor in determining NO_2 from the gas combustion source used in the chamber test.

TABLE 4. NO_2 SENSITIVITIES OF THE THREE MONITORS USED IN THE DECEMBER 1998 CHAMBER TESTS

	Sensitivity in mV/ppbv		
	Monitor A	Monitor B	Monitor D
Filtered	0.453	0.393	0.414
Unfiltered	--[a]	0.581	0.533

a: This mode inoperable in this monitor.

The NO_2 data from the chamber tests is shown in Figure 6, which plots the NO_2 values determined by the three monitors against the time of day during the chamber tests. The two separate tests are evident from the two peaks in the NO_2 levels; a single burner on medium setting produced over 400 ppbv of NO_2, and two burners on a high setting produced over 700 ppbv of NO_2. The data from the three monitors are plotted as data points, and overlap one another. Also shown as a solid line is the NO_2 signal of the conventional monitor (Monitor Labs 8840). Note that the NO_2 response shown for the 8840 in Figure 6 is really the sum of NO_2 and HONO: sharp decreases or increases in the conventional data were observed at times when a carbonate-coated filter was respectively added to or removed from the analyzer's inlet, due to the removal of HONO with the filter in place. The comparison of HONO data is presented below. Figure 6 shows good agreement among the results, a situation that is clearly different from the unexplained differences found in testing in the Chicago research house earlier in this program.

Figure 7 shows that the three monitors used in the tests agreed very well with one another: that figure shows the NO_2 results from monitors A and D plotted against the simultaneous NO_2 results from monitor B. The 1:1 line is shown, and it is evident that all three monitors measured very nearly the same NO_2 values. Figure 8 shows a different comparison, displaying NO_2 data from one of the monitors (Unit A) in comparison to the 8840 data. The 1:1 line is shown as the solid line, and the dashed line is the linear regression, which has the form:

$$\text{Unit A } NO_2 = 1.01\ (8840\ NO_2) + 9.4 \text{ ppbv, with } r^2 = 0.956.$$

The corresponding regressions for Units B and D have the forms:

$$\text{Unit B } NO_2 = 1.07\ (8840\ NO_2) + 8.5 \text{ ppbv, with } r^2 = 0.924.$$
$$\text{Unit D } NO_2 = 1.11\ (8840\ NO_2) - 1.8 \text{ ppbv, with } r^2 = 0.914.$$

These results show close agreement between the monitors and the conventional method for NO_2 determination. This agreement indicates that the electrochemical monitors are capable of accurate measurement of NO_2 at levels associated with operation of combustion sources indoors.

Figure 9 shows a comparison of the HONO results from monitors B and D, and from the conventional monitor when the carbonate filter was added to or removed from the inlet. In general, the HONO levels were quite low, because of the clean surfaces in the chamber and the

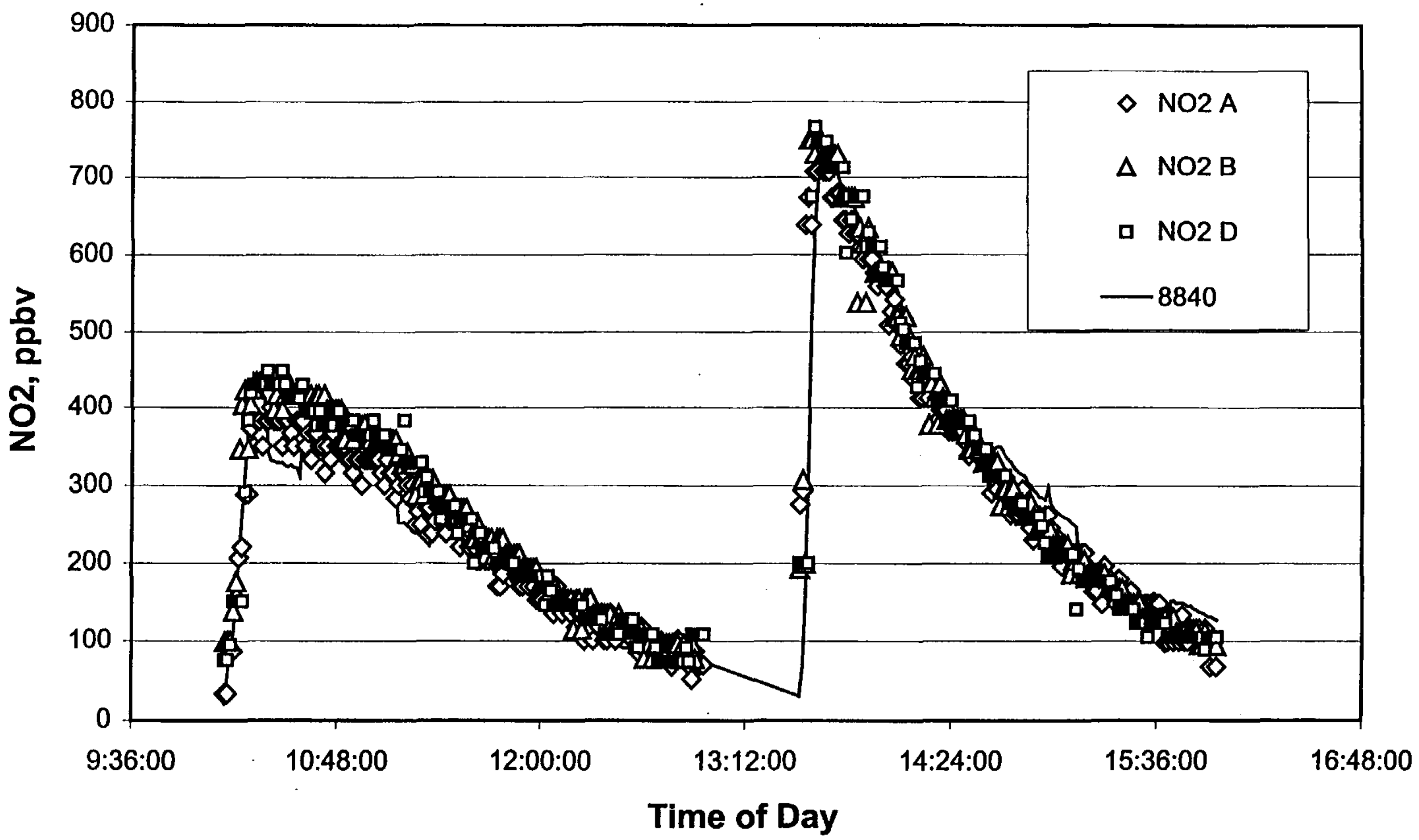


FIGURE 6. COMPARISON OF NO_2 FROM THREE MONITORS AND A CONVENTIONAL ANALYZER IN TESTS IN A 17.3 CUBIC METER CHAMBER

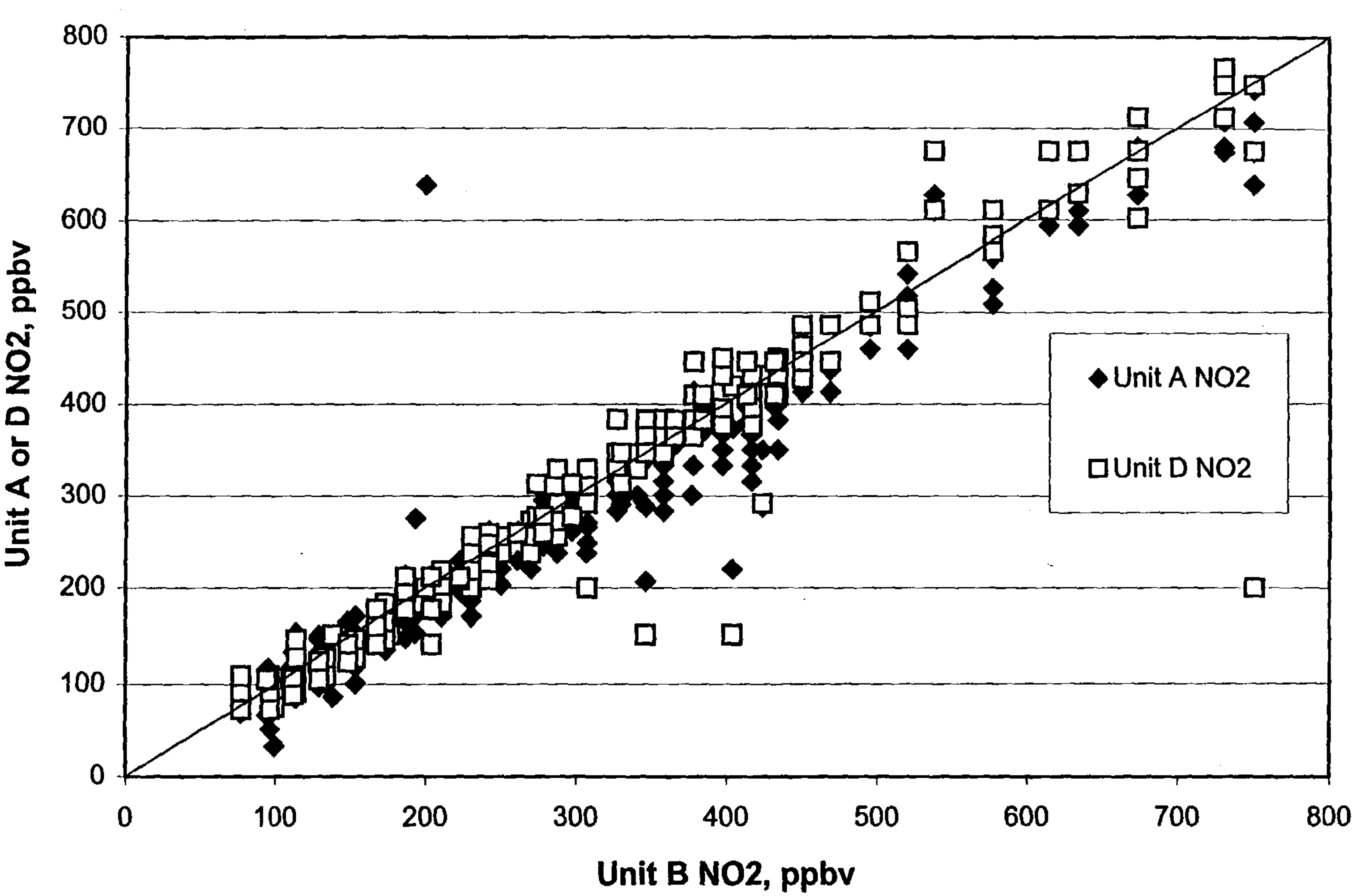


FIGURE 7. COMPARISON OF UNITS A AND D NO_2 VS UNIT B NO_2 IN TESTS WITH GAS COMBUSTION SOURCE IN A 17.3 CUBIC METER CHAMBER

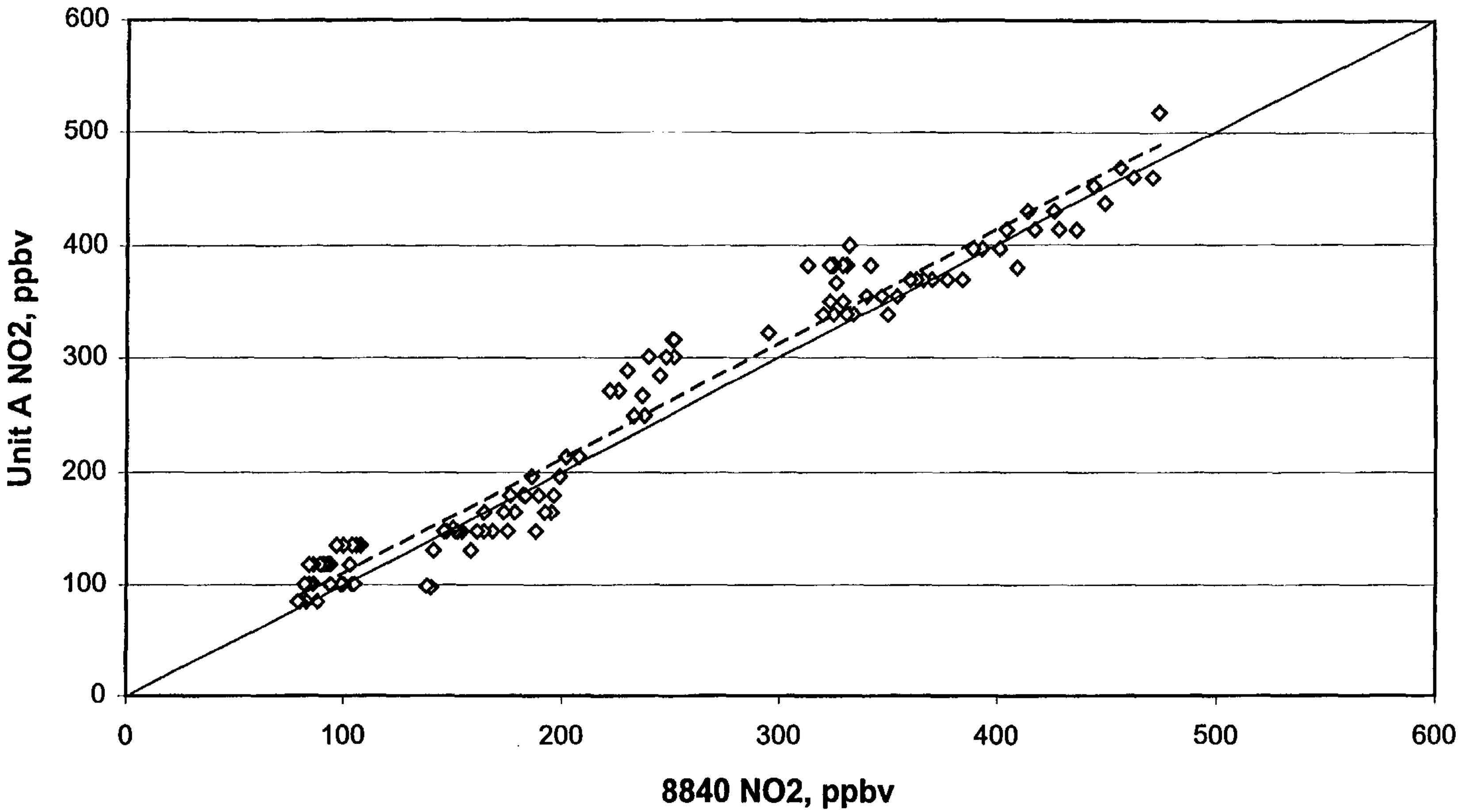


FIGURE 8. COMPARISON OF UNIT A NO_2 WITH CONVENTIONAL NO_2 FROM TESTS WITH A GAS COMBUSTION SOURCE IN A 17.3 CUBIC METER CHAMBER

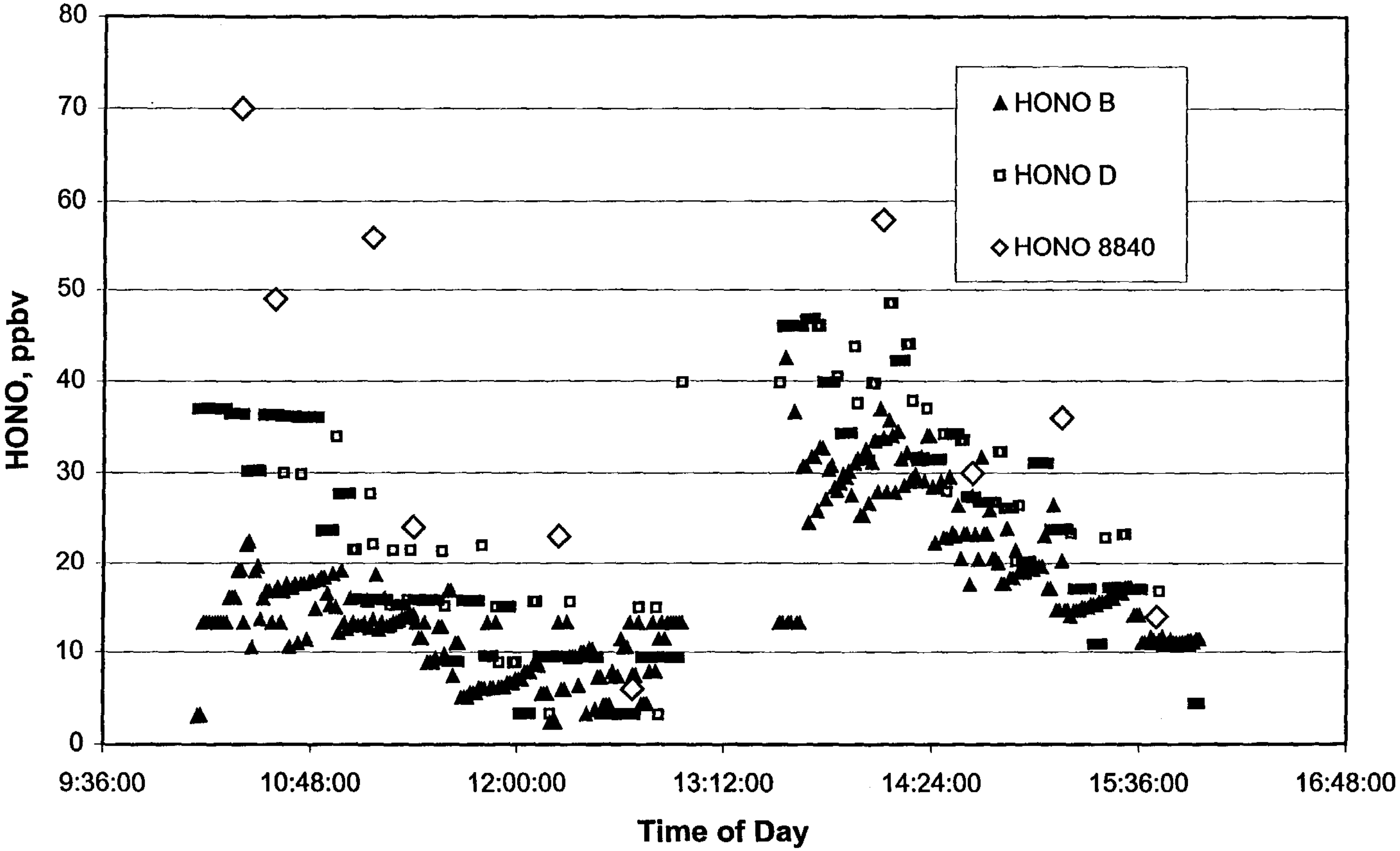


FIGURE 9. HONO DATA FROM TWO MONITORS AND A CONVENTIONAL ANALYZER IN TESTS WITH A GAS COMBUSTION SOURCE IN A 17.3 CUBIC METER CHAMBER

relatively short duration of the tests, which did not promote extensive HONO formation other than that emitted in the flame itself. The HONO results from the two monitors agree well with each other, but the conventional HONO data are somewhat higher, especially at the start of the first combustion test. This may indicate that some initial equilibration was needed at the start of the tests, since HONO agreement later in the test was good. The general finding of the chamber tests is good performance from the monitors, with no indication of any unusual effect of gas combustion that would invalidate measurements by the electrochemical approach.

3.3.3 Independent Assessment

The report prepared by Valley Research Corporation based on their assessment of one of the monitors is included as Appendix C. The primary finding of the assessment was that the monitor was reliable, easy to use, and appeared ready for field use. The following recommendations address relatively minor features of the monitor's design:

- Provision of better hardware for data transfer and greater convenience, such as longer cables, a small screwdriver, a carrying case, and better instructions on using a PC serial port for data transfer.
- An improved set of operating instructions, especially in the area of data collection, downloading, and transfer to the PC.
- Improved guidelines for use of the charcoal zeroing trap, and for positioning the instrument for monitoring.

Furthermore, it was also apparent from the VRC report that the instructions in the original operating manual were not complete, because only one channel of data was downloaded by VRC staff from each HOBO in the monitor. One of the HOBOs records two channels of analog data, and the other records both temperature and RH, but only one channel of analog data and the temperature data were reported by VRC. Accessing multiple data channels from a single HOBO is easily done using the software that runs the HOBO Shuttle, but clearly that information was not provided to VRC in the manual.

The revised operating manual included as Appendix B was modified to address several of the deficiencies noted above. Others, regarding hardware, will be addressed in future use of the NO_2/HONO monitors.

3.3.4 Final Field Testing – California

The final field tests were conducted in the three locations identified in Section 2.2.3 between April 5 and April 16, 1999. This field testing was conducted with only monitors A, B, and D, because of continuing problems with the amplification circuit in unit C. These three monitors operated in their normal two-channel automatic mode, allowing determination of both NO_2 and HONO. However, the Battelle field operator mistakenly failed to place a carbonate-coated filter in the inlet line of the conventional nitrogen oxides monitor, at any time during this field period. This departure from the planned procedure meant that the conventional monitor always measured the sum of NO_2 and HONO, and thus no direct comparison could be made with either NO_2 data or HONO data from the field sites. Therefore, the comparison of conventional and electrochemical monitors could only be done on the basis of the total of NO_2 + HONO.

The primary observation from the field testing was that indoor NO_2 + HONO levels were relatively low in all the test locations, despite the location of the monitors close to cooking and other combustion appliances. At all three sites, concentrations exceeded 200 ppbv only during brief periods when combustion sources were in operation. In the home and apartment, the background levels in the absence of appliance use were usually below 30 ppbv, and in the delicatessen background levels were usually about 50 ppbv. The higher background in the delicatessen probably results from the urban street level location of this site, whereas the relatively modest peak levels probably result from the ample ventilation provided in the commercial kitchen. The 10 mV resolution of the HOBO dataloggers led to a pronounced "quantization" of response at the low concentrations observed. However, the monitors showed excellent reliability in the field, and no data were lost as a result of instrument problems.

Table 5 shows the NO_2 sensitivities of the monitors as used in the California field tests. Sensitivities are shown in mV/ppbv, from calibrations done both before and after the field tests. These results illustrate the variable and individual behavior of the electrochemical sensors. The calibration done before the California field tests (Table 5) shows that all three monitors had declined in sensitivity since the final chamber tests (Section 3.3.2, Table 4), with Unit B showing the least decline and Unit A the most. Surprisingly, the calibration done after the California study (Table 5) showed mixed behavior, with in some cases an apparent increase in sensitivity to NO_2, relative to the pre-test calibration. No problems were found in the calibration procedure, and no obvious explanation is known for this unexpected result. It has been hypothesized that the humid environment of the delicatessen kitchen affected the response of the monitors, but this possibility seems unlikely, since efforts early in this program to restore the sensitivity of sensors by humidification were unsuccessful. Furthermore, the apparent increase in sensitivity was not observed in both modes of all three monitors. The behavior shown in Table 5 illustrates the primary shortcoming of the electrochemical sensors, namely the instability of their response. This behavior introduced some uncertainty in the reduction of the California field test data. The approach taken was to apply the sensitivities determined closest in time to the actual field periods. Thus the data from the private home and the apartment were reduced using the pre-test calibration (i.e., 4/1/99, Table 5), and the data from the delicatessen were reduced using the post-test calibration (i.e., 4/22/99, Table 5).

TABLE 5. NO_2 SENSITIVITIES OF THE THREE MONITORS USED IN THE CALIFORNIA FIELD TESTS

Date	Sensitivity in mV/ppbv		
	Monitor A	Monitor B	Monitor C
4/1/99[a]			
Filtered	0.19	0.40	0.22
Unfiltered	0.24	0.46	0.29
4/22/99[b]			
Filtered	0.33	0.32	0.17
Unfiltered	0.44	0.66	0.39

a: Before shipping to California for field tests.
b: After return to Battelle following field tests.

The comparison of NO_2 + HONO data from the California field testing is shown in Figures 10, 11, and 12, for the home, apartment, and delicatessen, respectively. Each figure consists of three parts, a, b, and c, showing the data from monitors A, B, and D, respectively. In the home (Figures 10a-c), the NO_2 + HONO readings from all three monitors were considerably lower than those from the 8840. The cause of this difference is not certain, although an error in correcting for the background readings of the monitors is one possibility, given the very low concentrations observed. Alternatively, a mismatch of the sample inlet locations for the monitors and the 8840 is possible, as indicated, e.g., by the absence of response from any monitor during an excursion of the 8840 to over 400 ppbv on April 7.

Figure 10a. Comparison of NO2 + HONO data from 8840 Conventional Analyzer and Monitor "A", in a Private Home

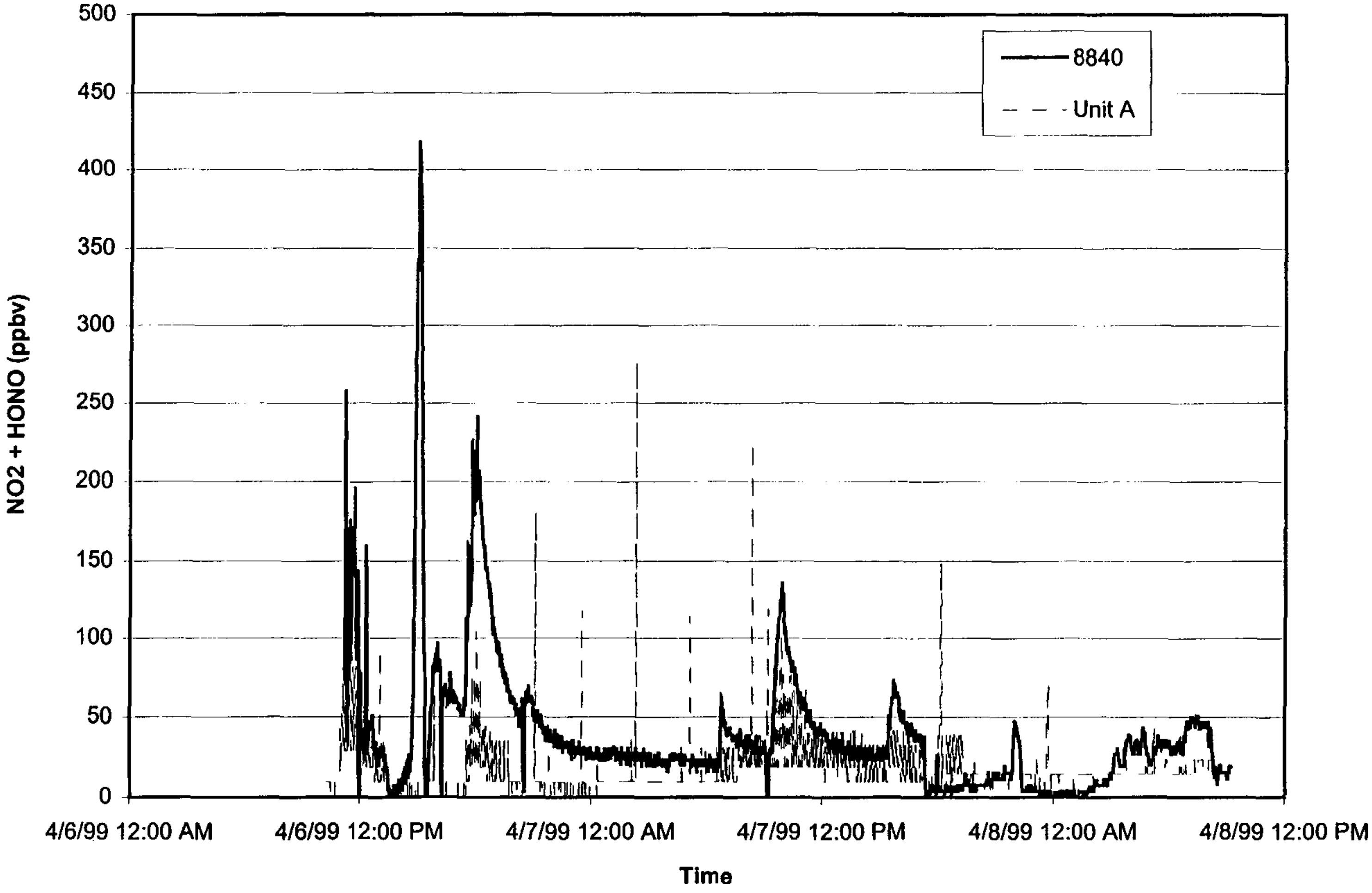


Figure 10b. Comparison of NO2 + HONO Data from 8840 Conventional Monitor and Monitor "B", in a Private Home

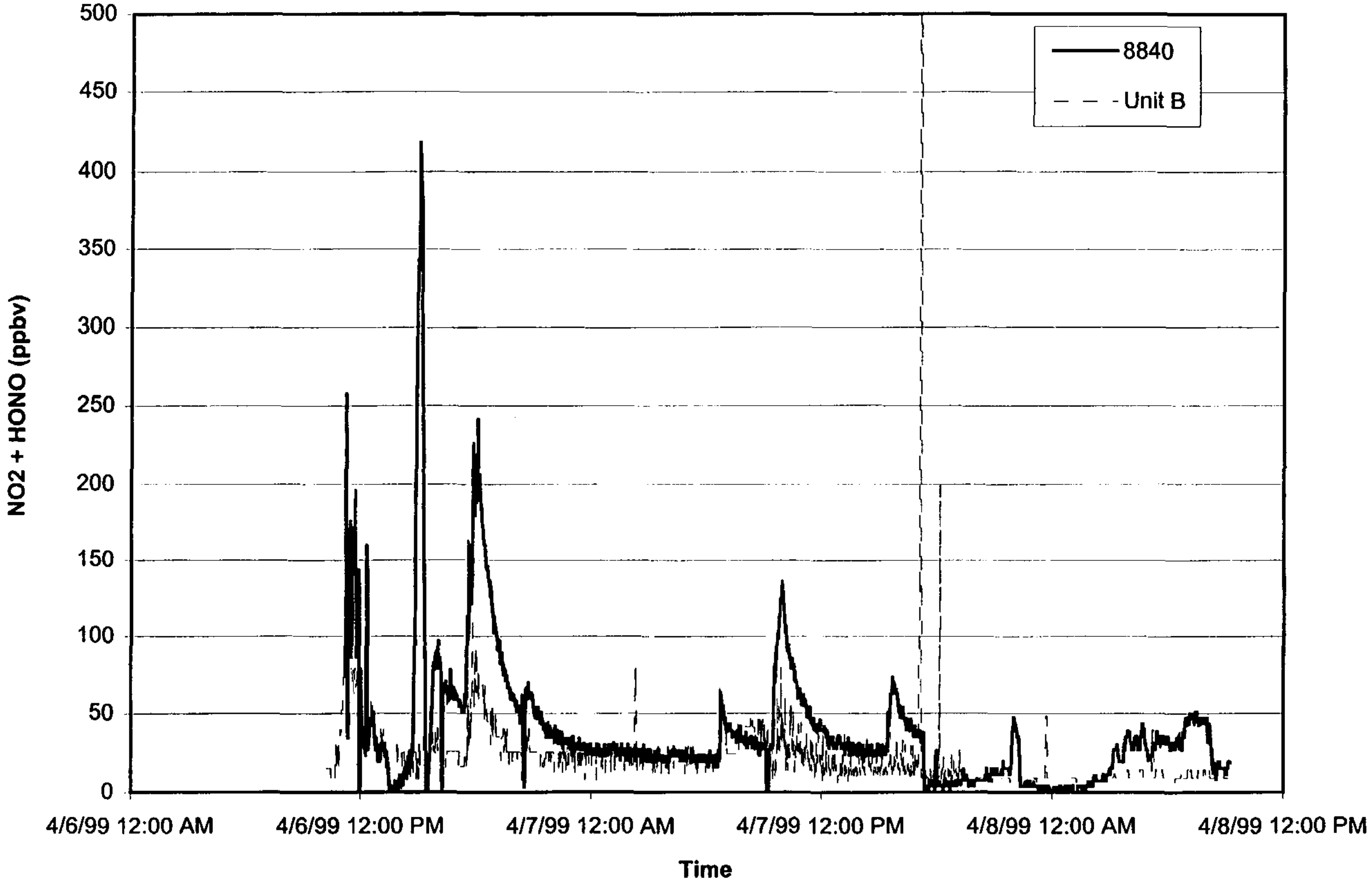


Figure 10c. Comparison of NO2 + HONO Data from 8840 Conventional Analyzer and Monitor "D", in a Private Home

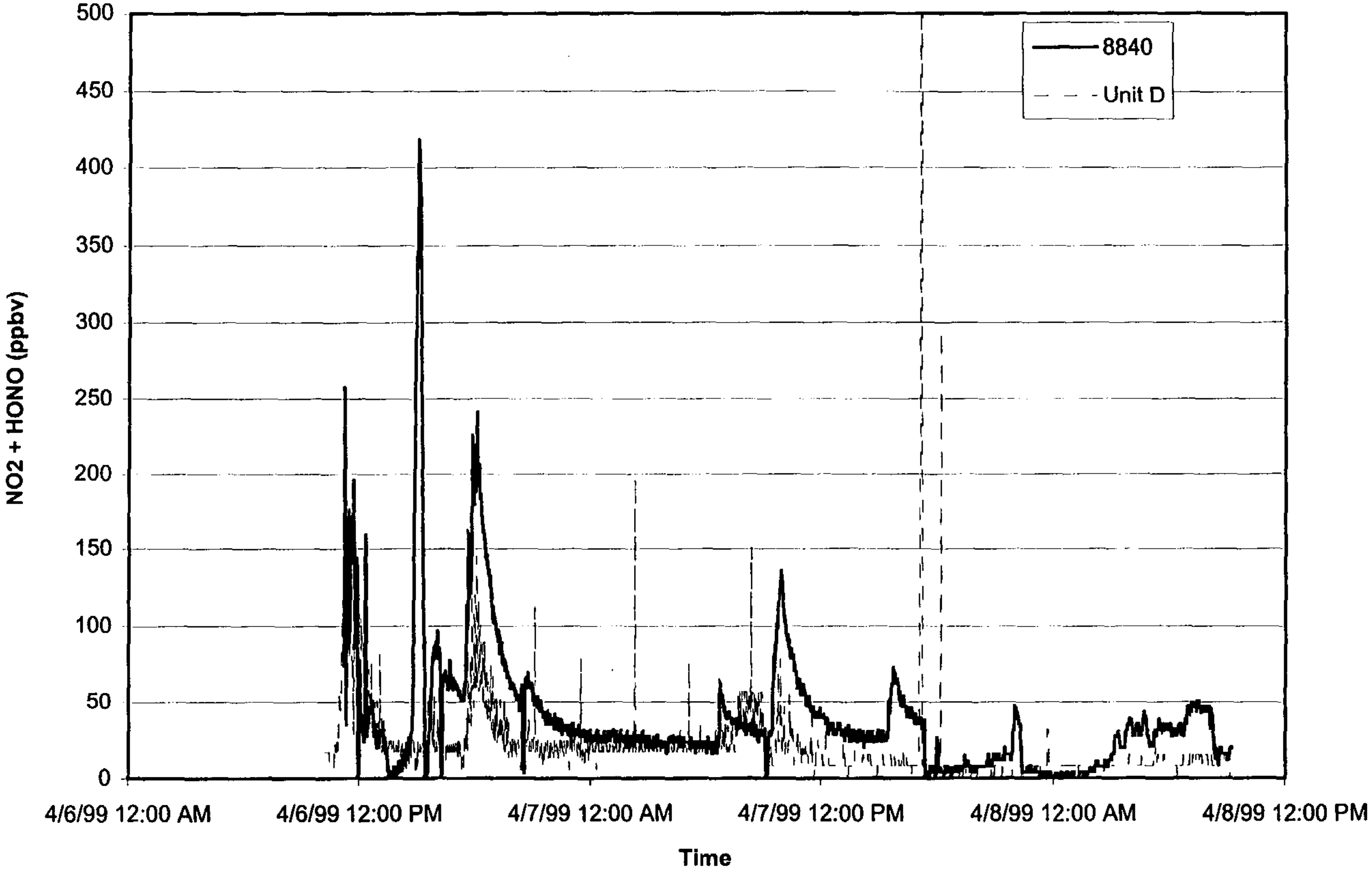


Figure 11a. Comparison of NO2 + HONO Data from 8840 Conventional Analyzer and Monitor "A", in an Apartment

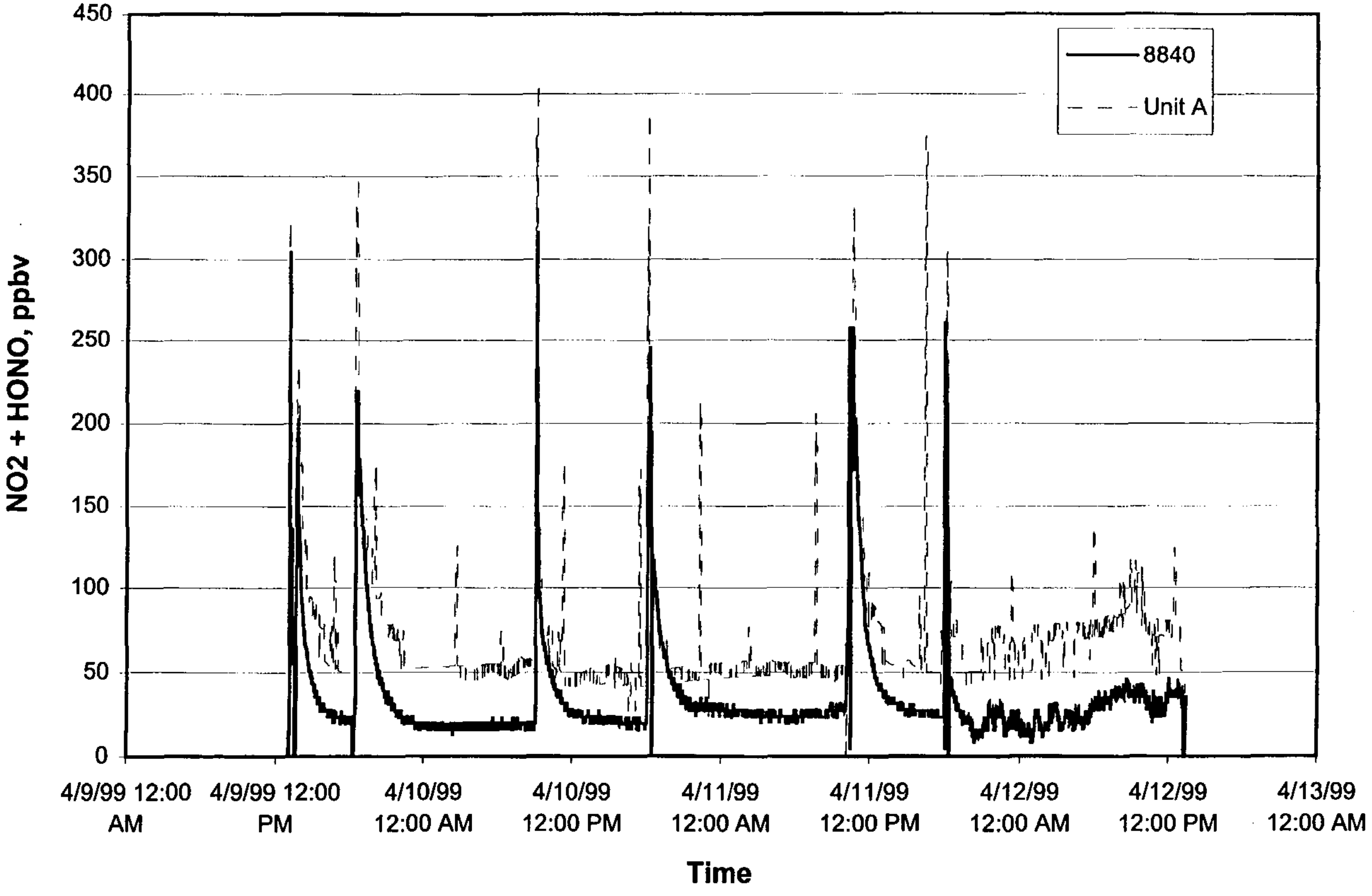


Figure 11b. Comparison of NO2 + HONO Data from 8840 Conventional Analyzer and Monitor "B", in an Apartment

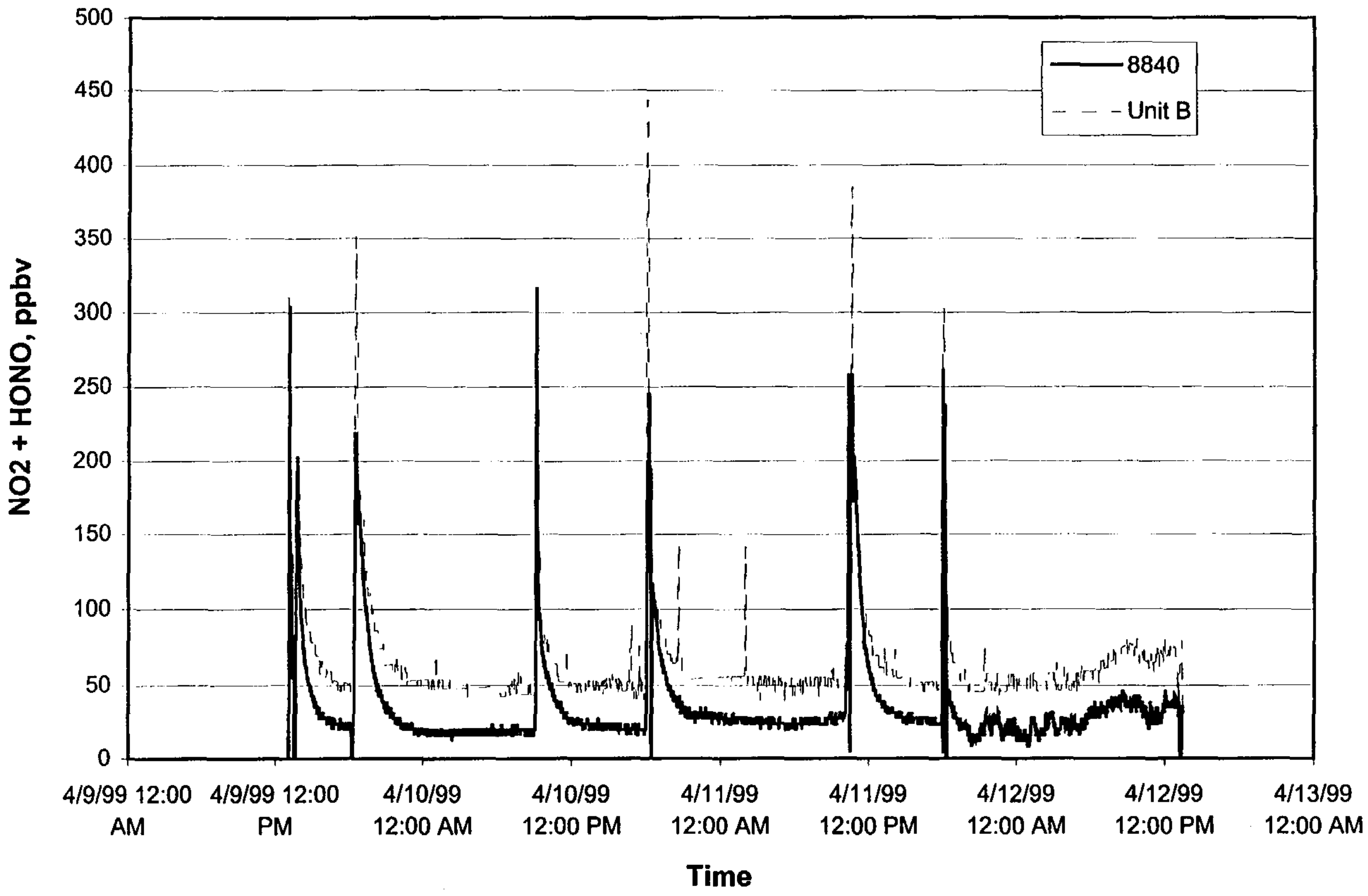


Figure 11c. Comparison of NO2 + HONO Data from 8840 Conventional Analyzer and Monitor "D", in an Apartment

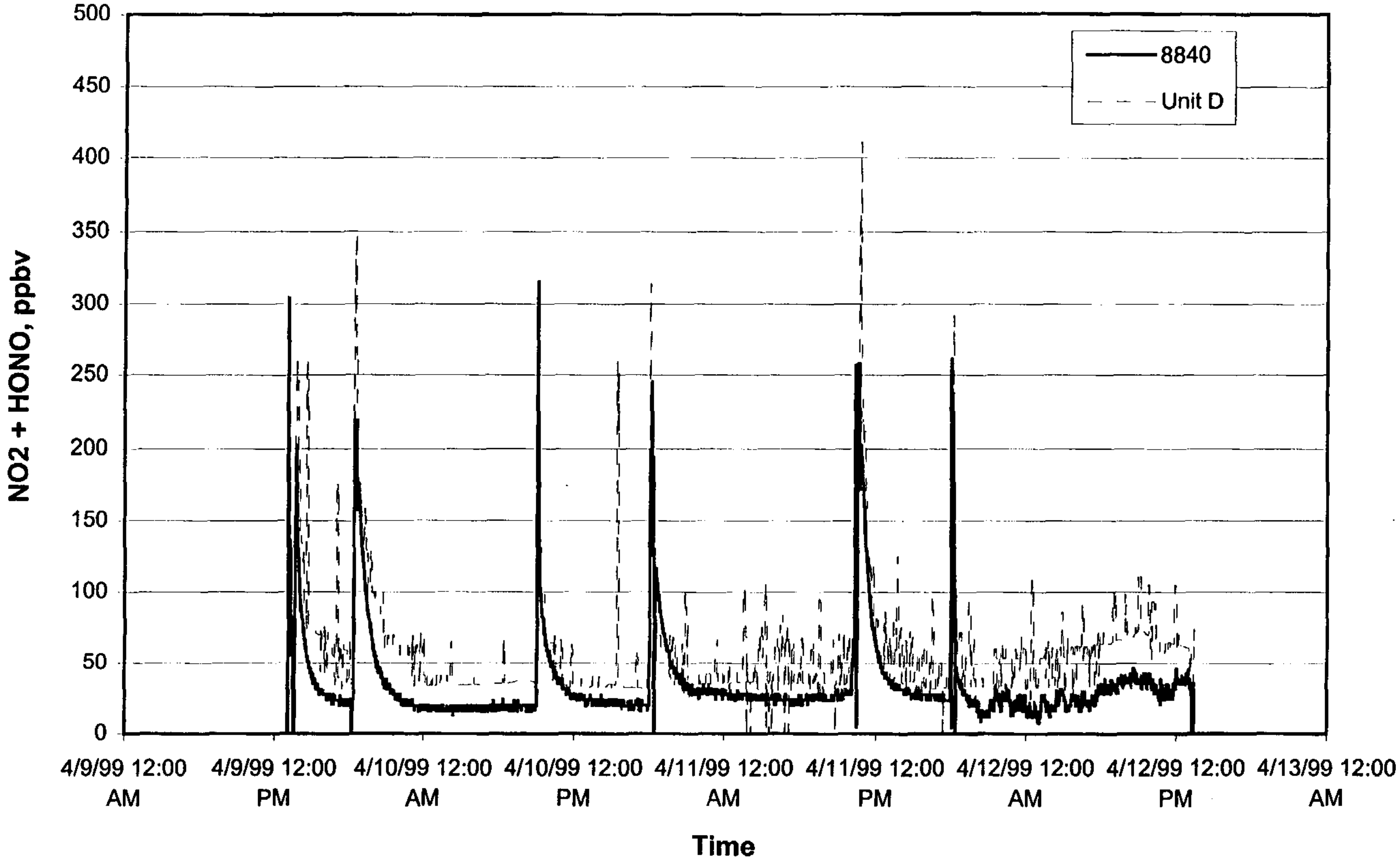


Figure 12a. Comparison of NO2+HONO Data from 8840 Conventional Analyzer and Monitor "A", in a Delicatessen

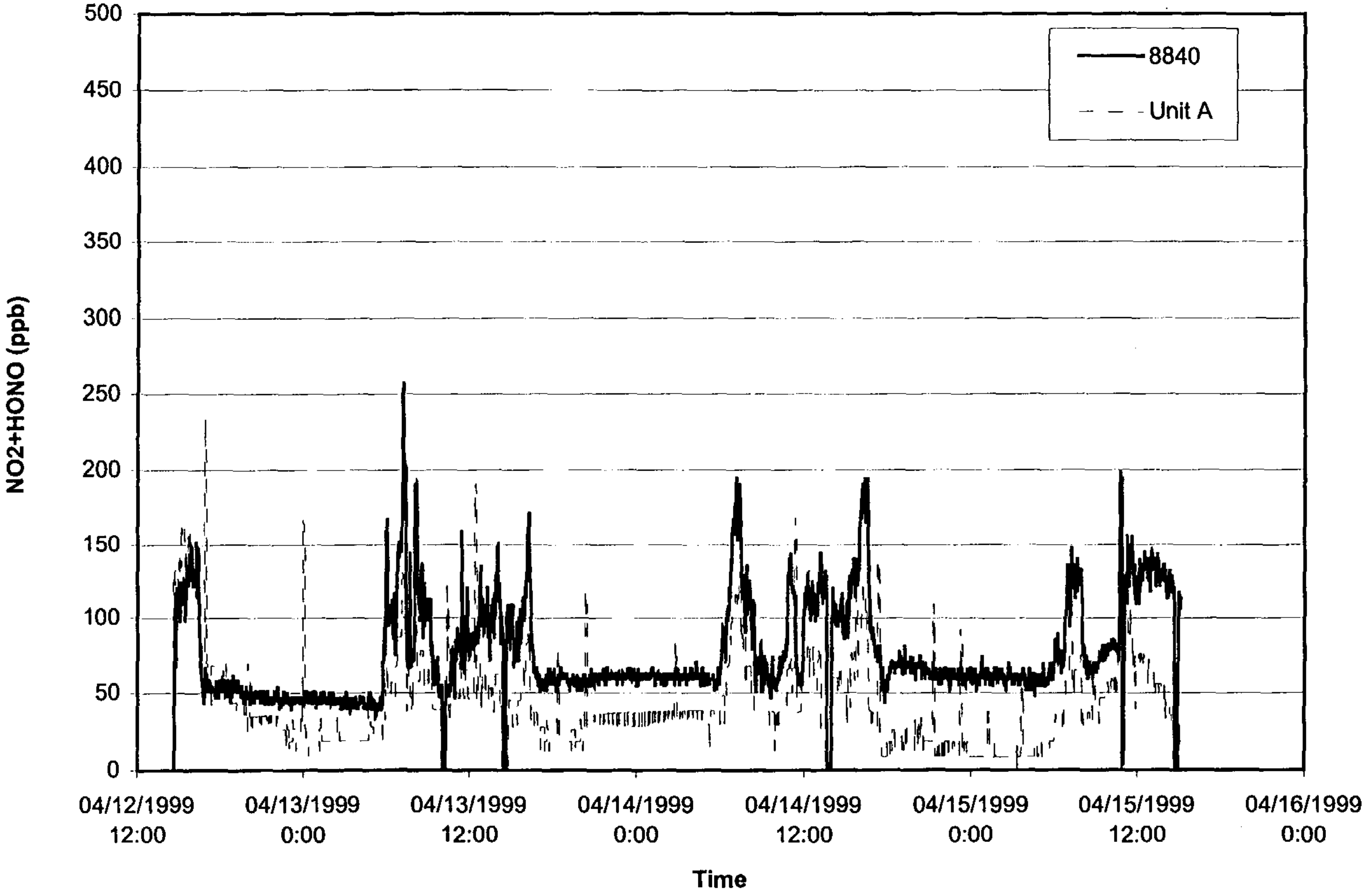


Figure 12b. Comparison of NO2+HONO Data from 8840 Conventional Analyzer and Monitor "B", in a Delicatessen

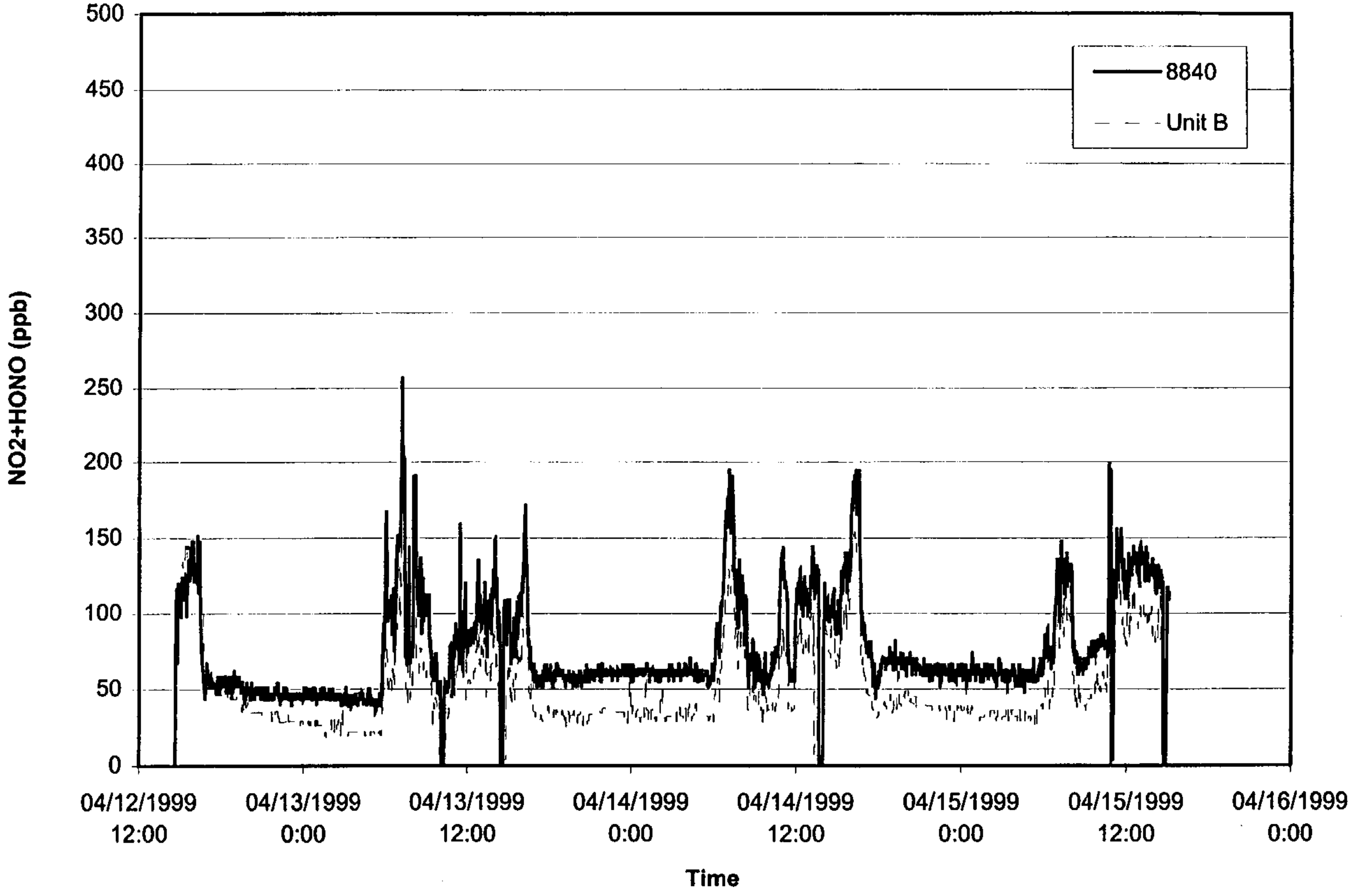
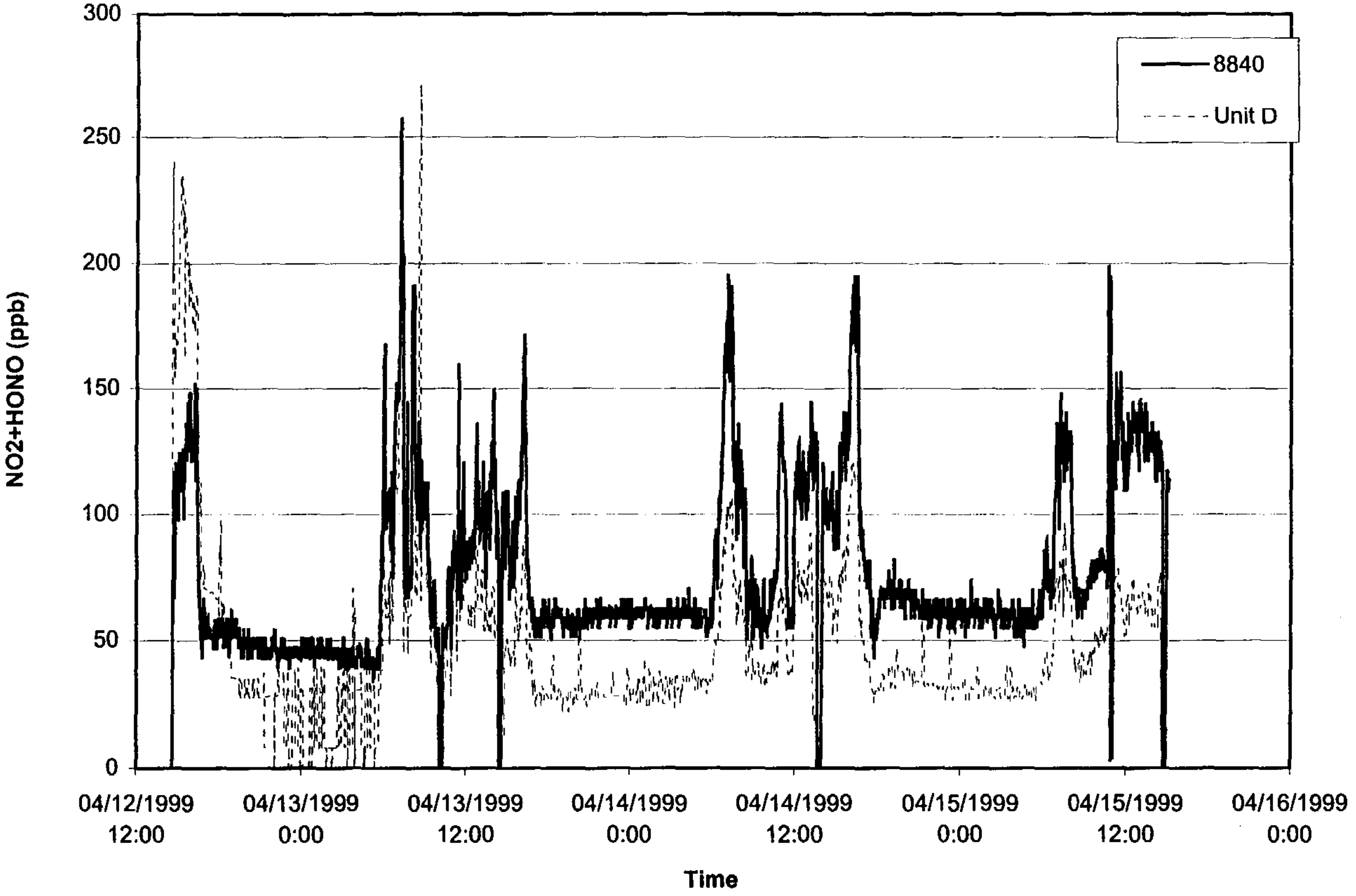


Figure 12c. Comparison of NO2+HONO Data from 8840 Conventional Analyzer and Monitor "D", in a Delicatessen



In the apartment (Figures 11a-c), better performance was observed, despite NO_2 + HONO levels that again were usually below 30 ppbv. In this part of the field test, the three monitors generally read higher than the 8840 by about 20 ppbv, but the occurrence and magnitude of all emission peaks were accurately tracked by all three monitors. Accuracy at levels of 20 to 30 ppbv (i.e., near the detection limit of the electrochemical monitors) was within only about a factor of two.

The NO_2 + HONO concentrations showed the highest average values in the delicatessen, and data from that site provide the most useful comparison of the conventional and electrochemical monitors. Figures 12a through 12c show comparisons of the sum of NO_2 + HONO from the conventional (8840) analyzer with the same sum from monitors A, B, and D, respectively, in the three days of sampling at the delicatessen. In periods of background concentrations in the delicatessen, all three monitors read lower than the 8840 by about 10 to 30 ppbv. In peak periods, with NO_2 + HONO levels of about 100 to 200 ppbv, the monitors indicated the temporal pattern of emissions accurately, but also read lower than the 8840 by about that same 10 to 30 ppbv. Agreement in peak concentrations was better for Units B and D than for Unit A. In light of the low concentrations present, the agreement is reasonable, especially considering that the sum of NO_2 + HONO is not determined directly by the electrochemical monitors, but is calculated from the difference between the two measurement modes, through application of the separate NO_2 and HONO calibration factors determined in the laboratory.

Figures 13 a through c show scatter plots comparing the NO_2 + HONO data from the delicatessen for Units A, B, and D, respectively, with those from the 8840. The 1-to-1 line and regression line are also shown. The data show a strong correlation of electrochemical results to conventional results, but with slopes considerably less than unity. Note that the results are dependent upon the choice of the calibration factors. If the pre-test rather than post-test calibration values (Table 5) were applied, the slope for Unit A (Figure 13a) would increase to 0.98, that for Unit B (Figure 13b) would remain almost unchanged, and that for Unit D (Figure 13c) would decrease slightly to 0.61. This observation exemplifies the uncertainty introduced by the variation in sensitivity of the electrochemical sensors.

Figure 14 shows a comparison of the HONO data from each of the three monitors in the delicatessen. Unit B indicated HONO at 10 to 15 ppbv throughout that portion of the test, whereas the other two monitors indicated essentially zero (± 10) ppbv HONO. These readings

Figure 13a. Comparison of NO2 + HONO Data from a Delicatessen, Unit A vs Conventional Monitor

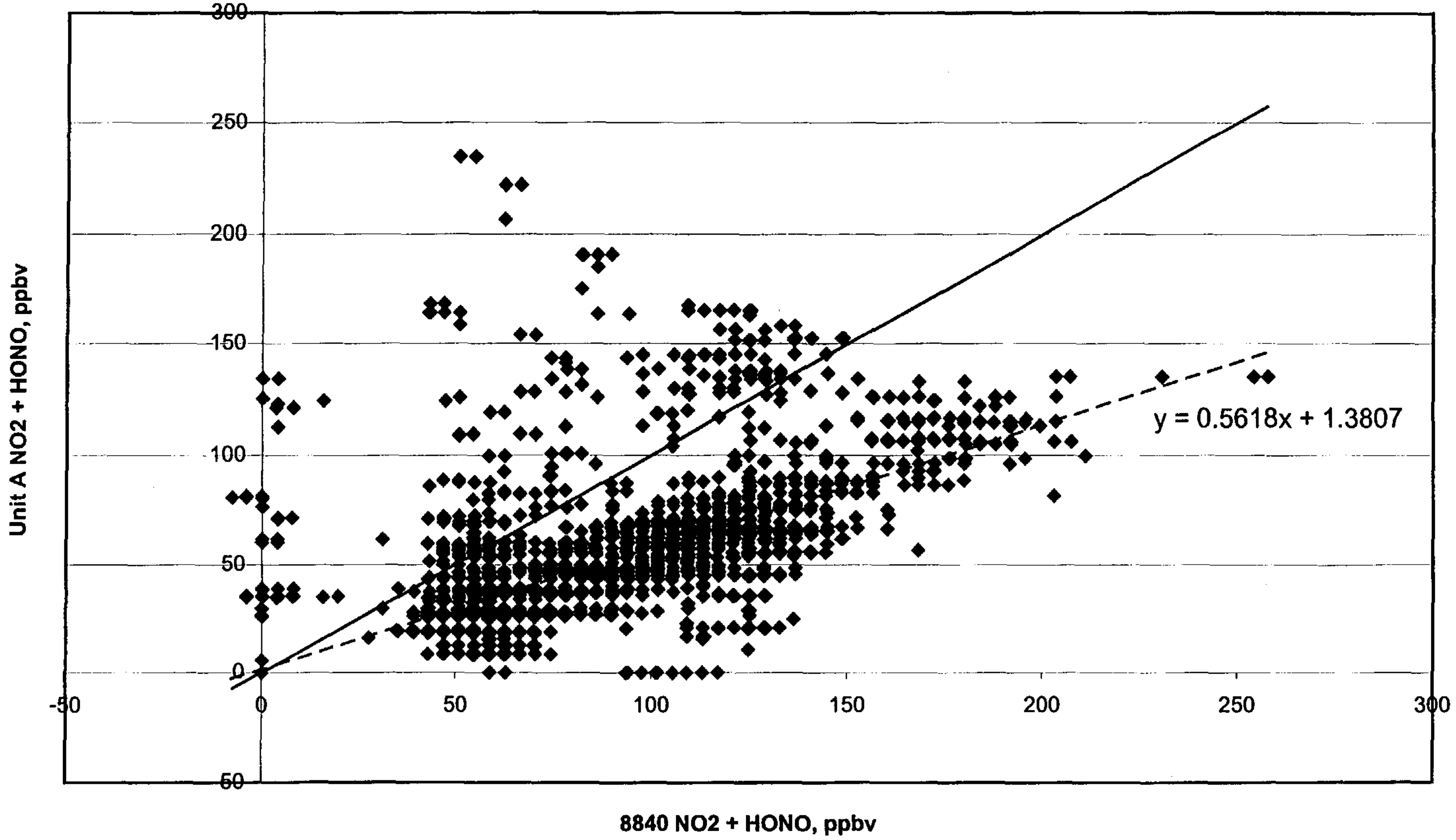


Figure 13b. Comparison of NO2 + HONO Data from a Delicatessen, Unit B vs Conventional Monitor

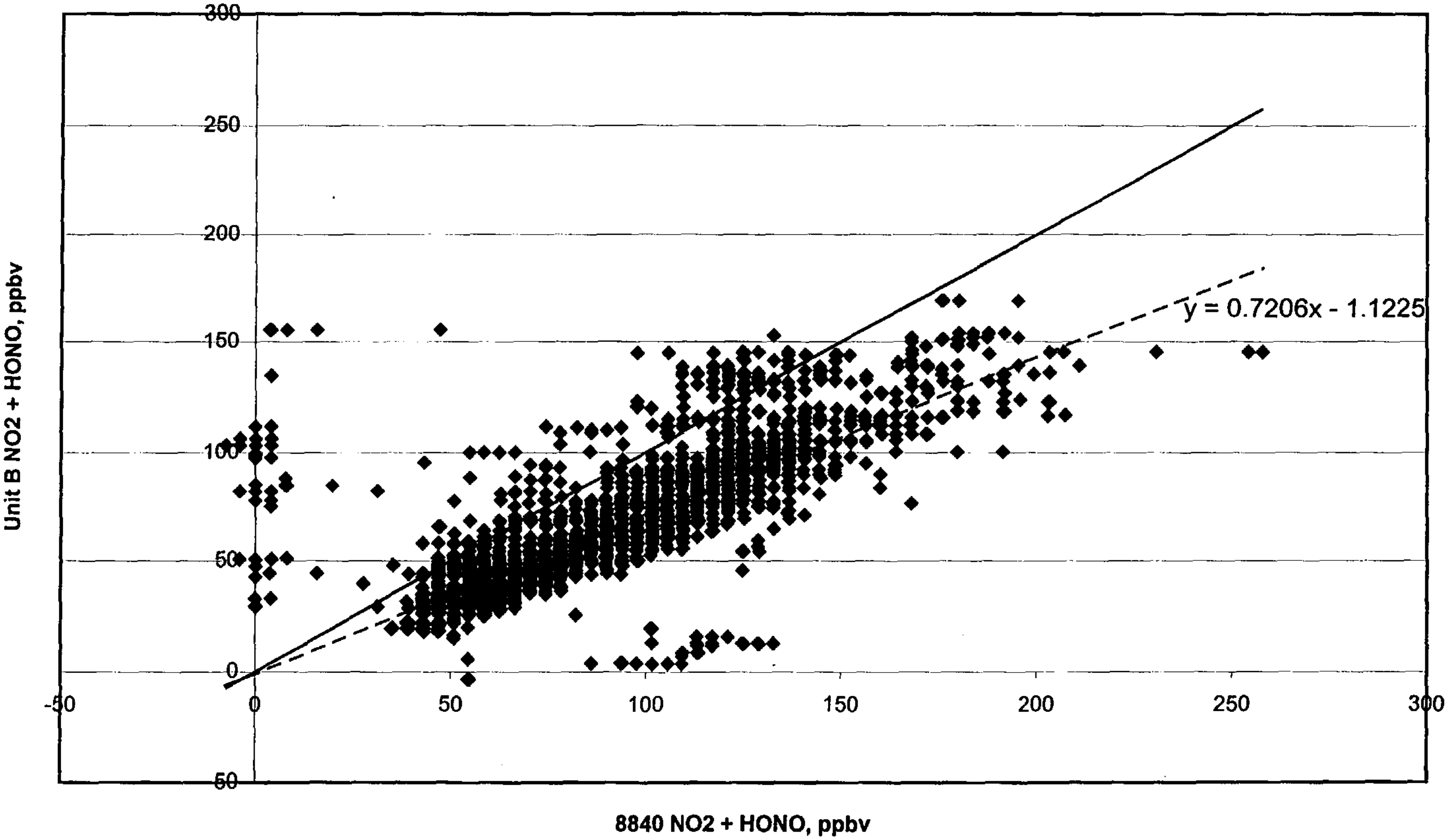


Figure 13c. Comparison of NO2 + HONO Data from a Delicatessen, Unit D vs Conventional Monitor

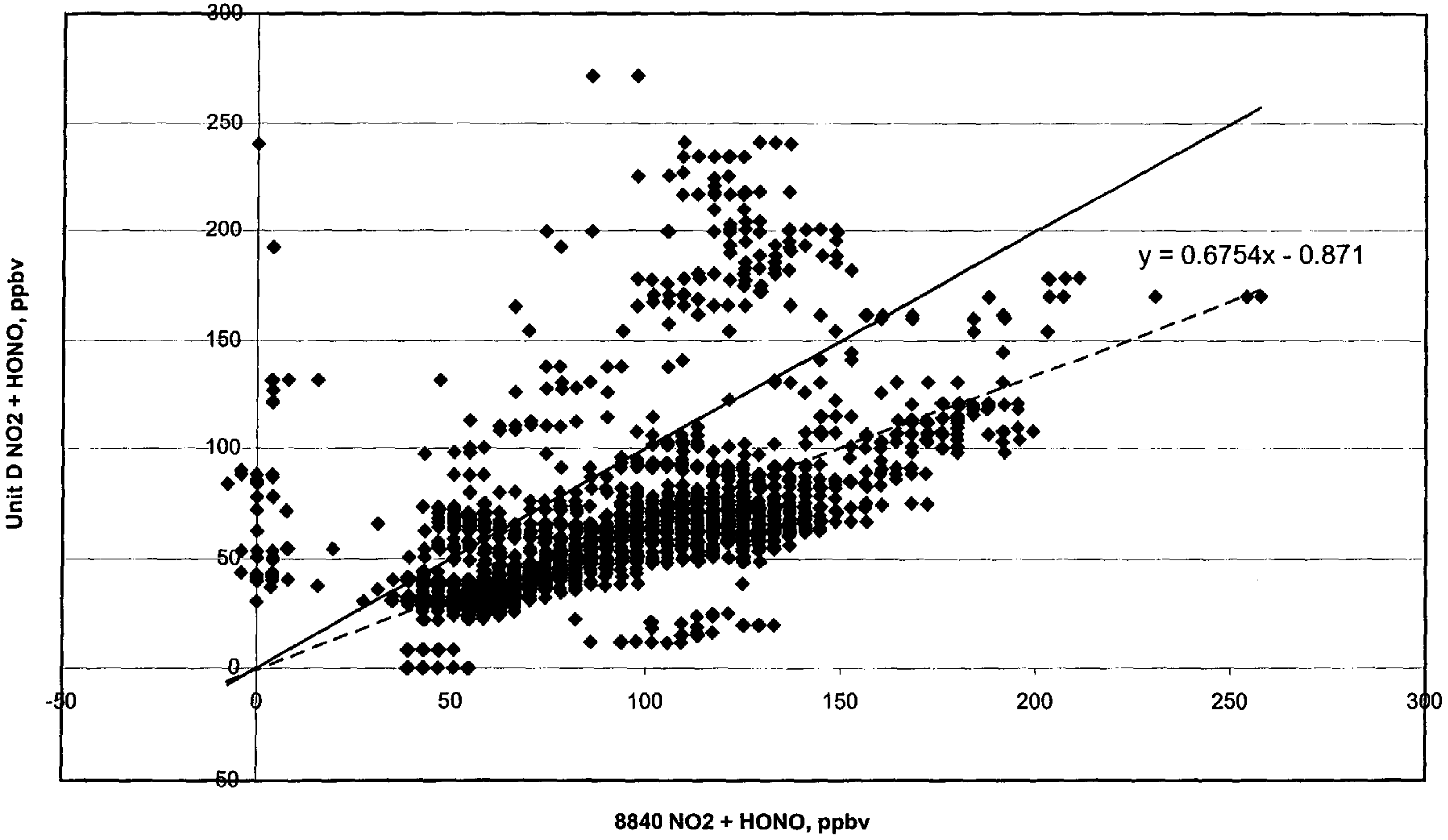
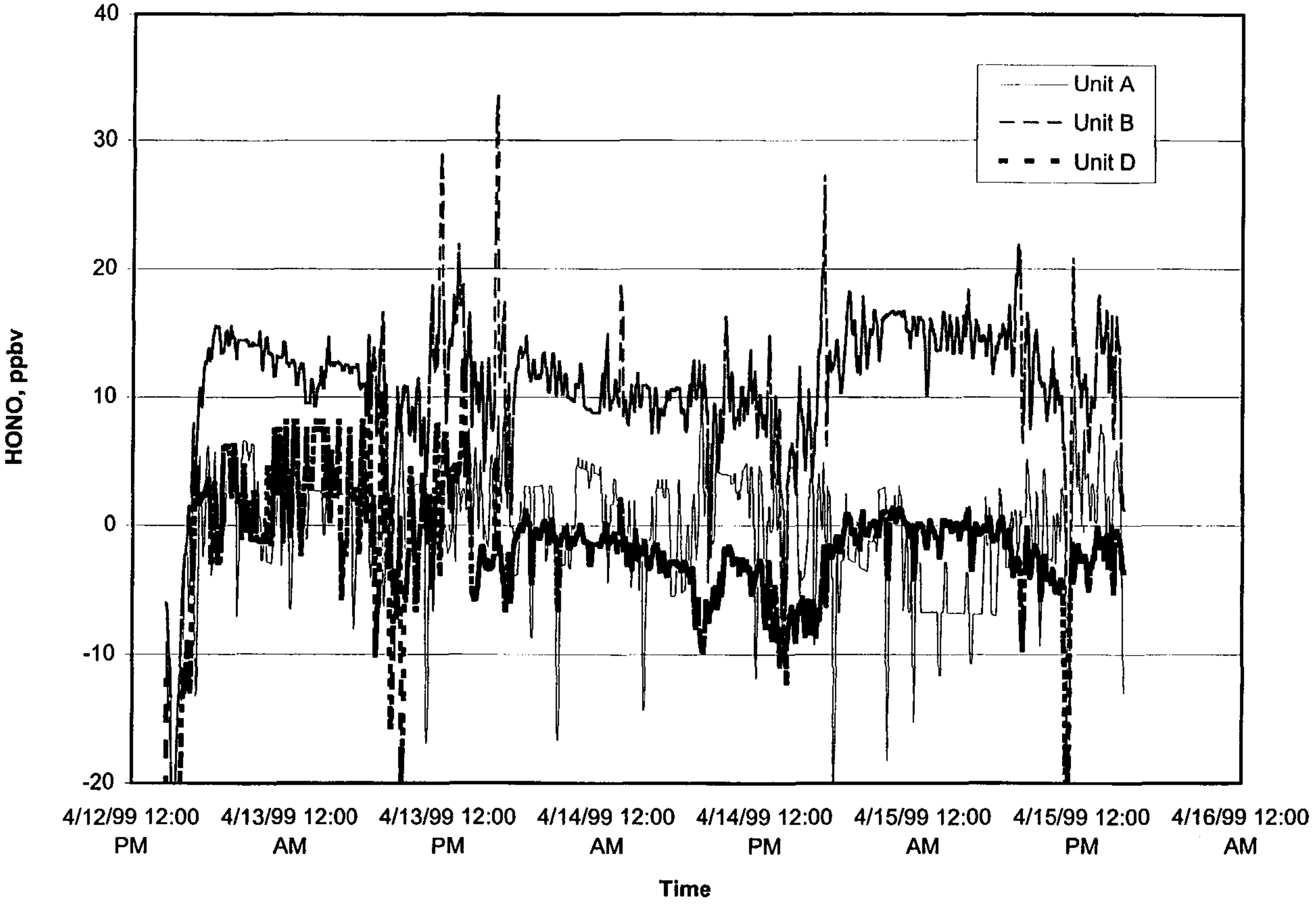


Figure 14. HONO Data from Monitors A, B, and D, from a Delicatessen



are below the practical detection limit of the monitors. Similar near-zero HONO levels were indicated by all three monitors in the private home and apartment as well, consistent with the low NO_2 + HONO levels observed. Unfortunately as noted above, a comparison to HONO determined by the conventional monitor cannot be made.

3.3.5 Final Field Testing – Columbus, Ohio

The California field tests provided no direct comparison of NO_2 data, so the Columbus field test was conducted to supplement the California data by focussing on NO_2. In the Columbus testing a carbonate-coated filter was always present on the inlet of the conventional monitor, allowing determination of NO_2 with that instrument. Cooking activities were deliberately conducted to produce indoor NO_2. In general the results of this test parallelled those from the California field test, in that better quantitative results were obtained with the B and D units because of their better sensitivity. The sensor in Unit A had NO_2 sensitivity of only 0.1 mV/ppbv when tested before this field study. As a result, that sensor was replaced with a previously used sensor, before calibration. Table 6 shows the sensitivities of each monitor, as calibrated immediately before and immediately after the Columbus field test. The calibrations are consistent, and the pre-test calibration was used for data reduction.

TABLE 6. NO_2 SENSITIVITIES OF THE THREE MONITORS USED IN THE COLUMBUS, OHIO FIELD TESTS

Date	Sensitivity in mV/ppbv		
	Monitor A	Monitor B	Monitor D
5/29/99[a]			
Filtered	0.16	0.44	0.27
Unfiltered	0.19	0.49	0.32
5/31/99[b]			
Filtered	0.13	0.51	0.31
Unfiltered	0.15	0.50	0.35

a: Before field test.
b: After field test.

Figures 15a-c show the data from this study, comparing NO_2 data from Units A, B, and D, respectively, with that from the 8840. As in the California residences, NO_2 levels were less than 30 ppbv in almost all periods when cooking was not done, and the observed levels exceeded

Figure 15a. Comparison of Conventional and Unit "A" Electrochemical NO2 Data from a Home in Columbus, Ohio

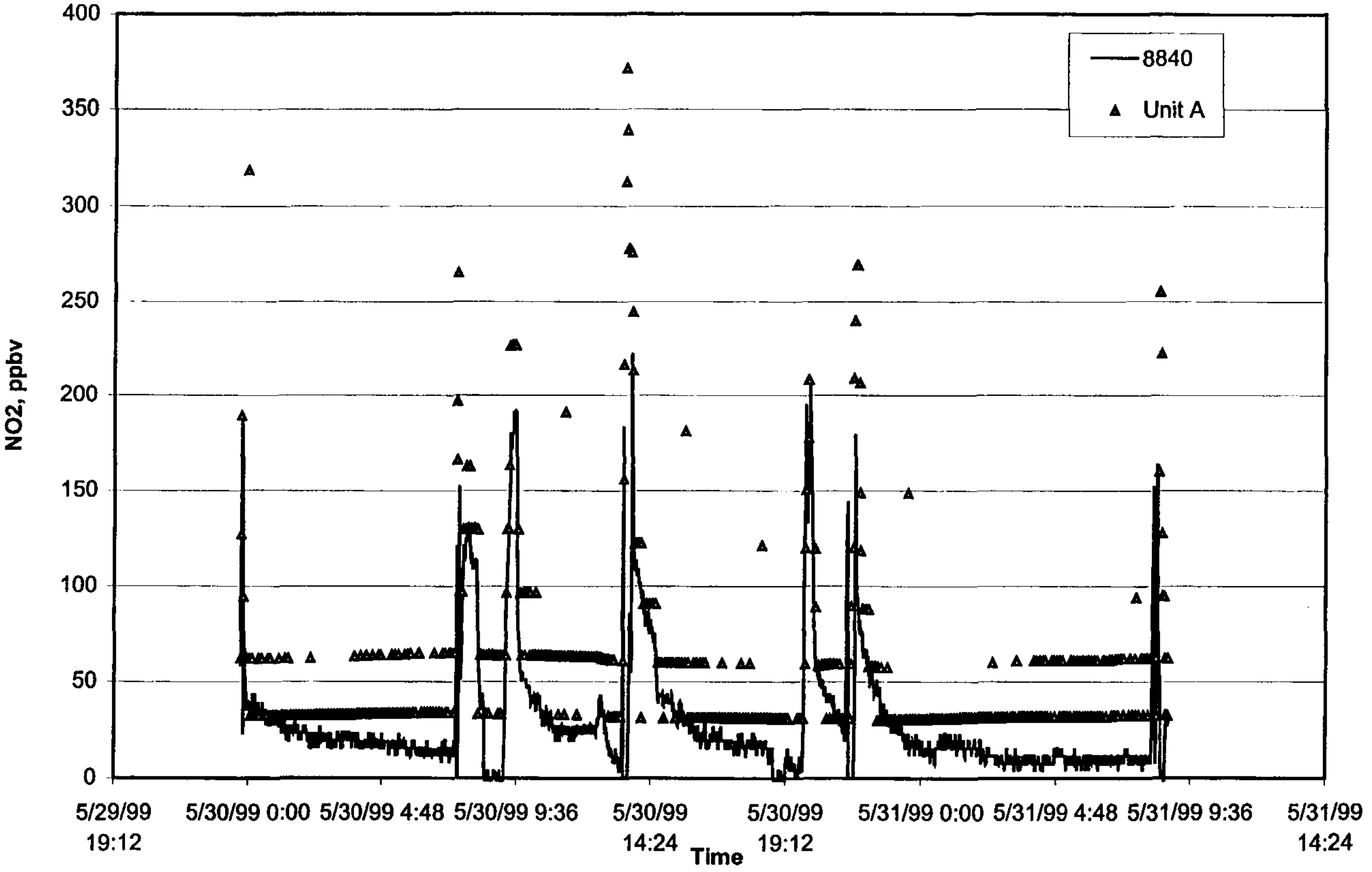


Figure 15b. Comparison of Conventional and Unit "B" Electrochemical NO2 Data from a Home in Columbus, Ohio

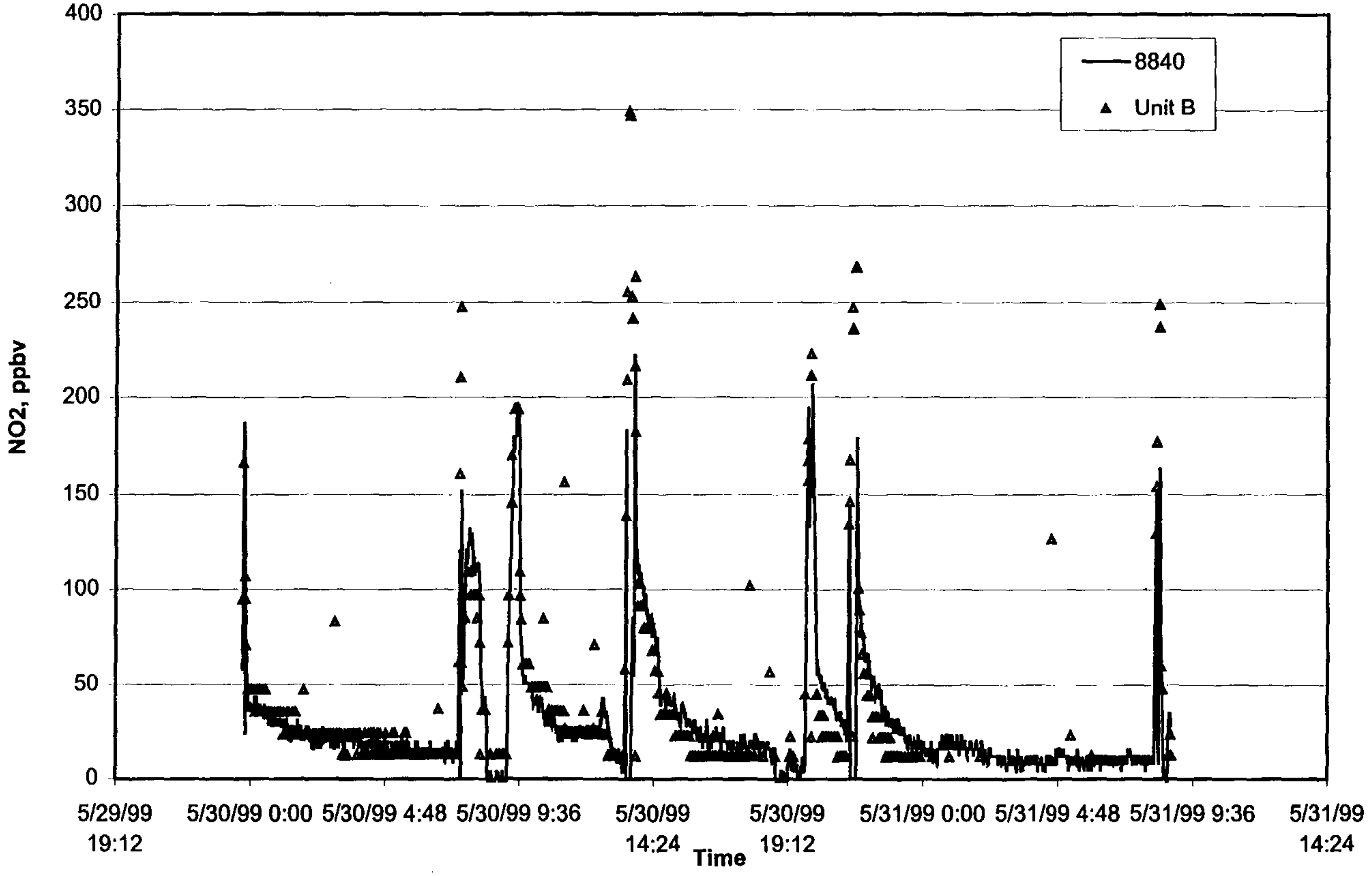
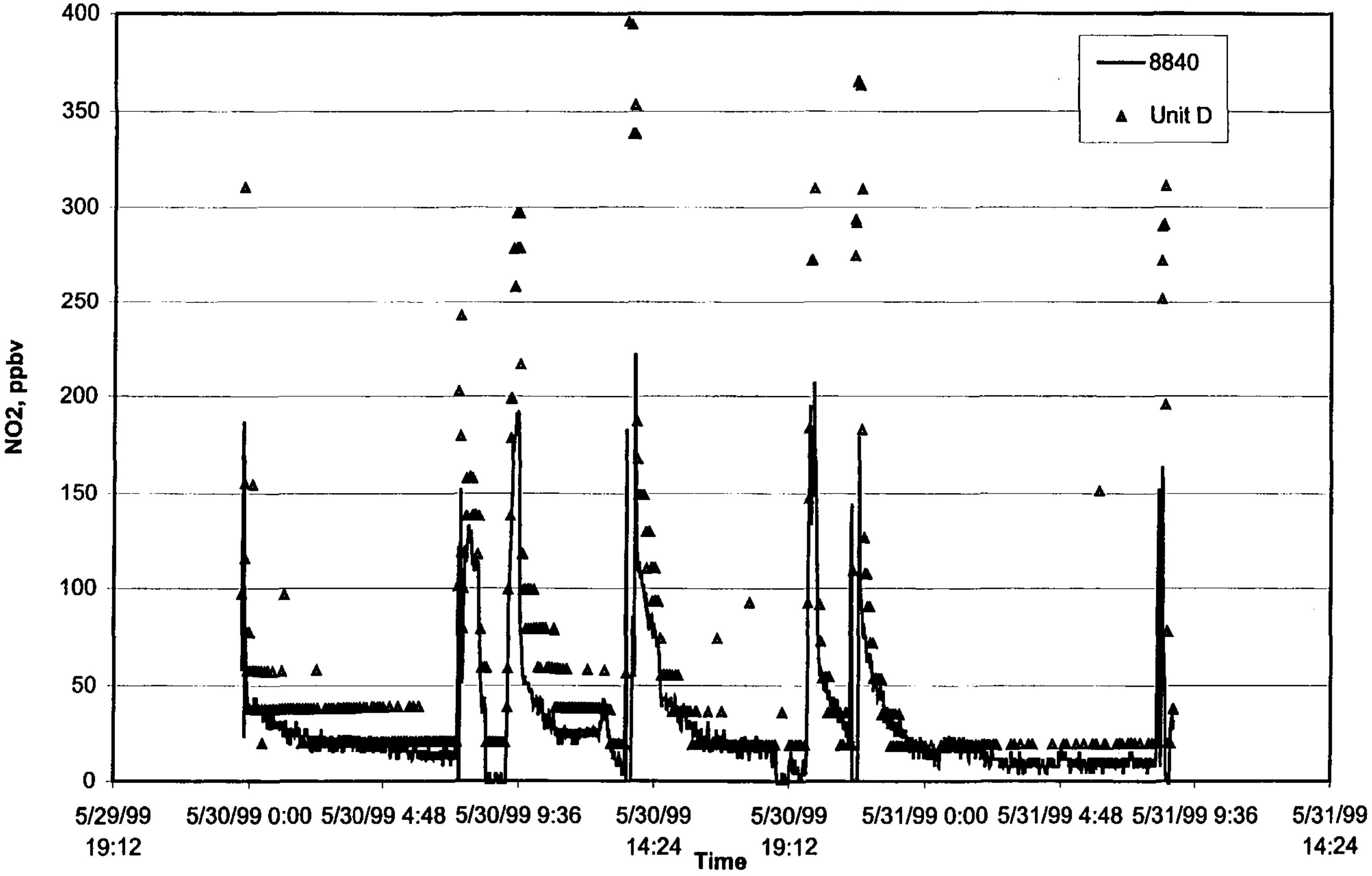


Figure 15c. Comparison of Conventional and Unit "D" Electrochemical NO2 Data from a Home in Columbus, Ohio



about 150 ppbv only when gas combustion was taking place. Figure 15a shows the quantization of Unit A response at low NO_2 levels, with Unit A indicating higher NO_2 levels than the 8840. This result is due to the low sensitivity of Unit A, and the consequent uncertainty in determining low NO_2 levels. In contrast, Figures 15a and 15b show good agreement between the monitors at the low levels observed, with the tendency for the electrochemical monitors to read higher in peak emissions, because of their faster time response. The agreement between the conventional and electrochemical NO_2 data for Units B and D is good, even when levels drop below 50 ppbv. These results show that the electrochemical monitors are capable of accurate determination of NO_2 indoors, provided that a sensor of adequate sensitivity is used.

Figures 16a through c show direct comparisons of the data from the electrochemical and conventional monitors in the Columbus field test, for Units A, B, and D, respectively. In each figure the regression line is shown. The slopes of the regressions are near unity for Units A and B (Figures 16a and b), with a positive offset for Unit A of about 25 ppbv. The slope for Unit D (Figure 16c) is 1.48, in part because of higher peak readings from that unit relative to the conventional monitor.

4.0 DISCUSSION

The variety of tests conducted on the prototype and second-generation NO_2/HONO monitors show that they generally meet the objectives set forth in Section 1.2. The monitors are small, readily portable, quiet, completely self-contained, and reliable in continuous operation. The HOBO dataloggers allow continuous unattended operation for over 10 days, with two analog outputs recorded every 60 seconds. The electrochemical monitors are also relatively inexpensive, primarily because of the low cost of the sensors themselves. The time response of a few minutes is certainly "substantially less than one hour", and no significant interferences occur as a result of the common indoor air pollutants associated with combustion sources. The two channel approach is successful in determining HONO, as well as NO_2, albeit with a somewhat complicated data reduction procedure, as described below. The monitors do require calibration with known sources of NO_2 and HONO, and laboratory tests to establish the temperature and relative humidity dependence of sensor response.

Figure 16a. Comparison of NO2 Data from a Home in Columbus, Ohio, Unit A vs Conventional Monitor

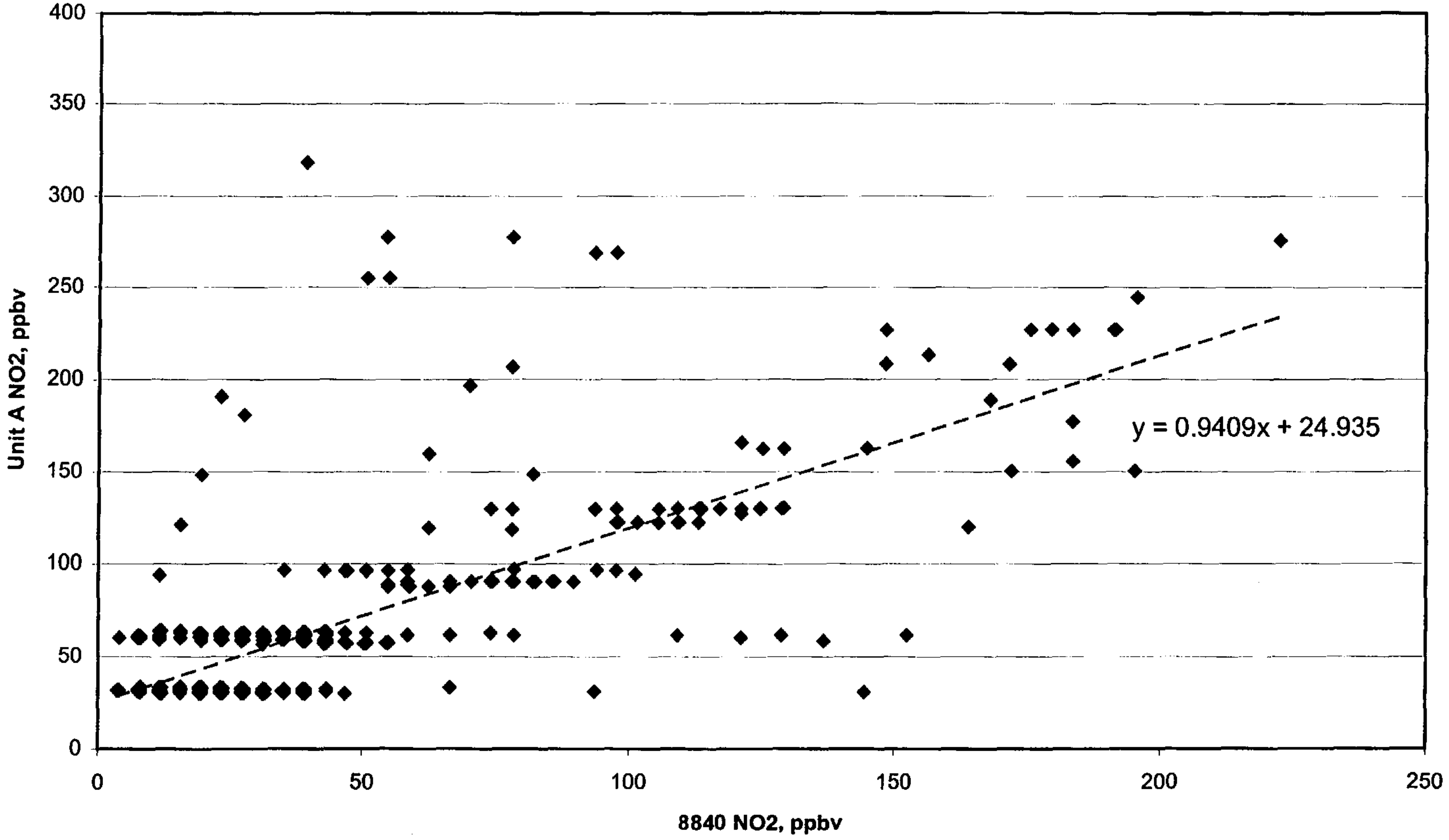


Figure 16b. Comparison of NO2 Data from a Home in Columbus, Ohio, Unit B vs Conventional Monitor

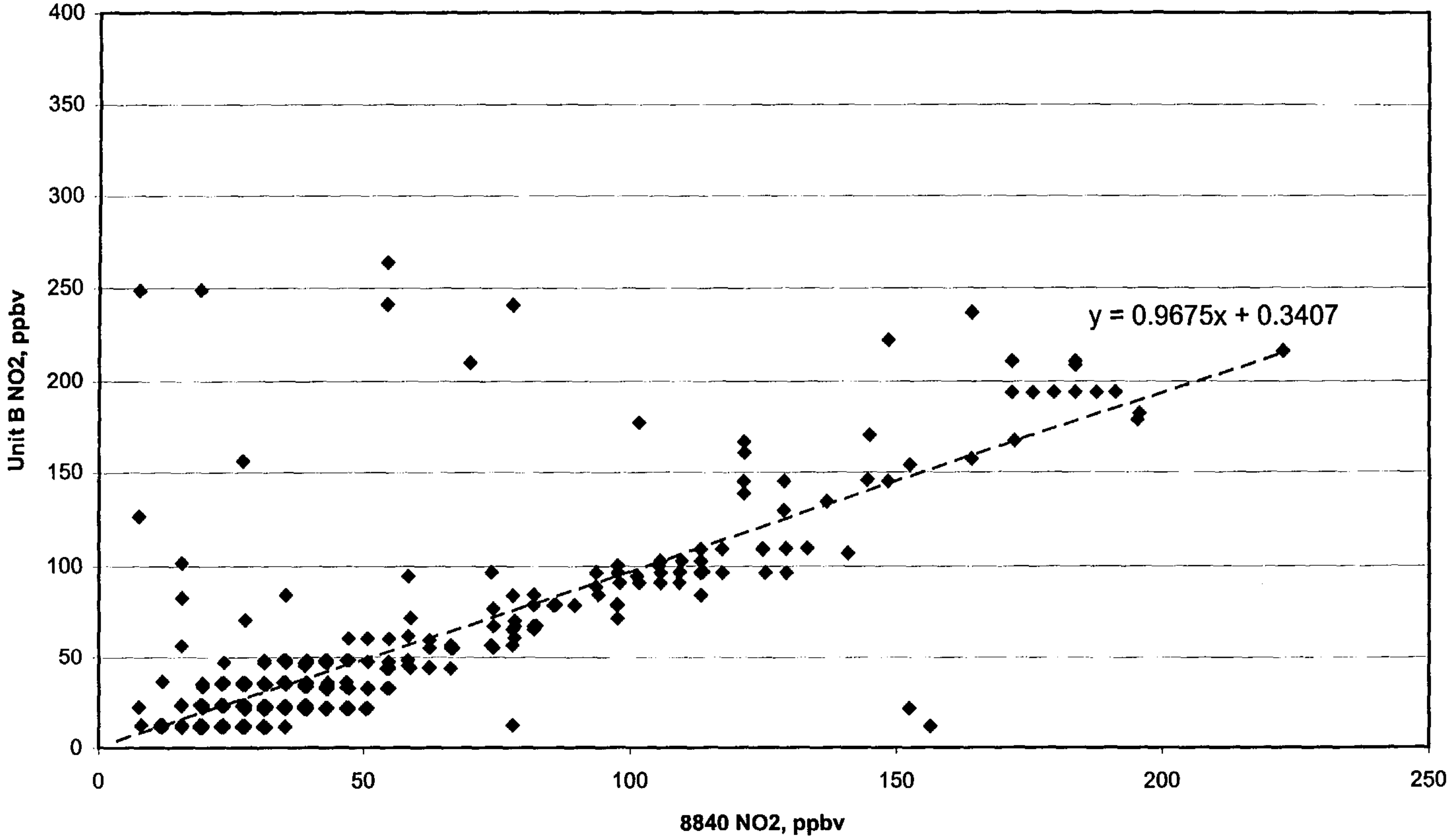
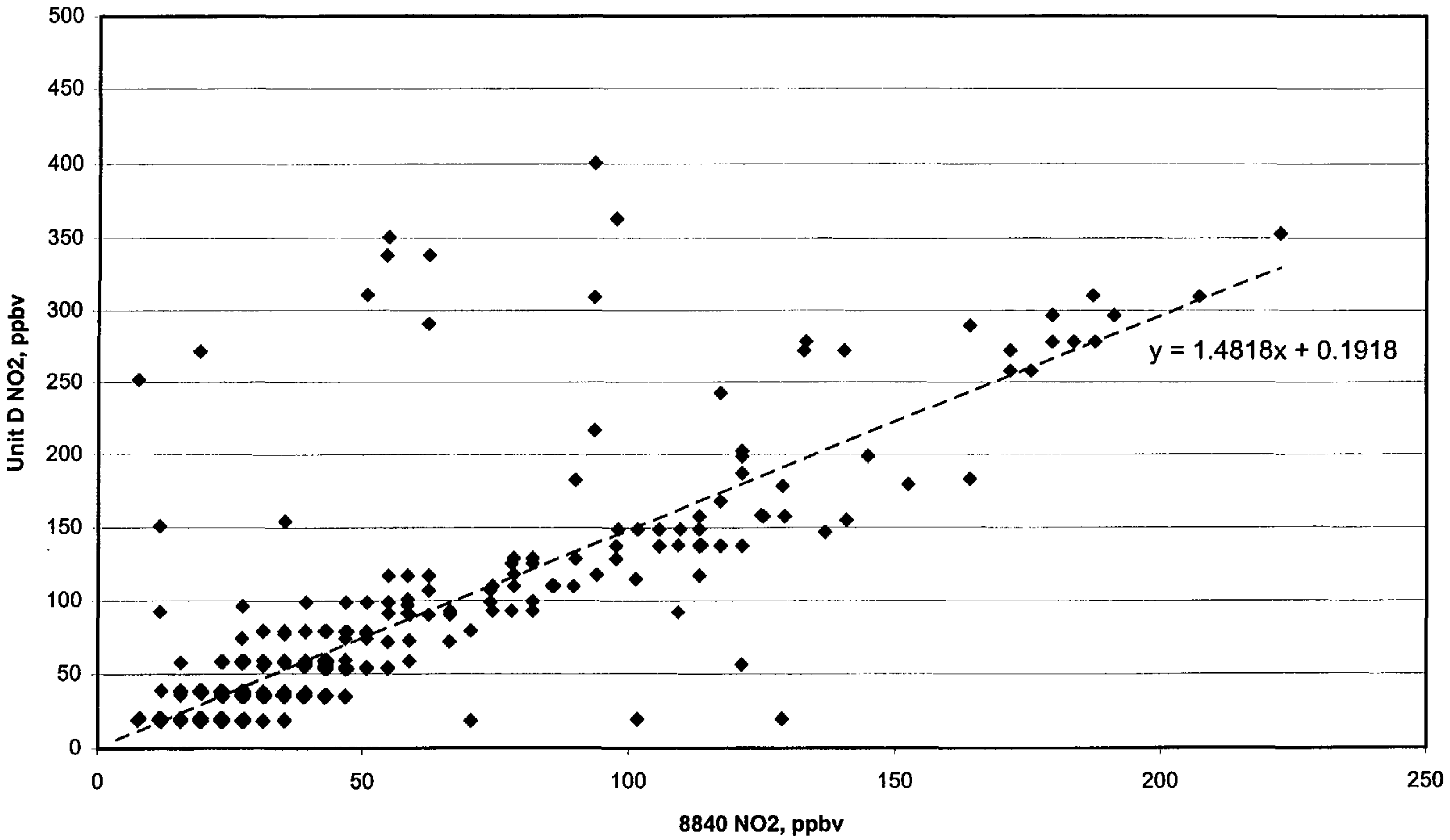


Figure 16c. Comparison of NO2 Data from a Home in Columbus, Ohio, Unit D vs Conventional Monitor



The accuracy and precision achievable with the monitors can be assessed relative to the conventional chemiluminescence method, using several different data sets. The slower time response of the conventional method does make comparisons of short-term response difficult. In addition, the results depend on the concentrations being measured, and on the sensitivity (and therefore the age) of the sensor being used. For example, the accuracy for NO_2 measurement can be assessed using the chamber test results with combustion sources (Figures 6 and 8). The linear regressions stated in Section 3.3.3 for those data indicate accuracy for NO_2 of about 1 to 11 percent, relative to the conventional method. Unit-to-unit precision of the three monitors used in that test was in a similar range, as shown in Figure 7. In field tests, the concentrations encountered were lower than those in the chamber tests, and so accuracy is somewhat worse. For example, the best accuracy indicated by the comparison of NO_2 + HONO data from the California field study (Figures 10 through 13) is within about 30 percent. For NO_2, in the Columbus field study, Units A and B had regression slopes of 0.94 and 0.97, respectively, relative to the conventional monitor (Figures 16a and b), at NO_2 levels usually 150 ppbv or less. For HONO, the results from the initial field tests (Figures 12 and 13 of Appendix A) indicate both accuracy and unit-to-unit precision within about 10 percent. These results are all highly encouraging. However, the sensitivity of the electrochemical sensor is the primary factor in obtaining accurate data. In addition, the validity of the data from the NO_2/HONO monitors also depends on the use intended for the data, and the amount of effort spent in reducing the data recorded by the HOBO dataloggers. In this regard, it is worthwhile to consider the different uses of the monitors, and the data processing requirements which arise.

The simplest use of the monitors is for NO_2 screening measurements, e.g., to provide a quick assessment of indoor NO_2 levels relative to the 250 ppbv one-hour standard. For such measurements, only single-channel operation (using the carbonate-filtered channel) is needed. Data reduction consists of downloading the recorded data from the HOBO into a spreadsheet program, applying the NO_2 calibration factor to convert the recorded data to ppbv, and visually scanning the data, for example by making a concentration-time plot of the sampling period. This approach provides an immediate indication of indoor levels, and an immediate decision as to the need for further monitoring. Somewhat greater accuracy can be achieved by correcting for temperature and relative humidity effects, but those corrections typically are not large, and in screening measurements could be neglected.

A more complex application is for continuous determination of NO_2, with only occasional single determinations of HONO. This can be accomplished by operating as above, and occasionally manually switching to the unfiltered channel to determine the sum of NO_2 and HONO for a brief period. Still more complex, but also more usual, is the routine determination of both NO_2 and HONO using automated two-channel operation of the monitor. This is the operating mode for which the monitors were designed. In either case, if HONO is to be determined, the following general sequence of data reduction steps must be carried out:

1. The recorded data (in mV) from the filtered channel of the monitor are converted to ppbv NO_2, using the NO_2 calibration factor (mV/ppbv) for that channel.
2. That ppbv NO_2 value is multiplied by the NO_2 calibration factor for the unfiltered channel, to calculate the portion of the analog signal (in mV) in that channel that is due to NO_2.
3. The analog signal calculated in step 2 is subtracted from the total analog signal recorded in the unfiltered channel; the difference is the analog signal due to HONO.
4. The analog signal determined by difference in step 3 is divided by the calibration factor (mV/ppbv) for HONO, to determine the HONO concentration.

In addition, the "holes" in the data (i.e., the periods of null data in each channel when the other measurement channel is operating) must be dealt with.

The example shown on the following pages will illustrate the process by which the raw data taken from the HOBO of monitor "A" is eventually converted into final concentrations of NO_2 and HONO. Steps 1, 2, and 3 show how the raw data is converted into a concentration of NO_2 in ppbv. Steps 4 and 5 illustrate the correction for temperature and humidity, and the way the 'holes' in the data are dealt with. Then steps 6 through 9 describe how the concentration of HONO in ppbv is calculated.

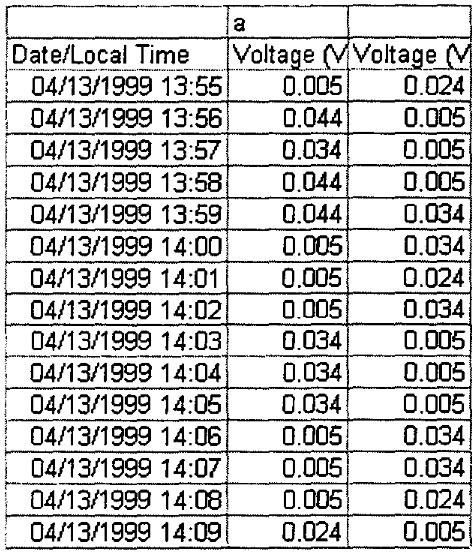
In the first step, the raw data from the HOBO is obtained. Channel 3 (Ch 3) is the data from the filtered (f) gas stream and channel 4 (Ch 4) is from the unfiltered (uf) stream. In step 2, the raw data from Ch 3, recorded in volts, is converted to millivolts (mV), the 5mV offset inherent in the HOBO is subtracted, and the NO_2 scale factor is used to convert the mV signal into an NO_2 concentration in ppbv. This is done by dividing the mV signal of Ch 3 by the scale factor that was previously determined experimentally in the lab. In step 4, the resulting NO_2 concentration is corrected for temperature and humidity. This correction is accomplished by taking the temperature and humidity data collected along with the NO_2 and HONO data and applying the correction factors previously established for the monitor in laboratory tests. Then in step 5, the null data or 'holes' that result from the two channel operation of the monitor are filled using a maximization routine. This routine looks for the maximum value in a nine point moving window and assigns the center point within the window that value. One drawback of this approach is the artificial broadening of maxima, that results in a tendency for monitor results to exceed conventional results. Any zero offset that was observed during the experiments (established by zeroing the monitor with the charcoal trap), can also be corrected in Step 5. The product of Step 5 is the final NO_2 data.

The next series of steps calculates the HONO concentration. Since HONO concentration is calculated using the difference between the filtered and the unfiltered channels, the first step in determining the HONO concentration is to determine how much of the signal from the unfiltered channel is attributable to NO_2. This is done by converting the final NO_2 concentration back to a mV signal, only this time, the NO_2 scale factor for the unfiltered channel is applied. Then this contribution is subtracted from the originally recorded signal on Ch 4, resulting in the mV signal from only HONO. This remaining mV signal is then divided by the previously determined scale factor for HONO to give the concentration for HONO in ppbv. Step 9 also fills in the 'holes' in the same manner as described previously.

Further data cleanup may also be needed due to other features of the two-channel operation. One feature is that the HOBO data acquisition cannot be accurately synchronized with the channel switching of the monitor. As a result, data are occasionally recorded before the monitor's response has fully stabilized in the measurement channel. Such data do not accurately represent either channel, and must be deleted. Also, a voltage transient often occurs in the monitor upon switching the three-way channel selection valve. When data acquisition by the HOBO coincides with this spike, unrealistically high single readings can be recorded. Examples of these spikes can be seen (e.g.) in Figures 10 through 12. These data can be edited out manually in the spreadsheet, but that is a time-consuming process. A solution to this problem would be an additional DC data signal, which switches on and off depending on the position of the three-way channel selection valve in the monitor. This signal would be recorded by the HOBO, and would provide a guide for avoiding the switching transient and eliminating data points too close to the channel switching times, as well as for rapid sorting out of the non-functional data.

Step 1

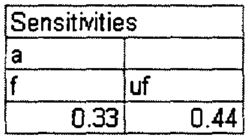
Raw data from monitor 'A' for CH3 (f) and Ch4 (uf)



	a	
Date/Local Time	Voltage (V	Voltage (V
04/13/1999 13:55	0.005	0.024
04/13/1999 13:56	0.044	0.005
04/13/1999 13:57	0.034	0.005
04/13/1999 13:58	0.044	0.005
04/13/1999 13:59	0.044	0.034
04/13/1999 14:00	0.005	0.034
04/13/1999 14:01	0.005	0.024
04/13/1999 14:02	0.005	0.034
04/13/1999 14:03	0.034	0.005
04/13/1999 14:04	0.034	0.005
04/13/1999 14:05	0.034	0.005
04/13/1999 14:06	0.005	0.034
04/13/1999 14:07	0.005	0.034
04/13/1999 14:08	0.005	0.024
04/13/1999 14:09	0.024	0.005

Step 2

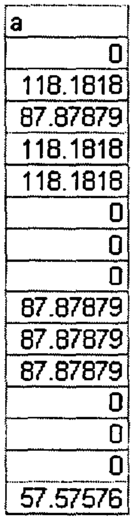
Subtract 0.005 from HOBO values and apply NO2 scale factor to CH3 (f) data



Sensitivities	
a	
f	uf
0.33	0.44

Step 3

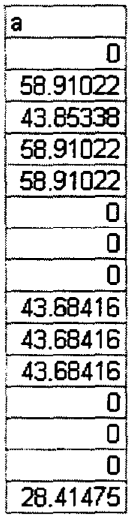
Obtain NO2 concentration in ppbv



a
0
118.1818
87.87879
118.1818
118.1818
0
0
0
87.87879
87.87879
87.87879
0
0
0
57.57576

Step 4

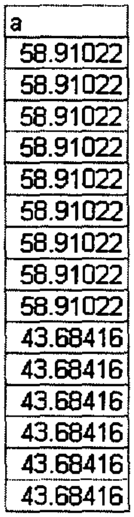
Correct for humidity and temperature



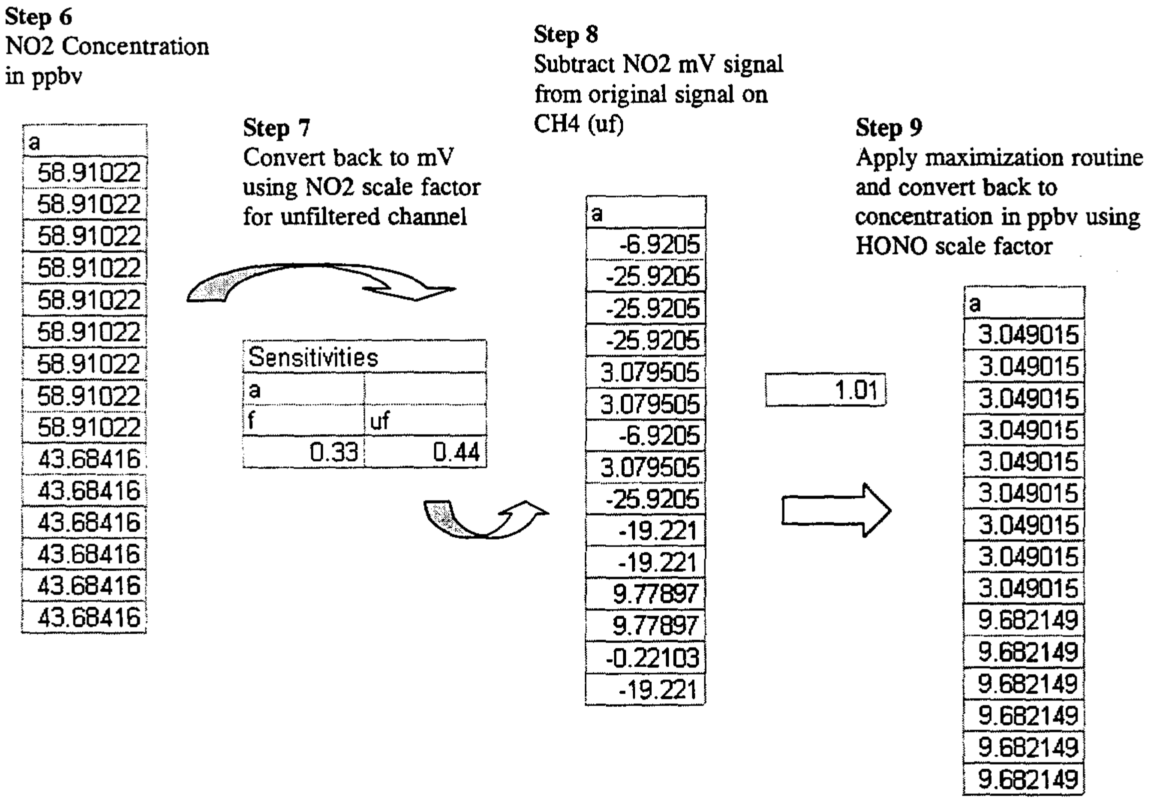
a
0
58.91022
43.85338
58.91022
58.91022
0
0
0
43.68416
43.68416
43.68416
0
0
0
28.41475

Step 5

Fill in empty data points using maximization routine and adjust for zero offset



a
58.91022
58.91022
58.91022
58.91022
58.91022
58.91022
58.91022
58.91022
58.91022
43.68416
43.68416
43.68416
43.68416
43.68416
43.68416



Step 6
NO2 Concentration
in ppbv

a
58.91022
58.91022
58.91022
58.91022
58.91022
58.91022
58.91022
58.91022
58.91022
43.68416
43.68416
43.68416
43.68416
43.68416
43.68416

Step 7
Convert back to mV
using NO2 scale factor
for unfiltered channel

Sensitivities	
a	
f	uf
0.33	0.44

Step 8
Subtract NO2 mV signal
from original signal on
CH4 (uf)

a
-6.9205
-25.9205
-25.9205
-25.9205
3.079505
3.079505
-6.9205
3.079505
-25.9205
-19.221
-19.221
9.77897
9.77897
-0.22103
-19.221

1.01

Step 9
Apply maximization routine
and convert back to
concentration in ppbv using
HONO scale factor

a
3.049015
3.049015
3.049015
3.049015
3.049015
3.049015
3.049015
3.049015
3.049015
9.682149
9.682149
9.682149
9.682149
9.682149
9.682149

These limitations of the monitors' data production process can be addressed by further development of the monitors. One such development is the addition of the valve position signal noted above. Another valuable development would be the improvement of the sensor amplification circuit used in the monitors. Discussions with electronics staff at Battelle have indicated that a better circuit could be designed and assembled, that would provide a larger analog output signal, while minimizing the noise in the circuitry. This improvement would provide greater output signals at low NO_2 levels, minimizing the effect of low sensor sensitivity and the 10 mV resolution of the HOBO dataloggers, and simplifying the data reduction process.

Finally, the performance of the NO_2/HONO monitors will always be dependent on the sensitivity of the NO_2 sensors themselves. TSI staff have indicated that production and development of the sensors will continue, and further effort is expected to reduce the long-term decay in response observed in this study. In routine use of the NO_2/HONO monitors, the loss of sensor response can be counteracted either by (1) frequent calibration of the monitors, or

(2) regularly scheduled replacement of the sensors. At this time, the former approach is recommended, because too little is known to establish a sensor replacement schedule that is appropriate for all sensors and all conditions of use. With the existing monitors, we recommend that after an initial multipoint calibration to establish a monitor's linear range, one-point NO_2 calibration checks be conducted once a week, and that a sensor be replaced when its NO_2 sensitivity falls below about 0.2 mV/ppbv. This will generally take place within 6 months of operation, depending on the initial sensitivity of the sensor. It may also be good practice to insert and calibrate new sensors at the start of any non-routine field study, such as a period of intensive measurements.

5.0 SUMMARY AND CONCLUSIONS

In this study a small, portable, rapid-response monitor was developed for determining nitrogen dioxide (NO_2) and nitrous acid (HONO) in indoor air. The monitor is based on a commercial electrochemical sensor that is capable of detecting as little as 5 ppbv of NO_2. This sensor also responds to HONO, with a sensitivity typically about three times as great as that for NO_2. This characteristic difference in sensitivity allows the monitor to determine HONO in the presence of a much larger concentration of NO_2. The measurement of NO_2 and HONO indoors is important because of the toxicity of these compounds, which originate from combustion sources such as gas cooking and heating appliances, and tobacco smoking. The intent of this study was to achieve NO_2/HONO monitoring with a time response much faster than that of the passive samplers used in previous in-home studies, and also faster than the one-hour period defined for California's 250 ppbv NO_2 standard.

For use in indoor monitoring of NO_2 and HONO in homes and businesses, the monitor was designed to be small and quiet. The monitor is 30 cm W x 20 cm H x 25 cm D, and weighs 4.8 kg. It is completely self-contained, needs no expendable reagents or supplies, and incorporates its own miniature dataloggers for recording of measurements and of temperature and relative humidity data.

Laboratory and test chamber evaluations were conducted of chemical interferences, temperature and relative humidity dependence, linearity, detection limits, and time response. Field tests were performed in a research house, in two occupied homes and one business in southern California, and in one occupied home in Columbus, Ohio. In those tests, a conventional chemiluminescent nitrogen oxides monitor, equipped to provide measurements of NO_2 and HONO, was used to obtain data for comparison.

The conclusions of this work are:

1. With a relatively new sensor exhibiting good sensitivity, the monitor has a detection limit of about 20 ppbv or less for NO_2, and can successfully determine NO_2 and HONO simultaneously in indoor air.

2. The linear range of the monitor typically extends to 2 ppmv of NO_2, more than sufficient for the planned indoor air monitoring application.

3. Chemical interferences from species likely to be present in indoor air, such as NO, CO, CO_2, SO_2, NH_3, and formaldehyde, are minimal. Interference from ozone does not appear to be significant in the presence of other indoor contaminants.

4. The response time of the monitor to a step change in NO_2 or HONO is about two minutes, more than fast enough to track indoor air emissions of these species from combustion sources.

5. The response of the electrochemical sensors is dependent on ambient temperature and relative humidity, increasing with both. In field tests, corrections for these effects often totaled 15 percent or less.

6. The sensitivity of the electrochemical NO_2 sensors decreases with time, at a rate of 20 percent or more per month, for reasons that are not yet understood. This behavior can require relatively frequent calibration checks, and will require replacement of each sensor once or twice per year.

7. The rapid electrochemical NO_2/HONO monitoring approach provided results within 10 to 20 percent of those from a conventional monitor, when operated with a relatively new and sensitive electrochemical sensor. In addition to using a sensitive sensor, other approaches to improving or maintaining accuracy are development of a better amplification circuit for the sensor, and adoption of a data recording device with better resolution than the 10 mV resolution of the HOBO datalogger.

6.0 RECOMMENDATIONS

Listed below are additional efforts that would substantially extend the NO_2/HONO monitor development conducted in this study.

1. Develop an improved circuit to convert and amplify the signal of the electrochemical sensors. The aims of this development are to produce a quieter circuit, and one that provides a larger analog signal.
2. Establish the cause of the gradual decay of sensitivity observed with the electrochemical NO_2 sensors, and adopt steps to minimize it.
3. Incorporate a low-voltage DC signal into the monitor to indicate the position of the three-way valve. Recorded by the HOBO datalogger, this signal would aid in processing the two channels of data in a spreadsheet.
4. Incorporate better components into the monitors. Specifically, the Teflon three-way valve and miniature air pump should be replaced with more reliable equivalents.
5. For outdoor monitoring, or indoor monitoring in the absence of combustion sources, develop a filter or trap that removes ozone while allowing NO_2 and HONO to pass through.
6. Perform further field testing with a monitor that has been modified by the foregoing improvements. This testing should address NO_2 levels near or above the one-hour standard of 250 ppbv, which were not encountered in the field tests in this program.

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