APPENDIX A

FIRST INTERIM REPORT
(Covering Assembly of the Prototype
NO_2/HONO Monitors and
Initial Laboratory Testing)

FIRST INTERIM REPORT ON LABORATORY TESTING

in

DEVELOPMENT OF SHORT-AVERAGING-TIME INDOOR NITROGEN OXIDE MONITOR

CARB Program No. 96-312

February 3, 1998

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INTRODUCTION

This is the first interim report on the results of project 96-312, "Development of a Short-Averaging-Time Indoor Nitrogen Dioxide Monitor", conducted by Battelle for the California Air Resources Board (CARB). This report presents the procedures and results of laboratory testing of three electrochemical sensor-based monitors for nitrogen dioxide (NO_2) and nitrous acid (HONO). Specifically, this report covers the laboratory testing that was done up to the point at which the monitors were subjected to preliminary field testing. The results of the preliminary field tests, and of additional laboratory tests, will be the subject of a second report.

This report was made necessary by a change in the schedule for this project. Originally, it was planned that nearly all the laboratory testing would be completed before the preliminary field testing was conducted. However, preliminary field testing was conducted earlier than planned, in order to coordinate with an ongoing project in a research house in Chicago. As a result, laboratory testing was interrupted, and was completed after the field testing. This report documents the laboratory testing that justified the readiness of the monitors for the preliminary field trial.

PROCEDURES AND EQUIPMENT

Monitors Tested

The three monitors tested were assembled using type NO2-SNL electrochemical NO_2 sensors produced by TSI Inc., of St. Paul, Minnesota. These sensors were chosen based on previous experience in our laboratories (Spicer et al., 1994), and on discussions with the manufacturer. In particular, the previous observation that the sensors were more sensitive to HONO than to NO_2 (Spicer et al., 1994) made them attractive for determining both species in indoor air. The sensors incorporate a proprietary electrode design that results in extremely low baseline current, allowing detection of low ppbv levels of NO_2, in contrast to other sensors for which detection limits are often in the ppm range.

Each sensor was fitted into a Teflon sampling block, designed and made in this project, with inlet and outlet ports to provide passage of sample air over the face of the sensor. The electronics supplied by TSI as a sensor evaluation kit were used to provide bias voltage to the sensor, and to provide amplification and current-to-voltage conversion of the sensor signal. This resulted in an analog output signal (approximately 0 – 2 V) from the sensor. A small diaphragm air pump was used to pull air through the Teflon sensor block. A miniature Teflon 3-way solenoid valve, and a potassium carbonate (K_2CO_3) - coated glass fiber filter in a Teflon holder, were installed in the sample air flow line upstream of the sensor. Passage of air around the $CO_3^=$ filter allowed measurement of NO_2 and HONO, whereas passage through the filter caused removal of HONO from the air stream. The switching of the solenoid valve was controlled by an adjustable timer and accomplished by means of a relay. The analog output signal was directed to different output jacks on the rear of the instrument, depending on the position of the valve. Thus the sensor responses to filtered and unfiltered sample air were shown by separate and alternating analog outputs. For the testing described here, the valve timing was set to switch between filtered and unfiltered modes of sampling at 10 – minute intervals.

The components outlined above were installed into an aluminum chassis of dimensions 12 in. W x 4 in. H x 7 in. D. Power switches and controls for automatic or manual valve switching were installed in the front panel of the chassis, and the air intake and analog outputs were mounted in the rear panel. The instrument operates on 120 V AC power, however all

internal circuits use low-voltage DC power for safety. A battery and continuous battery charging circuit were installed in each chassis, to isolate the sensor electronics from trace AC leakage currents from the DC power supply. Air flow control was achieved by placing a crimped section of stainless steel tubing in the air flow path just upstream of the air pump, and air flow is indicated by a miniature rotameter located at the front of the chassis. The resulting instruments have sample air flows of 870, 880, and 850 cm^3/min, for monitors 1 through 3, respectively, and each weighs approximately 8 pounds. Figure 1 is a schematic of the layout of the three NO_2/HONO monitors tested in this effort.

Initial tests with this layout of the monitors showed that the internal temperature during normal operation was about 10°C above the room temperature, i.e., about 33 to 35°C at room temperature of 22 to 23°C. This internal temperature is in the upper half of the optimum temperature range stated by the manufacturer for operation of the sensors. As a result, no effort was made to provide temperature control on the sensor housing. It was judged that a temperature control circuit would provide little additional stability beyond the temperature environment already present in the monitor, and would add complexity to the monitor. This judgment will be reconsidered, if necessary, based on the results of field and further laboratory tests.

General Testing Approach

In the laboratory testing reported here, the general approach was to test the three monitors simultaneously with a single target species or potential interferent. In nearly all tests the three monitors sampled from a common manifold, and thus sampled identically the same sample mixtures. The sole exception was in testing with HNO_3. In the HNO_3 tests the monitors were supplied with the test mixture one at a time, because of the difficulty of transporting low concentrations of HNO_3 through sampling lines. High purity air, generated by an Aadco Pure Air Generator in the laboratory, was used as the dilution matrix in all tests. In all but initial preliminary tests, the sample air supplied to the monitors was humidified, by addition of a second flow of pure air that had been passed through a heated water tank. In the testing described here, the monitors were operated at room temperature (i.e., 20 to 22°C). The range of relative humidities used in testing was from about 5 to 85 percent.

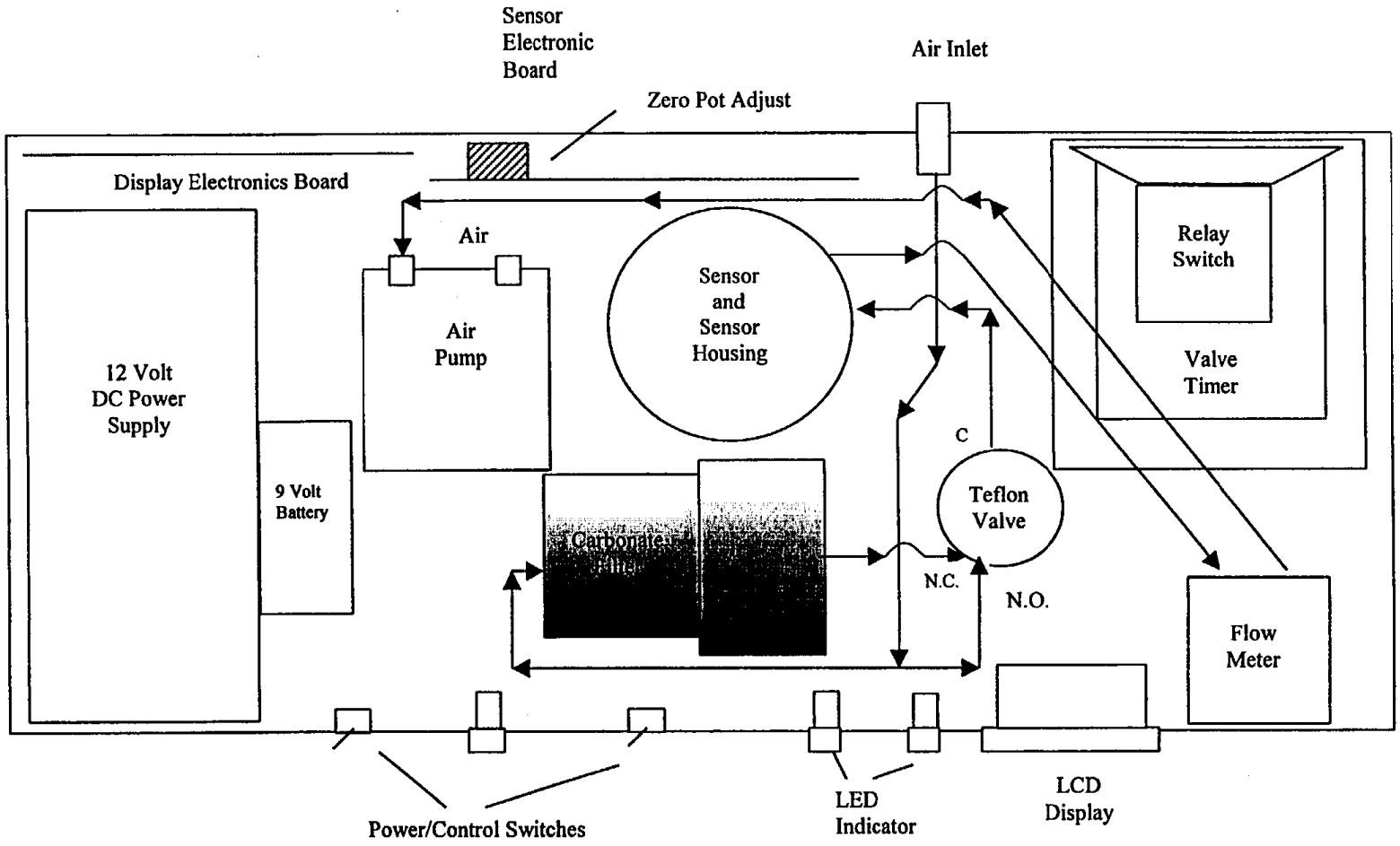


FIGURE 1. SCHEMATIC OF THE ELECTROCHEMICAL NO_2/HONO MONITORS

The target species of interest in this study were nitrogen dioxide (NO_2) and nitrous acid (HONO). The potential interferants tested were nitric oxide (NO), carbon monoxide (CO), carbon dioxide (CO_2), ozone (O_3), formaldehyde (HCHO), sulfur dioxide (SO_2), nitric acid (HNO_3), and peroxyacetylnitrate, i.e., $CH_3C(O)O_2NO_2$ (PAN). Table 1 shows the concentration ranges of interest for each of the target and interferant compounds. In collaboration with CARB staff, these ranges were chosen to cover the maximum concentrations of the indicated species that might be expected to occur indoors. Published indoor air quality studies indicate that the maximum target levels in Table 1 greatly exceed the interferant levels generally found in California homes (Wilson et al., 1993; Spengler, et al., 1994). Furthermore, an initial review of indoor data from the preliminary field tests (which followed the laboratory efforts reported here) confirm that indoor levels are likely to be below the maxima in Table 1. For example, even with continuous operation of unvented gas hearth products on maximum settings for up to 12 hours, producing temperatures up to 100°F in the small research house, the maximum levels of several species were as follows: NO_2, 1.1 ppm; NO, 2.4 ppm; CO, 7.2 ppm; CO_2, 6,300 ppm; SO_2, 55 ppb; and HCHO, 295 ppb.

TABLE 1. CONCENTRATION RANGES OF INTEREST FOR TARGET AND INTERFERANT COMPOUNDS

Compound	Range
NO_2	50 ppbv to 2 ppm[a]
NO	10 ppbv to 2 ppm
HONO	1 to 100 ppbv
HNO_3	1 to 15 ppbv
PAN	1 to 10 ppbv
O_3	5 to 150 ppbv
CO	1 to 100 ppm
CO_2	10 to 5,000 ppm
HCHO	5 to 400 ppbv
SO_2	up to 500 ppbv

(a) Response to be tested at one temperature and one RH value at concentrations up to 3 ppm.

For the interferant compounds, testing usually began with the maximum concentration level of interest. If no response was observed at that level, then it was inferred that no interference would result from that species at lower concentrations, and no further tests were

conducted. For certain species, such as HNO_3 and PAN, even the maximum levels shown in Table 1 were difficult to prepare. As a result, tests at the maximum levels shown in Table 1 were supplemented or replaced by tests at substantially higher levels.

The concentrations of the target and interferant species supplied to the monitors were established in either of two ways. For some species (i.e., NO, NO_2, CO, CO_2, O_3, and SO_2), certified standard sources of the species were used. For all but O_3, these standards were compressed gases in the form of Standard Reference Materials (SRM's) obtained from the National Institute of Standards and Technology (NIST), or comparable commercial standards, whose content in most cases was confirmed by comparison to a NIST standard. For ozone, a commercial primary standard ozone generator was used. For other species (i.e., HONO, HNO_3, PAN, and HCHO) certified standards do not exist. For these species prepared concentrations were confirmed by analysis of the sample stream with an independent analytical method. The sources and confirmation techniques used are described below.

Target and Contaminant Sources

Water Vapor – The humidification of the sample air stream was accomplished using the apparatus shown schematically in Figure 2. A flow of high purity air, controlled by a mass flow controller, was passed through an 8 liter aluminum vessel wrapped with heating tape, and containing several liters of deionized water. The temperature of the vessel was controlled at 46 (+/- 1) °C, and the water level was monitored by means of an external sight tube. Air flows of 0.1 to 2 L/min were humidified in this vessel, and then mixed with a dry air stream containing the target or interferant species of interest. Final relative humidities of 5 to 85 percent at room temperature were readily prepared with this apparatus.

The one exception to this humidification approach was the testing for PAN. Gaseous PAN was prepared by injecting microliter quantities of PAN in decane solution into a gas sampling bag. The high purity air in the bag was humidified by addition of microliter quantities of water directly into the bag.

Relative humidity was determined using a Model 911 Dew-All Digital Humidity Analyzer (Edge Tech, Milford, Mass.). This analyzer uses the cooled mirror principle to determine dew point and relative humidity of the air stream.

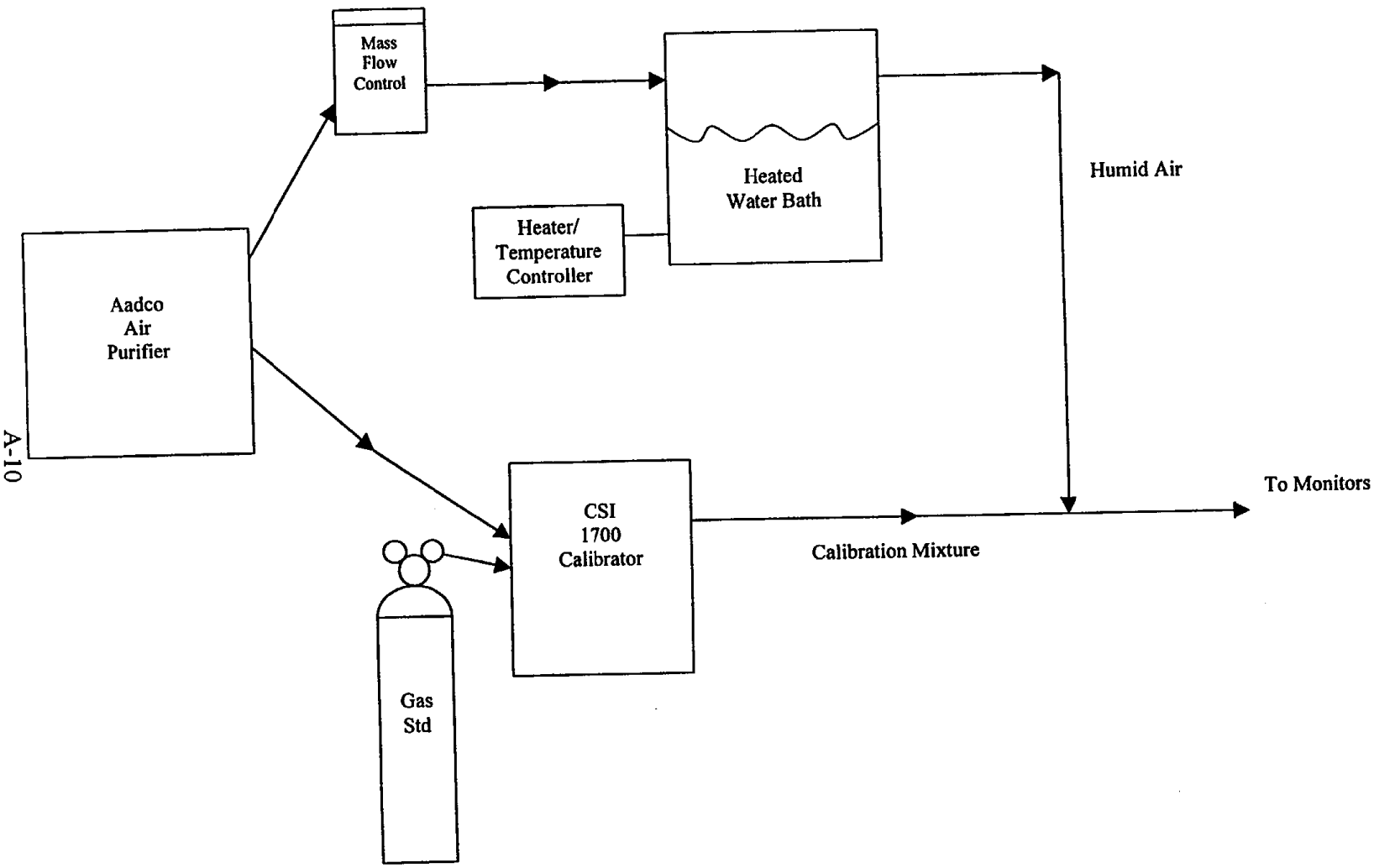


FIGURE 2. SCHEMATIC OF AIR HUMIDIFICATION SYSTEM USED IN LABORATORY TESTS

Gas Dilution – A Columbia Scientific Industries (CSI) Model 1700 Gas Calibrator was used to dilute target and contaminant species to the desired levels for testing. This device has mass flow controllers for air and calibration standard flows, digital readout of flow rates, and an internal ozone source and mixing chamber for gas phase titration of NO with ozone.

Nitric Oxide – The NO source for these tests was an "Acublend Master Gas" Certified Standard of 49.7 ppm NO in nitrogen, obtained from Scott Specialty Gases. The concentration of this standard was confirmed by comparison with a NIST SRM of 47.7 ppm NO in nitrogen (SRM 1683b), using a Monitor Labs Model 8840 Nitrogen Oxides analyzer.

Nitrogen Dioxide – The NO_2 source for these tests was a Certified Working Standard cylinder of nominally 51.3 ppm NO_2 in nitrogen, obtained from Scott Specialty Gases. The concentration of this standard was checked by comparison with the Scott 49.7 ppm NO standard (see above), using the same Monitor Labs Model 8840 Nitrogen Oxides analyzer. This comparison showed that the actual concentration of the NO standard was 46.1 ppm, rather than 51.3 ppm. The corrected standard concentration was applied in evaluating all test data.

Sulfur Dioxide – The source of SO_2 was a NIST SRM of 47.7 ppm SO_2 in nitrogen (SRM 1693a).

Carbon Monoxide – A cylinder of 8.0 percent CO in nitrogen (Matheson Gas Products) was used as the source of CO for dilution, in order to achieve the relatively high maximum level shown for this compound in Table 1. This standard had been compared in previous studies to NIST standards, including SRM 2636a, containing 242.7 ppm CO in nitrogen.

Carbon Dioxide – A Certified EPA Protocol Standard of 7.99 percent CO_2 in nitrogen (Scott Specialty Gases) was used as the source for CO_2.

Formaldehyde – A Certified Standard cylinder of 10.0 ppm HCHO in nitrogen (Liquid Carbonic Specialty Gases) was used as the source for testing of HCHO interference. No NIST standard exists for HCHO, so the standard concentration was checked by analysis with Battelle's continuous gas-phase HCHO monitor (Kelly and Fortune, 1994; Kelly, 1996). The continuous monitor has shown excellent agreement with other measurements, including the DNPH derivatization/HPLC method denoted as EPA TO-5 (Kelly, 1996).

Ozone – The primary ozone standard in these tests was a Dasibi 1008PC Primary Ozone Calibrator. This device uses the UV absorption principle to determine ozone, and incorporates both an ozone monitor and an ozone source. Known ozone levels are produced by a feedback

circuit that uses the 1008PC monitor to control the intensity of the lamp in the ozone source. The 1008PC was used to calibrate a Thermo Environmental Model 49 ozone monitor, which was then used to determine the ozone levels produced by the ozone source in the CSI 1700 calibrator. The combination of the CSI 1700 source and the Model 49 monitor was then used in all subsequent tests with ozone.

Nitric Acid – A permeation tube of nitric acid maintained in a high temperature permeation tube oven was the source for HNO_3. The tube was 7 cm long, and had a certified permeation rate of 900 ng/min at 90°C (Vici-Metronics). The tube was held in the permeation oven of a Metronics Model 340 dynamic calibrator. Because of the extreme difficulty of transporting vapor phase HNO_3 through tubing, the outlet flow from the calibrator was delivered through a 0.75 m length of 6.35 mm O.D. tubing heated over its entire length to 45 (+/- 1°C). The HNO_3 test mixture was provided to each of the three monitors one at a time, via this heated line.

Nitrous Acid – HONO vapor was produced in known concentrations by converting HNO_3 to HONO through contact with a bed of solid $NaNO_2$ coated on glass beads (Spicer et al., 1993, 1994). The HNO_3 permeation tube described above was used as the HNO_3 source. Nitric acid vapor from the permeation tube was carried through the heated line to an unheated 20 ml volume glass trap containing 5 mm glass beads coated with $NaNO_2$. Complete one-to-one conversion of nitric to nitrous acid took place in the trap, and the resulting HONO concentrations were then confirmed by sampling with the Model 8840 nitrogen oxides analyzer.

PAN – Known concentrations of PAN were prepared by injecting microliter quantities of a solution of PAN in decane into humidified high purity air in a 40-liter Tedlar gas sampling bag. Because of the difficulty of accurately injecting microliter quantities of the PAN solution into the bag, it was judged preferable to increase the target PAN concentration somewhat above the 10 ppbv shown in Table 1. The PAN was synthesized in decane solution, and the resulting solution concentration was then determined by vaporizing known quantities of the solution into the cell of a Fourier transform infrared (FTIR) absorption instrument. The solution used in this study was found to contain 4.5 μg PAN/μL of solution. Because of the potential for PAN to decompose in solution or in the bag, the PAN level in the bag was also determined directly using a gas chromatographic approach with electron capture detection. In the two tests performed, the bag PAN levels were found to be 20 ppbv and 16 ppbv, respectively, by the GC technique. Sampling

of the bag contents was completed within 15 minutes after injection of the PAN solution into the bag, so that decomposition of PAN is believed to have minimal effect on the test results.

RESULTS AND DISCUSSION

General Comments

The results of the laboratory tests conducted up to the point of preliminary field testing are summarized below, arranged by individual target or interferant species. Before proceeding to specific test results, some general comments on the behavior of the three monitors are in order.

The electrochemical sensor-based monitors exhibited both consistent and individual behavior. They showed consistent behavior in that their response to various interferants was essentially the same; i.e., there was no indication of different interferant behavior in one monitor compared to the others. All the monitors showed excellent reliability, operating for weeks at a time in the laboratory without incident, and with no problems in either manual or automatic modes of operation.

On the other hand, each monitor also exhibited individual characteristics. Most notable is that each monitor has its own sensitivity to NO_2, which appears to be a characteristic of the sensor used, and is not greatly affected by factors such as the bias voltage applied to the sensor. As will be illustrated below, the three monitors exhibited NO_2 sensitivities in the order of monitor #1 > monitor #3 > monitor #2. The sensitivity differences also led to differences in the extent of the linear range for NO_2. Since the air flows, physical configurations, and data acquisition procedures are the same for all three monitors, such differences are attributed to the sensors themselves. A similar difference was found in the sensitivity to HONO. Despite these individual differences, all three monitors showed ample sensitivity for the intended purpose of indoor air measurements.

Another individual characteristic was the rate of change of the NO_2 sensitivity. Although all three monitors showed a loss of sensitivity during the period covered by this report, the extent of that loss differed sharply among the three. These observations suggest the need to consider the unique characteristics of each sensor in their selection and use.

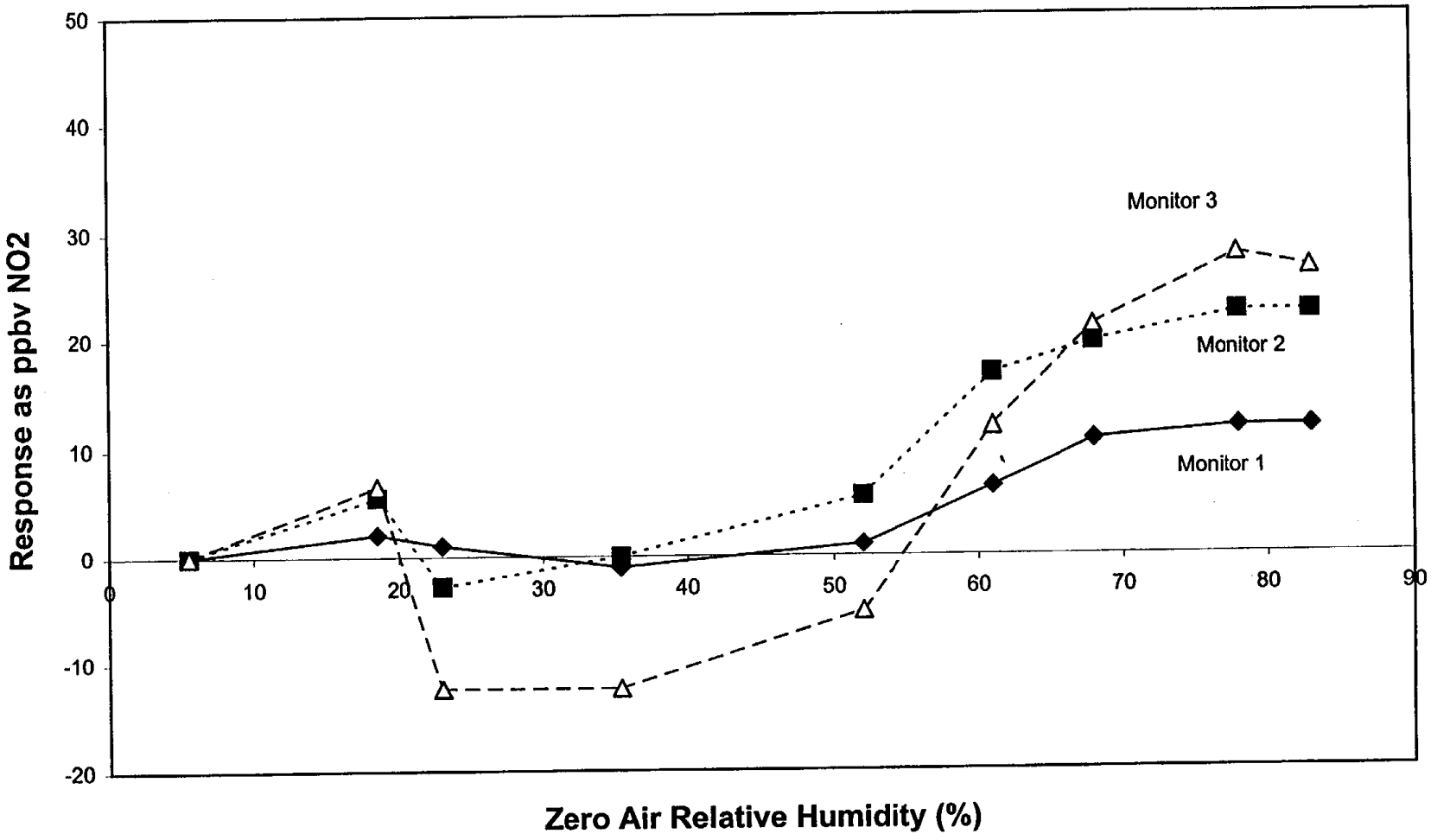
Relative Humidity

The impact of the relative humidity of the sample air on the baseline (i.e., zero air) response of the monitors was assessed, by altering the degree of humidification of high purity air supplied to the monitors. The mV readings from the monitors were converted to NO_2-equivalent values using the results of an NO_2 calibration conducted on the same day. The results are shown in Figure 3, in terms of the NO_2-equivalent shift in the baseline signal (relative to that at 5.5 percent RH) that occurred at various RH levels. Figure 3 shows that the RH effect on the baseline signal is similar for the three sensors and relatively small, amounting to at most 30 ppbv NO_2 equivalence (i.e., approximately 20 mV absolute signal) over the full range from 5.5 to nearly 85 percent RH. Noise and drift in the monitors' baseline signal over the duration of this test undoubtedly affect the measurement of these small changes in baseline signal. For example, an apparent negative dependence on RH is suggested for Monitor 3 at RH between 20 and 40 percent; this is unlikely to be a real effect. In any case, the main conclusion from Figure 3 is that humidity effects on the baseline signal are small. Note that in actual operation it would be improbable to encounter such a wide range of relative humidity in a short time period, and furthermore the monitor's baseline signal would be measured in operation at the ambient conditions. Thus the real impact of RH on baseline readings will be less than the maximum differences indicated in Figure 3.

The effect of the relative humidity on sensitivity for NO_2 was also assessed by conducting calibrations at more than one humidity on a single day. This was done on November 7, when the monitors were calibrated at room temperature in air of 5.5 percent, 20 percent, and then 38 percent RH. The sensitivities (in mV per ppbv NO_2) of all three monitors increased with increasing RH in these tests. At the successive RH values of 5.5, 20, and 38 percent, monitor 1 showed sensitivities of 0.768, 0.794, and 0.863 mV/ppbv; monitor 2 showed 0.320, 0.337, and 0.355 mV/ppb; and monitor 3 showed 0.575, 0.631, and 0.644 mV/ppbv. These results show a consistent increase in sensitivity of 11 to 12 percent from the lowest to the highest RH values tested.

Further tests are planned to assess the RH effect on NO_2 sensitivity over a wider range of RH values (i.e., to at least 80 percent RH).

Figure 3. Zero Air Response versus Relative Humidity



NO_2 Response

The detection limits of the sensors were assessed by monitoring the noise in the signal while sampling humidified high purity air, and by sampling of very low concentrations (i.e., < 10 ppbv) of NO_2. The latter tests showed that, at least when new, the sensors could detect NO_2 at levels below 5 ppbv, in agreement with the manufacturer's claims. However, the noise in the baseline signal was found to be at least +/- 5 mV, and gradual drift in the baseline signal was also observed over the course of a day. As a result of these factors, quantitation of the NO_2 concentration is only possible above about 10 ppbv, assuming the monitor's baseline signal is determined at intervals of a few hours. Under rapidly changing ambient conditions, the detection/quantitation limits may be higher.

The linearity of the three prototype monitors was tested by a multipoint calibration, at about 30 percent RH and room temperature, over the full range of NO_2 concentrations listed in Table 1. Figures 4a through 4c show the results of that calibration for monitors 1 through 3, respectively. These figures show that all three monitors give linear response to NO_2, up to the point at which the output of the sensor electronics is saturated, i.e., at about 1,800 mV output. For monitors 1 and 3 (Figures 4a and 4c), saturation is reached at NO_2 levels of about 2,250 ppbv and 2,450 ppbv, respectively. Monitor 2 (Figure 4b) showed the lowest sensitivity, and thus did not reach electronic saturation over the range of concentrations tested. The linear regression fits to the data in Figures 4a through 4c have the form:

Monitor 1: $mV = 0.827 \times ppbv\ NO_2 + 18\ mV;\ r^2 = 0.998;\ N = 9$

Monitor 2: $mV = 0.355 \times ppbv\ NO_2 + 11.4\ mV;\ r^2 = 0.998;\ N = 11$

Monitor 3: $mV = 0.708 \times ppbv\ NO_2 - 14.9\ mV;\ r^2 = 0.9998;\ N = 9.$

The sensitivity of all three monitors (i.e., 0.355 to 0.827 mV/ppbv) is sufficient for determination of NO_2 at indoor air levels, and the linear range of all the monitors exceeds the upper limit of expected indoor air NO_2 levels (ca. 1 ppm). Comparison of these results indicates that there is a tradeoff between the sensitivity of the sensor and its linear range, due to the saturation point of the sensor output electronics.

Figure 4a. Wide-Range NO2 Calibration, Monitor 1

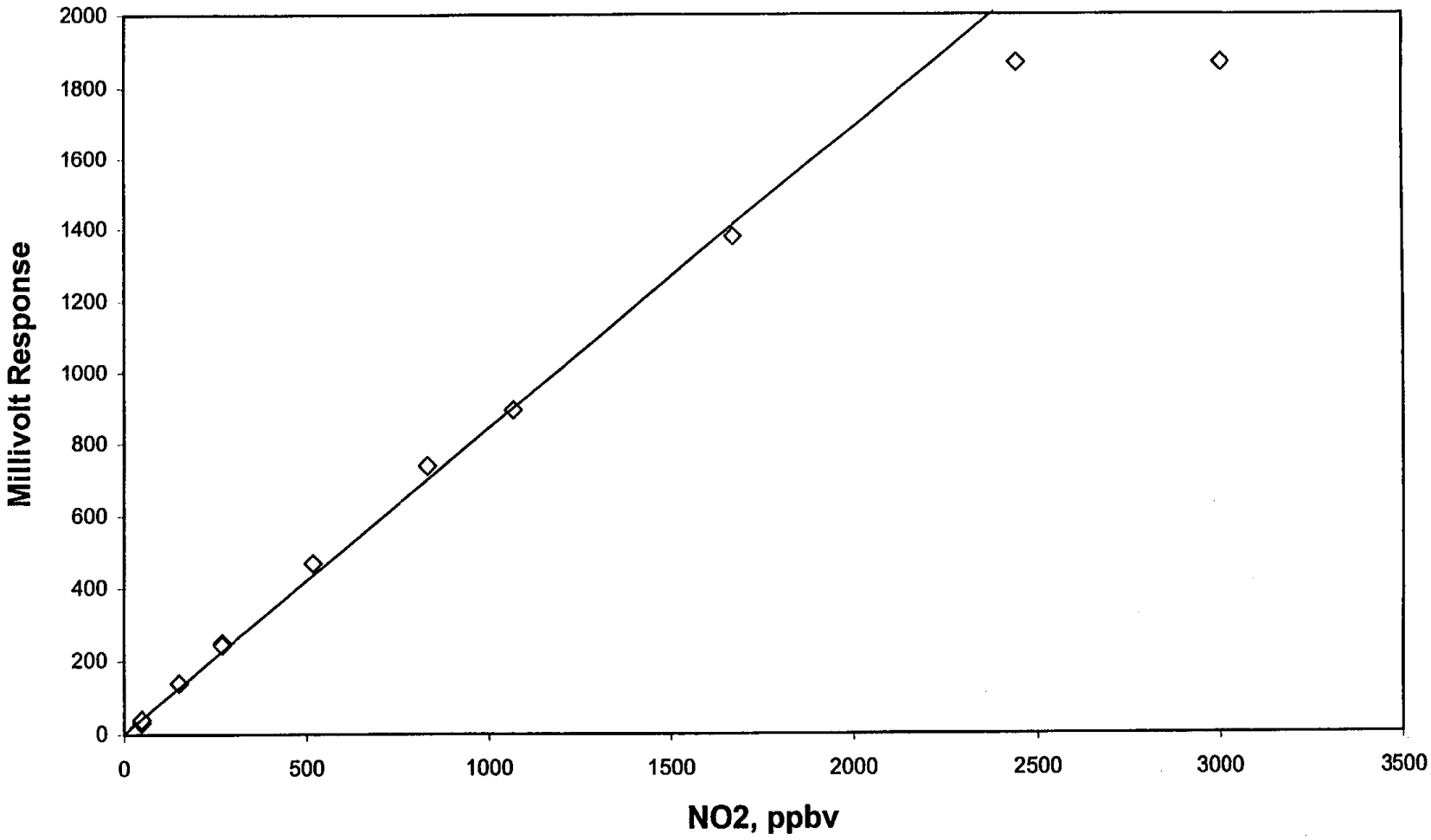


Figure 4b. Wide-Range NO2 Calibration, Monitor 2

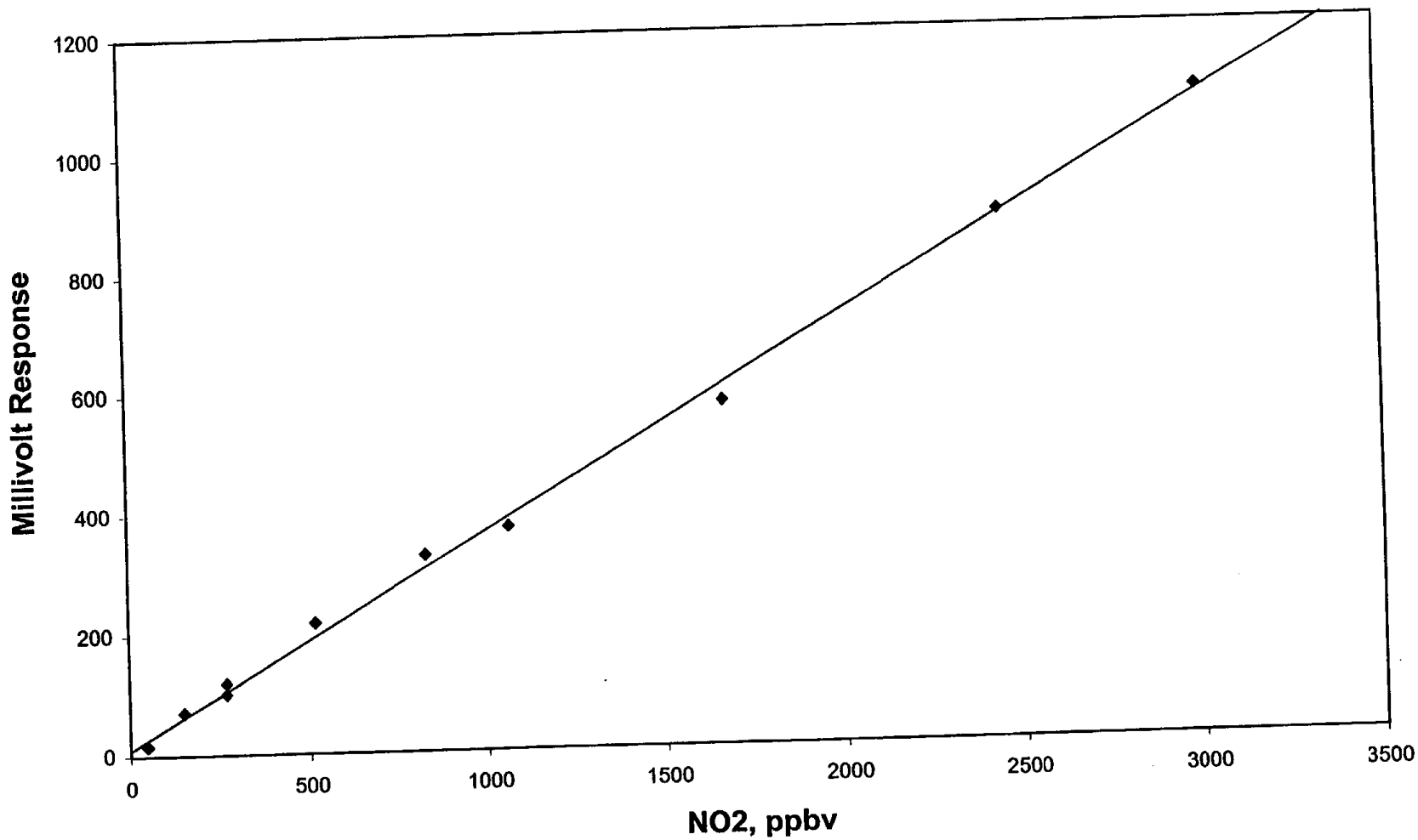
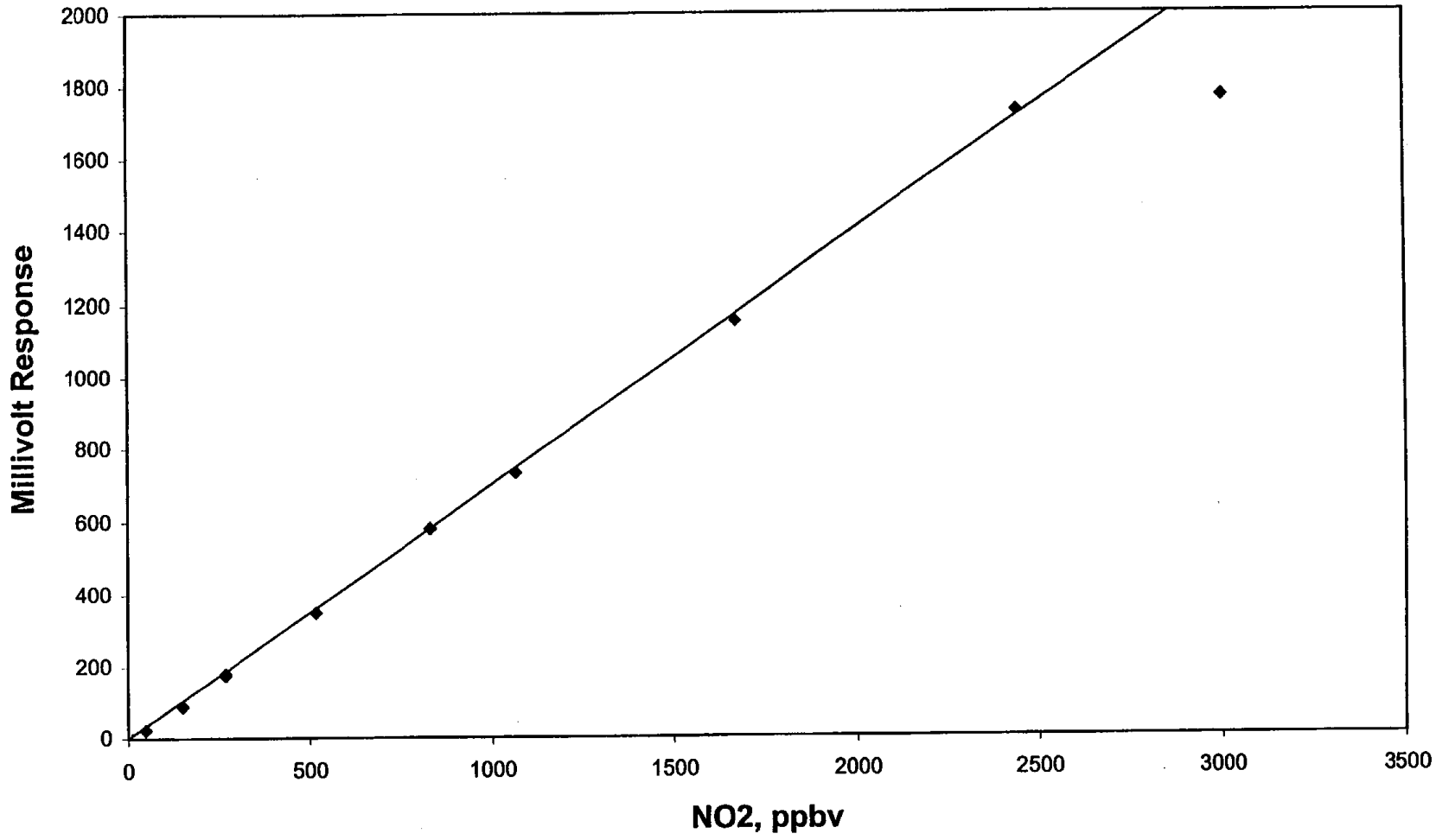


Figure 4c. Wide-Range NO2 Calibration, Monitor 3

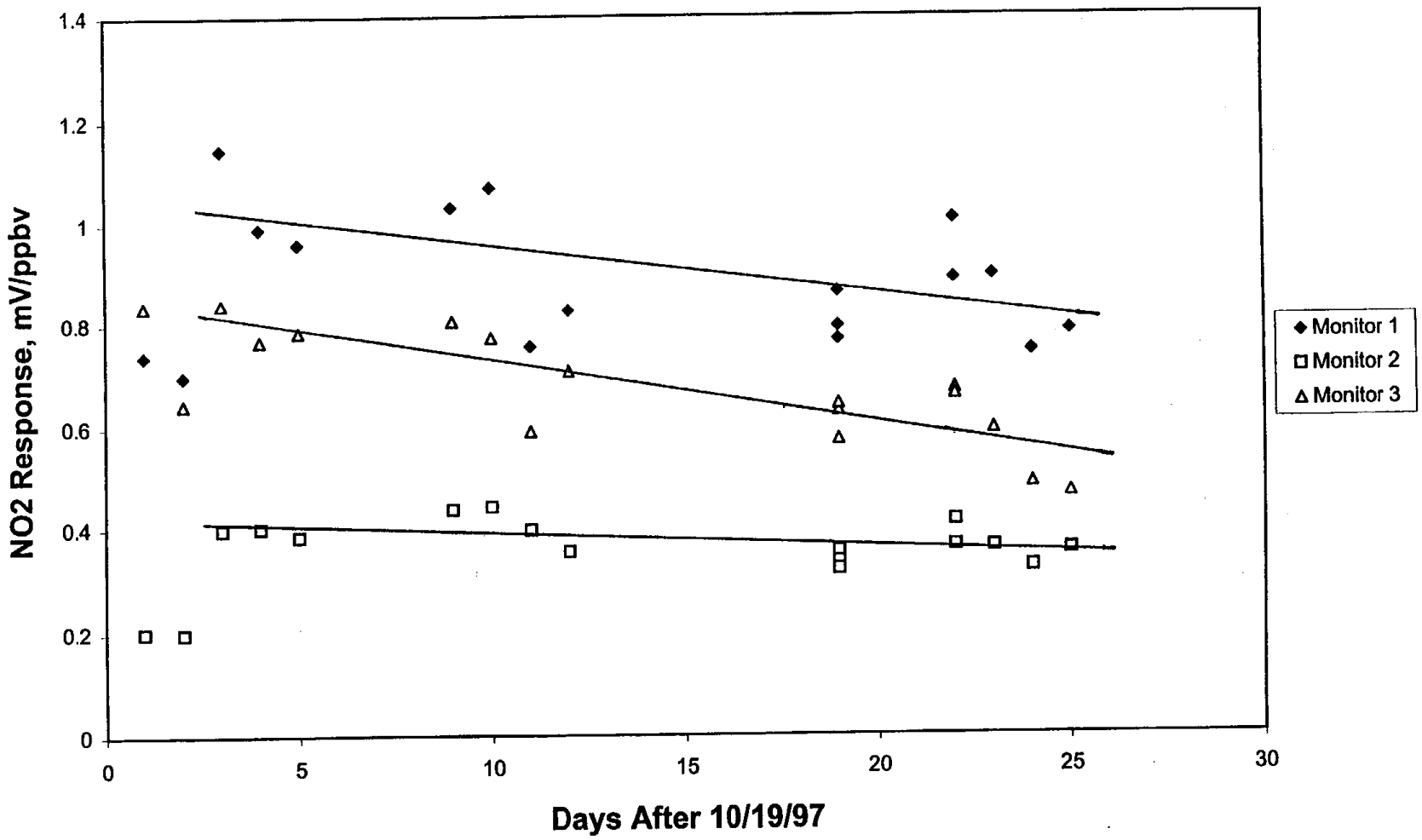


The time response of the monitors was found to be faster than expected. Upon switching between the filtered or bypass modes of measurement, the response of each monitor was found to stabilize within two minutes, i.e., the time to go from 5 percent to 95 percent of the final reading was less than two minutes. In the laboratory, data were displayed at 30-second intervals using LabTech Notebook software, and it was generally observed that even the first data point displayed after switching modes was often within 10 to 20 percent of the final reading. This response time is comparable to that stated by the manufacturer.

The long-term stability of the monitors' sensitivity for NO_2 was documented by means of the NO_2 calibrations done on every day of laboratory testing. Figure 5 summarizes the results, showing the monitors' sensitivity (in mV/ppbv NO_2) on every day of laboratory testing, from October 20 until November 13, immediately before the preliminary field tests. Results from both single and multipoint calibrations are shown; the slopes of linear regressions to the data are plotted for the multipoint calibrations. Over the entire test period shown (17 calibrations) the average response sensitivities for monitors 1 through 3 were 0.880 (± 0.133), 0.356 (± 0.069), and 0.676 (± 0.113) mV/ppbv, respectively. The variation in each corresponds to ± 15 percent, ± 19 percent, and ± 17 percent, as relative standard deviation, respectively. However, the first two calibration results were somewhat lower than the later results, and contributed substantially to the variance. For example, excluding the first two calibrations, the average response of monitor 2 was 0.376 (± 0.038) mV/ppbv, i.e., a relative standard deviation of 10 percent. The degree of variation observed reflects the behavior of the sensors in response to the test program, as well as small variation in the calibration process itself.

Figure 5 also shows that once the monitors stabilized after the first few calibrations, each monitor exhibited a characteristic sensitivity for NO_2, but with a gradual loss of sensitivity during the period. This decrease in sensitivity also contributes to the variances noted above. The lines in Figure 5 are linear regressions to the data, and indicate that monitors 1 through 3 lost sensitivity at a rate of about 28 percent per month, 20 percent per month, and 43 percent per month, respectively, after the first few days of testing. Although the sensitivity of all three monitors at the end of this testing period was more than sufficient for indoor monitoring, the rate of decrease of sensitivity greatly exceeds that reported by the manufacturer, i.e., 5 percent per month. Furthermore, the rates of the sensitivity decrease differ widely among the three sensors, indicating that each sensor must be considered individually in accounting for this decrease. It is

Figure 5. Summary of NO2 Calibrations, 10/20 - 11/13/97



noteworthy that the response speed of the monitors was not degraded as the sensors aged and gradually lost sensitivity.

A consistent difference in signal between the filtered and unfiltered modes of measurement was also observed with each sensor, even when sampling air containing only NO_2. This difference was in the direction of filtered response < unfiltered response, with a typical ratio greater than 0.9. The origin of this effect appears to be small flow differences in the two paths, due to the pressure drop of the carbonate coated filters. Operation without a filter results in equal flows and equal responses in the two channels. In normal operation this effect is accounted for by applying separate NO_2 calibration factors to the two modes of data.

HONO Response

The monitors' sensitivity to HONO was found to be much higher than their sensitivity to NO_2. This finding is consistent with that reported by Spicer, et al., (1994), for an earlier version of the sensors. An illustration of this result is shown in Figures 6a through 6c, which show the results of NO_2 and HONO calibrations conducted on the same day for monitors 1 through 3 , respectively. All three sensors show markedly higher mV responses, for HONO concentrations between 60 and 130 ppbv, than for the corresponding levels of NO_2. However, the ratio of HONO to NO_2 sensitivity was not the same for all three monitors. Based on the slopes of linear regressions to the HONO and NO_2 data, that ratio was 2.51, 5.75, and 3.16, for monitors 1 through 3, respectively. The ratio of HONO to NO_2 response was lowest for the monitor (i.e., # 1) having the highest NO_2 response, and highest for the monitor (i.e., # 2) having the lowest NO_2 response. This finding indicates that the HONO sensitivity is less variable from sensor to sensor than is the NO_2 sensitivity. For example, the regression slopes for HONO ranged from 1.48 mV/ppbv (monitor # 3) to 2.05 mV/ppbv (monitor # 2), whereas the NO_2 slopes ranged from 0.36 mV/ppbv (# 2) to 0.785 mV/ppbv (# 1). These results confirm the observation made with NO_2, that the sensors exhibit individual characteristics.

Figure 6a. NO2 and HONO Calibrations, Monitor 1

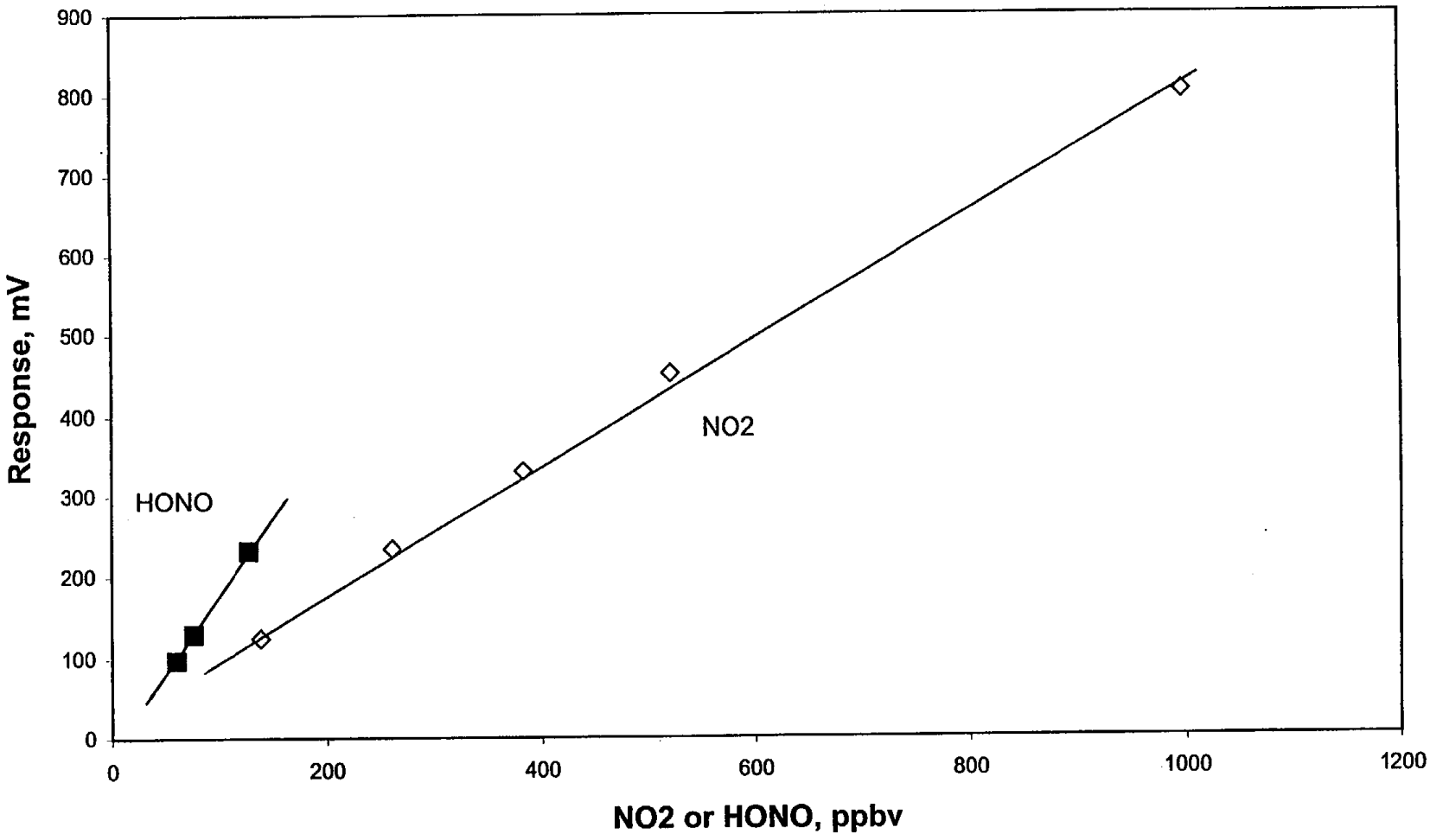


Figure 6b. NO2 and HONO Calibrations, Monitor 2

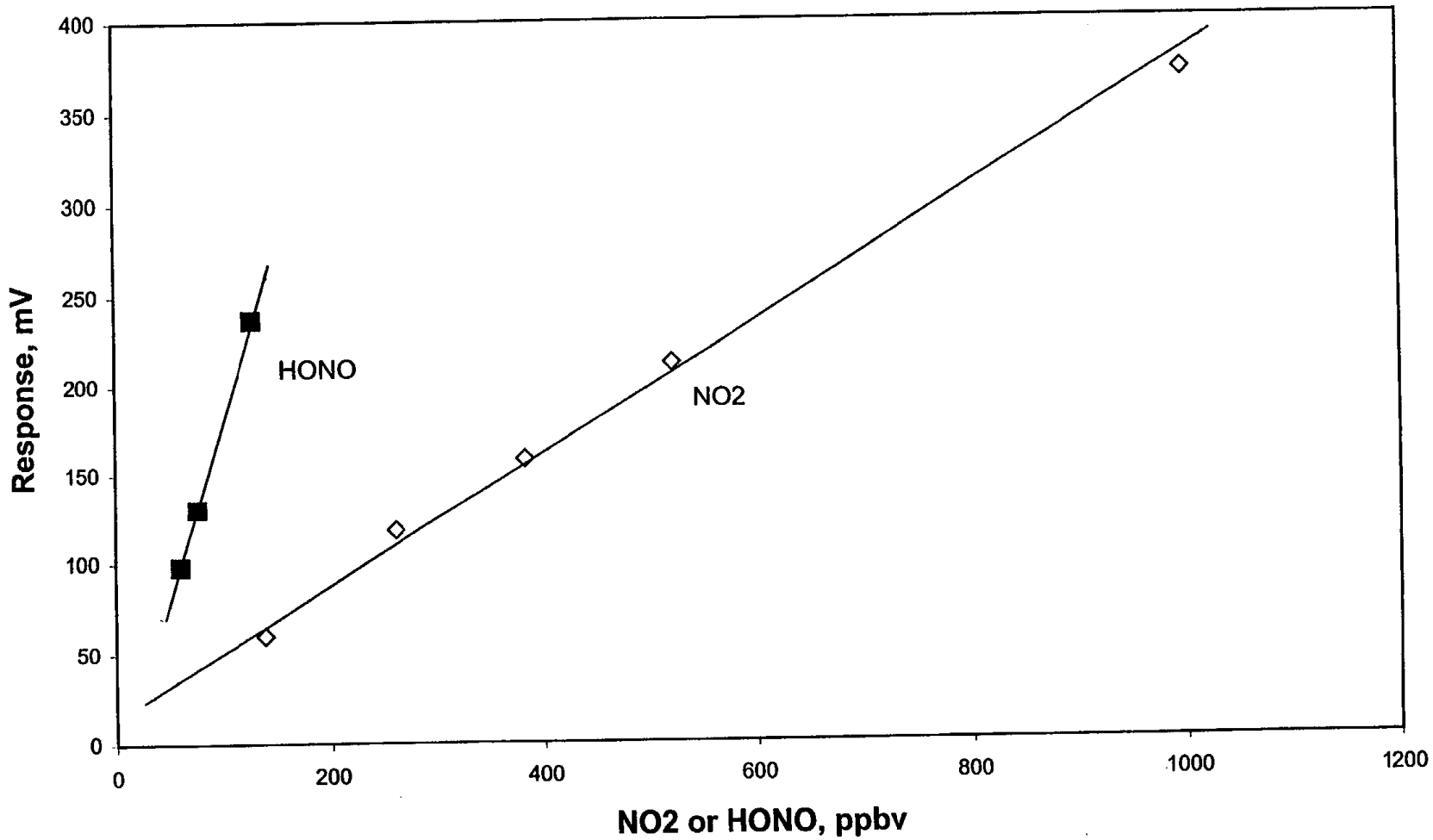
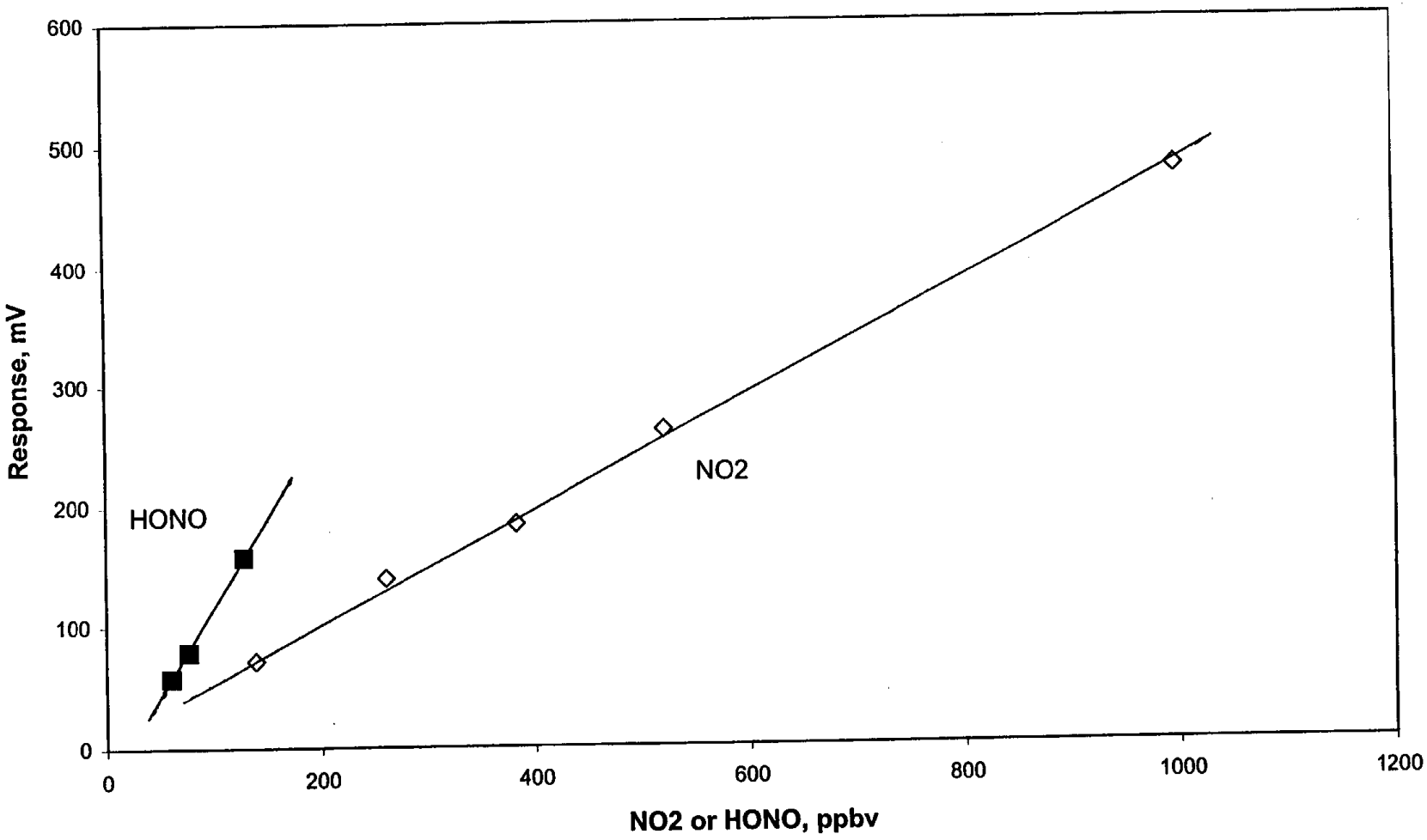


Figure 6c. NO2 and HONO Calibrations, Monitor 3



Initial tests showed that the carbonate filters were 100 percent efficient at removing HONO from the sample air. No effect was seen when a carbonate filter was connected to the inlet of a commercial chemiluminescent nitrogen oxides monitor sampling NO_2 in air, indicating that the filters cause minimal removal of NO_2. The total capacity of the filters for HONO is undoubtedly large, but was not determined in the laboratory tests reported here.

Interferant Compounds

Nitric Oxide - NO was tested as an interferant at concentrations from 338 to 2,020 ppbv, at room temperature of 22°C, in high purity air humidified to 20-25 percent RH. Response to NO was in the same direction (i.e., in terms of the output signal) as that for NO_2, but was much lower. At 338 ppbv, responses on all three sensors were indistinguishable from the zero air reading, and at the highest NO concentration tested the maximum individual responses of the three sensors were equivalent to 31 ppbv, 27 ppbv, and 37 ppbv NO_2 on monitors 1, 2, and 3, respectively. Thus the sensors have a selectivity of 70:1 or more toward NO_2 relative to NO. At common indoor NO levels of 1 ppm or less, NO will have a minimal effect on the measured NO_2 value.

Carbon Monoxide – Interference from CO was evaluated at 107 ppm, at 22°C and with RH of 27 percent. The response to CO was opposite to that for NO_2, i.e., signal dropped slightly with the high concentration of CO present. The maximum extent of this effect was equivalent to 3.9 ppbv, 5.0 ppbv, and 10 ppbv NO_2 on monitors 1, 2, and 3, respectively. Thus the sensors have a selectivity of at least 10,000:1 toward NO_2 relative to CO. At indoor CO levels of a few ppm, this interference will be negligible.

Formaldehyde – Testing of HCHO as an interferant was conducted at at 22°C and with RH of 20 percent. A concentration of 437 ppbv HCHO was prepared, and produced no detectable response whatsoever on the monitors, i.e., no signal beyond the few mV noise level in the zero air readings. Thus no significant interference will result from indoor HCHO.

Sulfur Dioxide – Interference from SO_2 was tested at a maximum concentration of 513 ppbv, at 22°C and with RH of 27 percent. As was the case for CO, the response of the sensors to SO_2 was weak and in the opposite direction to that for NO_2. The maximum individual response on each sensor in three trials with SO_2 was equivalent to 8 ppbv, 33 ppbv, and 22 ppbv NO_2, on

monitors 1, 2, and 3, respectively. Thus the selectivity of the sensors for NO_2 relative to SO_2 is 15:1 or more. The SO_2 level tested was far above any expected indoor levels; even at indoor SO_2 levels of up to 50 ppbv the extent of SO_2 interference would be limited to a few ppbv NO_2 equivalent.

Carbon Dioxide – Testing of CO_2 as an interferant was conducted using a concentration of 5,350 ppm, at 22°C and with RH of 37 percent. The response to CO_2 was equivalent to at most 4 ppbv, 10 ppbv, and 5 ppbv NO_2, on monitors 1, 2, and 3, respectively. This degree of interference (i.e., a selectivity toward NO_2 of at least 500,000:1) is completely negligible for indoor sampling.

Nitric Acid – Initial attempts to conduct interference tests with HNO_3 at the 15 ppbv level shown in Table 1 showed no response from any of the monitors. However, because of the known difficulties in transporting HNO_3 vapor through tubing, there was concern that the initial tests merely indicated that HNO_3 was lost from the vapor phase during the brief passage through the monitors' plumbing to the sensors. As a result, an additional test was done in which 150 ppbv of HNO_3 was supplied to the monitors in air having a 20 percent RH at 22°C. For this test, the output of the HNO_3 permeation tube was fed to only one of the monitors at a time, through a Teflon line that was heated over its entire length up to the rear bulkhead of the monitor. Even after extended sampling of the HNO_3 mixture, no detectable response was observed on any of the sensors. This finding does not unequivocally establish whether the sensors are insensitive to HNO_3 (which is likely), or whether even high very high levels of HNO_3 are lost in passage through the monitor. However, these results do indicate that the low levels of HNO_3 found indoors will not be an interferant with the NO_2/HONO monitors.

PAN – No response outside the baseline noise range was shown by either monitor 2 or monitor 3 when sampling from the bag containing PAN in humidified air. Monitor 1 showed a small difference in response relative to zero air, equivalent to about 20 ppbv NO_2. Thus if monitor 1 was responding to PAN, its sensitivity was about equal to that for NO_2. However, it seems unlikely that monitor 1 was responding to PAN, given that the other two monitors showed no response at all. These unusual observations could be explained by a small leak that allowed monitor 1 to sample a small amount of room air while sampling from the PAN bag. As a result, further testing with PAN is planned for after the preliminary field study. In any case, the small

response observed to a PAN level that exceeded the maximum target concentration (Table 1) is not likely to be a significant interference indoors.

Ozone – The ozone response of the sensors was tested on five separate occasions at levels of 46 to 200 ppbv in air of 20 to 45 percent RH. All three sensors exhibited response to ozone approximately equal to that for NO_2, but with markedly different time response. The sensor signal increased slowly when ozone was supplied in the sample air, and in particular decreased very slowly when the ozone was removed. When a high ozone level was sampled, as much as an hour was required for the zero signal to return to normal after the ozone was withdrawn. This behavior was completely different from the response to any other target compound or interferent, and suggests that the mode of detection of ozone was different.

In these tests, two approaches were tried to eliminate the ozone interference. First, an ozone removal trap of the kind used with the Scintrex Luminox NO_2 detector was placed on the inlet of each sensor in turn. This trap was found to restrict the flow of sample air to the sensor, so an accurate measure of ozone removal could not be obtained. Second, a 30 cm length of tubing composed of natural polyisoprene gum rubber, having an inner diameter of 12.7 mm, was inserted upstream of the sensors. This approach was tried because of previous reports that natural rubber was effective at removing ozone (Schmidt, et al., 1995). Initial trials showed that the rubber tubing was effective in removing ozone while having minimal effect on NO_2 or HONO. However, optimization of this approach was not achieved prior to the preliminary field studies. Tubing of a smaller diameter would likely be needed to serve as a denuder tube for use in a monitor.

SUMMARY AND CONCLUSIONS

The tests described here showed that the electrochemical sensor-based monitors provide highly sensitive, rapid, and linear detection of NO_2, and substantially greater sensitivity to HONO. Interferences from other compounds likely to be present indoors are minimal, and initial tests show only a small dependence of baseline signal over a wide range of relative humidity. The monitors operated reliably during extended laboratory testing, and are rugged and compact enough for field use. Separation of HONO from NO_2 is readily achieved with the carbonate-coated filters. The gradual loss of sensitivity observed with all the sensors is a concern. It is

worth noting that the temperatures, humidities, and general sampling conditions which the sensors encountered in these tests were well within the normal ranges recommended by the manufacturer. Thus the decreasing sensitivity cannot be attributed to extreme testing conditions.

The reason for the different sensitivities toward HONO and NO_2 is not clear. The sensor manufacturer has never conducted tests with HONO. The greater sensitivity for HONO may have to do with the greater water solubility of that compound (i.e., a Henry's law coefficient about 5,000 times larger than that of NO_2; Schwartz, 1986), which would promote its uptake into the sensor's electrolyte solution. On the other hand, the chemical species undergoing reduction is believed to be NO_2, not nitrite ion (NO_2^-) as would result from HONO dissolution, so this factor would tend to limit HONO sensitivity. The observed relative response to HONO and NO_2 probably results from the counteracting effects of these (and perhaps other) factors. The apparent greater uniformity of HONO response among different sensors, relative to the NO_2 response of those same sensors, is also puzzling. A series of questions has been directed to the manufacturer of the sensors to explore these issues.

These preliminary tests indicate some likely modifications to the monitors. An important one may be the adoption of a denuder, rather than a filter, for removal of HONO. A denuder would likely eliminate the small differences in response that are apparently due to the pressure drop of the coated filter. Addition of a denuder for ozone removal is another likely modification, though ozone is unlikely to be present at significant levels in indoor air.

Although further laboratory tests remain to be completed beyond the testing reported here, it was judged likely that field tests would identify areas for further study that laboratory tests alone could not. On this basis, and on the basis of the laboratory tests reported here, it was concluded that the electrochemical sensor-based monitors were sufficiently demonstrated to justify a few days of preliminary field testing, in parallel with conventional nitrogen oxides measurements for comparison.

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APPENDIX B

SECOND INTERIM REPORT
(Covering Initial Field Testing and
Extensive Laboratory Testing of the
Prototype NO_2/HONO Monitors)

SECOND INTERIM REPORT

on

DEVELOPMENT OF SHORT-AVERAGING-TIME INDOOR NITROGEN OXIDE MONITOR

California Air Resources Board Program No. 96-312

June 18, 1998

Prepared by

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SECOND INTERIM REPORT

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DEVELOPMENT OF SHORT-AVERAGING-TIME INDOOR NITROGEN OXIDE MONITOR

California Air Resources Board Program No. 96-312

from

BATTELLE

June 18, 1998

1. INTRODUCTION

This report presents laboratory and preliminary field test results from California Air Resources Board (CARB) Program No. 96-312. The purpose of this program is to develop a short-time-response portable monitor for nitrogen dioxide (NO_2) and nitrous acid (HONO) in indoor environments. The approach taken in this program is to use a sensitive electrochemical sensor for NO_2 as the basis for a portable monitor. Laboratory and field testing are conducted to evaluate the monitors and to obtain real-world monitoring data. The electrochemical NO_2 sensors are also sensitive to HONO, so a two-channel mode of operation was adopted to allow measurement of both species.

The purpose of this interim report is to summarize the results of development efforts on the NO_2/HONO monitors, and to make recommendations on the directions for further development. Thus this report summarizes all the observations made in developing and testing the NO_2/HONO monitor. Included here are quantitative results from laboratory and preliminary field tests, as well as qualitative findings on operational characteristics such as reliability, ruggedness, ease of use, etc. The intent of this report is to describe all aspects of the current NO_2/HONO monitor, so that its suitability to meet CARB's needs may be assessed, and further developments may be recommended.

Preparation of this report constitutes Task 5 of the program; the topics covered include the following project tasks:

Task 1 – Develop Prototype Monitors

Task 2 – Laboratory Testing

Task 3 – Preliminary Field Tests

Task 4 – Analyze Test Results

As originally proposed, Tasks 1-5 were to take place essentially in sequence. However, in fact Task 2 was only partially completed before Task 3 was conducted, and then Task 2 efforts were resumed. This change occurred because of an opportunity to use a research house for the preliminary field tests, during November 1997. Because of that change in schedule, an interim report was previously submitted on the study results up to the start of the preliminary field tests. That report is included here as Appendix A.

This report is organized according to the actual chronological sequence of program activities. Section 2 summarizes the prototype development and initial laboratory tests (Tasks 1 and 2), which took place between the start of this program in March, 1997, and mid-November, 1997. Section 3 describes the preliminary field tests (Task 3), which took place in November, 1997. Section 4 presents results from subsequent further lab tests (Task 2), conducted up to the time of this report. Section 5 presents the conclusions of the study to date, including the advantages and limitations of the monitors, and Section 6 presents recommendations for the further development of the monitors.

2. PROTOTYPE DEVELOPMENT AND INITIAL LABORATORY TESTS

Three prototype NO_2/HONO monitors were assembled, using small, inexpensive, yet highly sensitive, commercially available electrochemical NO_2 sensors as the detection device. Each monitor uses a single NO_2 sensor, with a three-way valve to alternate air sampling between two measurement channels: through a Na_2CO_3-coated filter for measurement of NO_2, and by passing the filter for measurement of NO_2 + HONO. The prototypes were tested in the laboratory for sensitivity, linearity, interferences, stability, and temperature and humidity effects. Laboratory testing was then interrupted, to take advantage of an opportunity to use a well-characterized research house in Chicago for preliminary field tests, in conjunction with a separate Battelle study of indoor gas combustion emissions. At that point, an interim report (Appendix A) was prepared describing all activities conducted in Tasks 1 and 2 prior to the preliminary field tests.

The main findings of the initial lab tests described in Appendix A are that the monitors provide high sensitivity and linear response, and substantially greater sensitivity to HONO than to NO_2. This is an advantage, since HONO is determined by difference relative to the NO_2 response with the prototype monitors. The monitors also showed minimal interferences from a variety of potential indoor contaminants, and operated reliably in the laboratory. However, the sensitivity of the monitors was also found to decrease over time, at a rate substantially greater than that stated by the manufacturer. Nevertheless, the results of the initial laboratory tests were sufficient to justify moving to preliminary field tests of the monitors.

A description of the three prototype NO_2/HONO monitors, and details of the initial laboratory tests, are presented in Appendix A.

3. PRELIMINARY FIELD TESTS

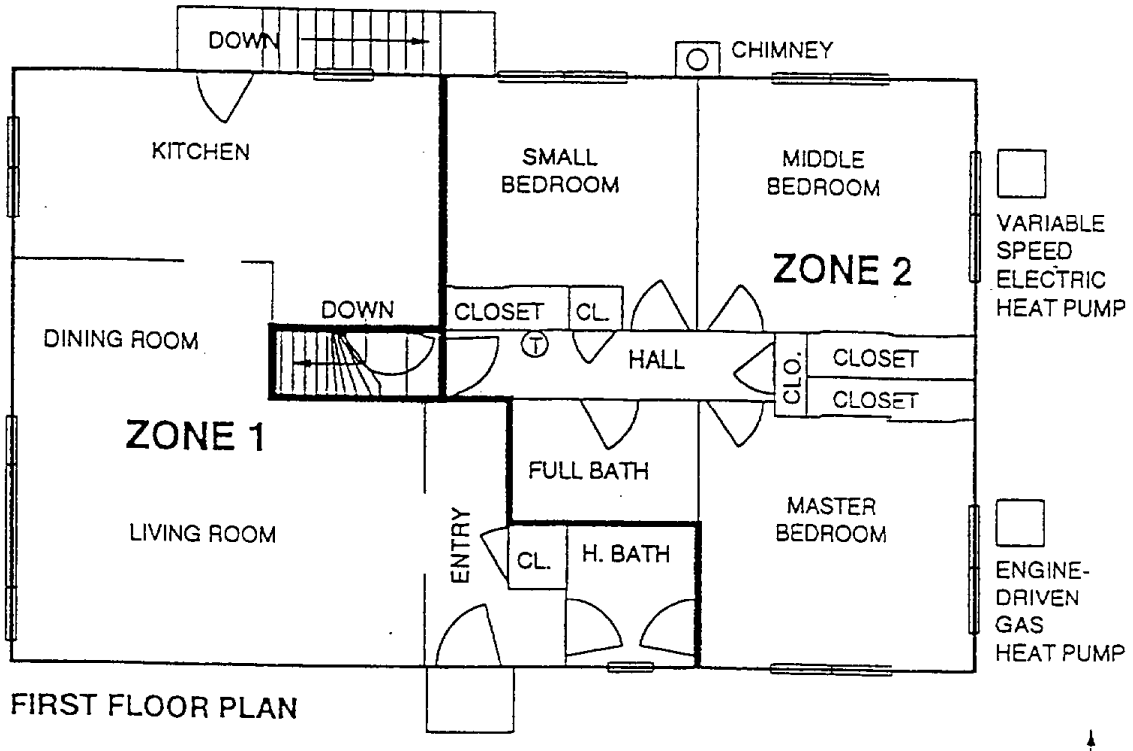
3.1. Location

The preliminary field tests of the three prototype NO_2/HONO monitors were conducted from November 14 to 18, 1997 at the Gas Research Institute (GRI) conventional research house, located at 6247 North Harlem Avenue, northwest of downtown Chicago. This house has been used for numerous indoor air studies by Battelle and other organizations. The present preliminary field tests were conducted in conjunction with a Battelle study for GRI of emissions from unvented gas hearth products. The preliminary field tests of the NO_2/HONO monitors included periods of operation of the hearth products, and of a gas range and oven.

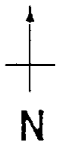
The GRI conventional research house is a one-story single family dwelling with three bedrooms, a full basement, and a detached garage. It is representative of many existing houses in the eastern half of the U.S. Figure 1 shows the floor plan of the research house, and Table 1 shows the characteristics of the house. During the preliminary field tests, the NO_2/HONO monitors and additional equipment were operated primarily in the living room and kitchen, and briefly in the hallway leading to the rear bedrooms. The main floor has hardwood floors, except for the living room, which is carpeted, and the kitchen, which has vinyl floor tile. All interior walls are plaster covered with oil-based paint, and the house is sparsely furnished with conventional furnishings. For the preliminary field tests, the main floor of the house was not divided into two separate zones, as suggested by Figure 1, but was fully connected as in a conventional home.

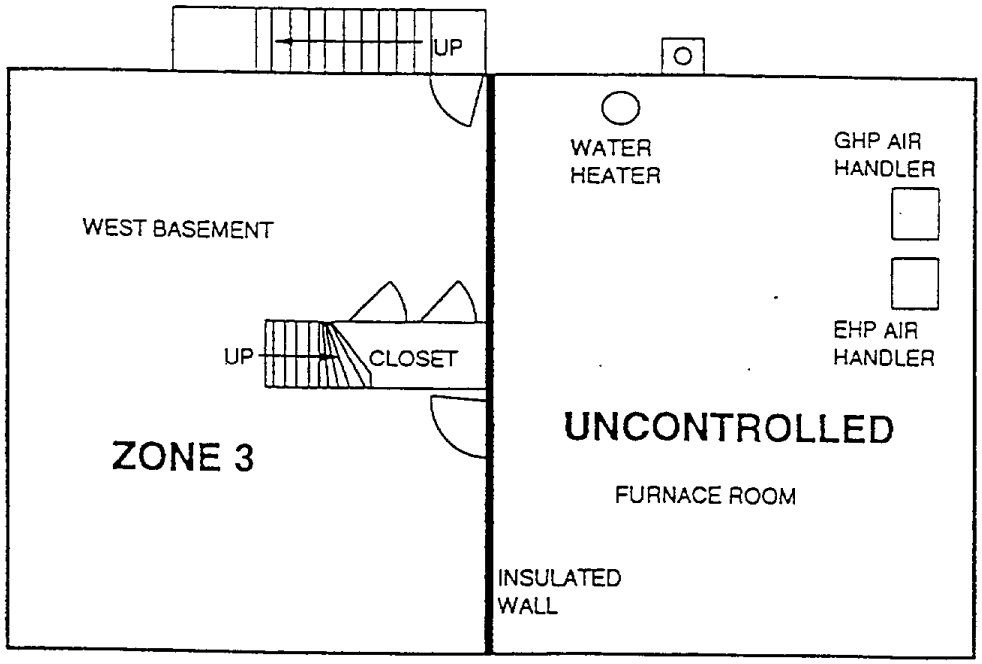
3.2. Equipment

The three prototype monitors were operated in the research house along with a Thermo Environmental Model 49 ozone (O_3) monitor and a conventional Monitor Labs 8840 chemi-luminescent nitrogen oxides (NO/NO_x) monitor. The analog outputs of all three NO_2/HONO monitors and of the ozone and nitrogen oxides monitors were recorded using a Keithley 575 A/D converter unit and a personal computer (PC) running LabTech Notebook software.



FIRST FLOOR PLAN





BASEMENT FLOOR PLAN

FIGURE 1. CONVENTIONAL RESEARCH HOUSE FLOOR PLANS

TABLE 1. CONVENTIONAL RESEARCH HOUSE CHARACTERISTICS

Location	Chicago, Illinois		
Year Constructed	1957		
Style	One Story with full Basement 3 Bedrooms, 1-1/2 Baths 2-Car Detached Garage with Office		
Floor Area	1,150 ft^2 per floor Living Room Bedroom West Basement Furnace Room	 592 ft^2 558 ft^2 575 ft^2 575 ft^2	
Construction	Frame – Half Brick Veneer, Half Cedar Siding R-11 Ceiling Insulation R-7 Wall Insulation Plaster Walls, Painted with Oil-Base Paint Wood Double-Hung Windows, Wood Doors Weatherstripped Storm Windows and Doors Uninsulated, Poured Concrete Basement		
Zone Volumes	(Excluding/Including Closets, Cabinets, Furnishings and Appliances)		
	Living Room Bedroom West Basement Furnace Room	4,160/4,736 ft^3 3,688/4,464 ft^3 4,092/4,600 ft^3 4,114/4,600 ft^3	119/134 m^3 104/126 m^3 116/130 m^3 116/130 m^3
	Total House	16,054/18,400 ft^3	455/521 m^3

Each NO_2/HONO monitor has two analog outputs (representing NO_2 and NO_2 + HONO, respectively). The NO_2/HONO monitors each alternated between NO_2 and NO_2 + HONO measurement modes about every 10 minutes, thus only one of the analog outputs was active at any time. The ozone monitor has one analog output, and the nitrogen oxides monitor has two outputs (representing NO and NO_x, respectively). Thus a total of nine data channels were recorded, at 30-second intervals, throughout the field period. Small AC leakage potentials traced to the data system caused spurious signals early in the field study. Grounding the chassis of the NO_2/HONO monitors to the AC ground of the PC and the Keithley unit minimized this problem. The NO_2/HONO, O_3, and NO/NO_x monitors were mounted on a wheeled cart, and connected to the data system and to electric power by long cables to allow movement from room to room in the test house. Figures 2 and 3 show the instrument package in the kitchen and in the bedroom hallway of the test house, respectively.

During some parts of the field study only a Teflon particulate filter was used on the inlet of the 8840 nitrogen oxides monitor; in such cases the NO_x channel represents the sum of NO, NO_2, and HONO. In the other parts of the study, a potassium carbonate-coated glass fiber filter

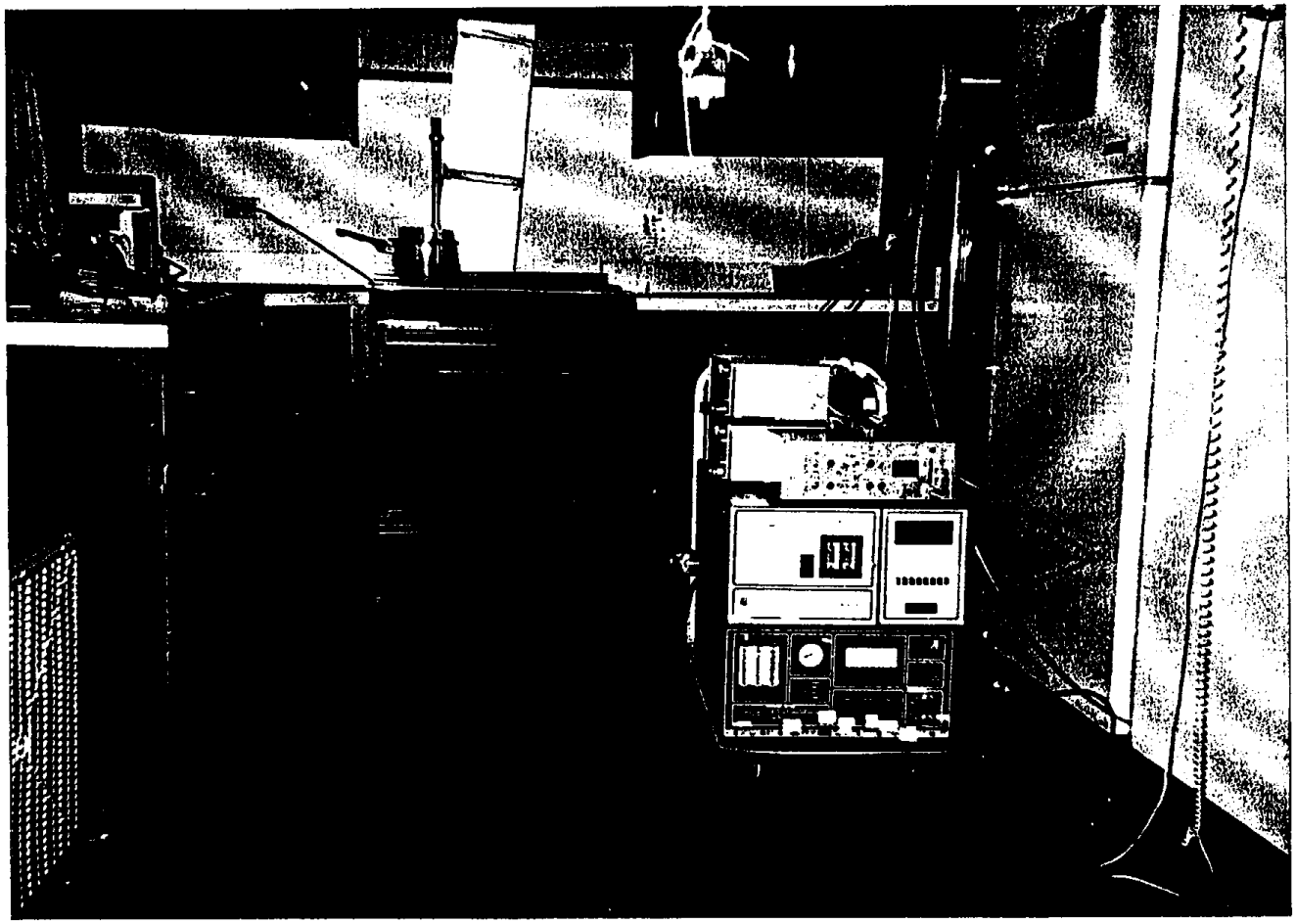


FIGURE 2. THE NO_2/HONO, O_3, AND NO/NO_X MONITORS LOCATED IN THE KITCHEN OF THE RESEARCH HOUSE DURING SIMULATED COOKING ACTIVITIES

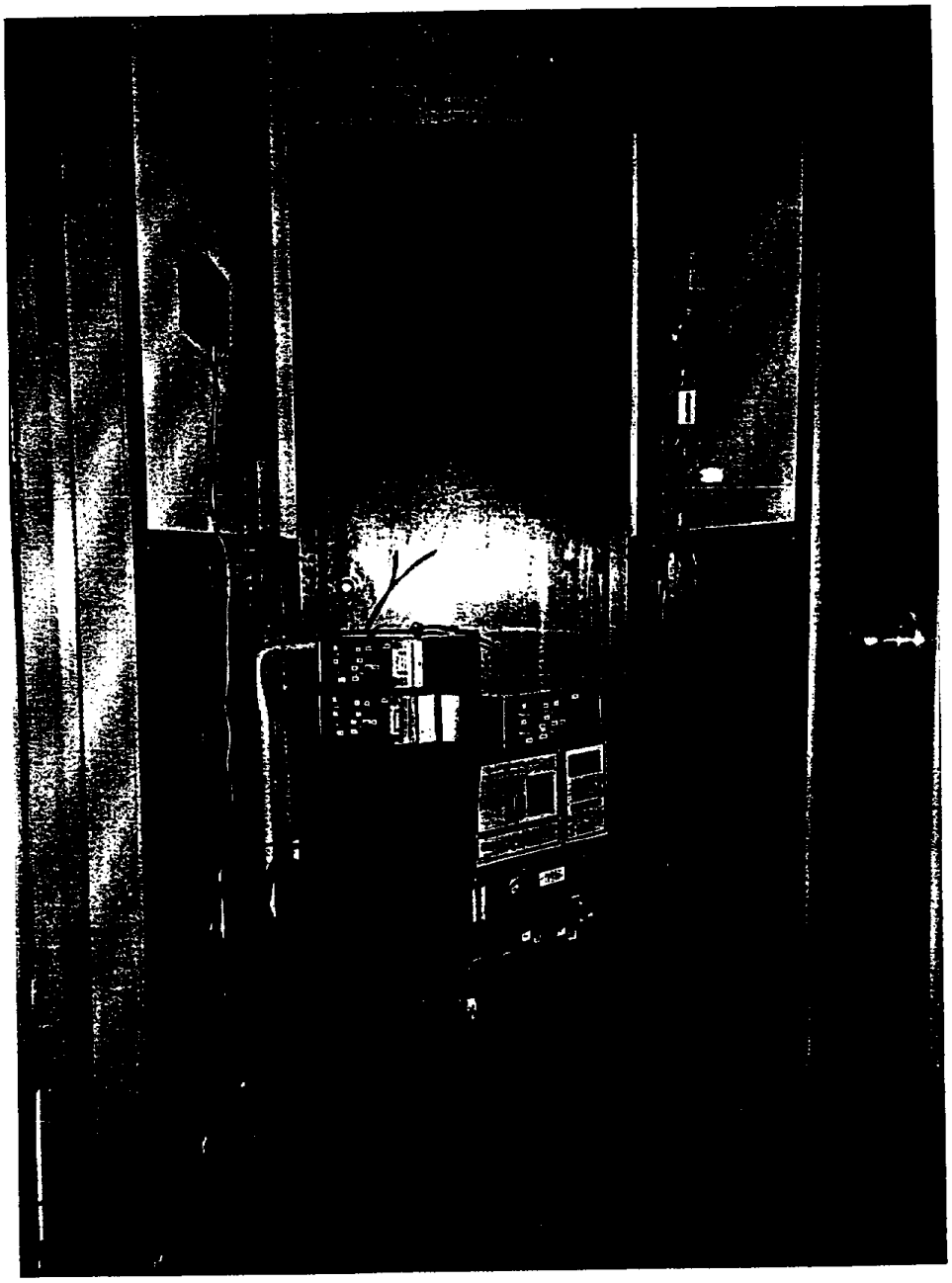


FIGURE 3. THE NO_2/HONO, O_3, AND NO/NO_X MONITORS IN THE BEDROOM HALLWAY OF THE RESEARCH HOUSE

was also used on the 8840 inlet to selectively remove HONO; in those periods the NO_x channel represents the sum of only NO and NO_2. Subtraction of the NO signal from the NO_x signal thus provided data for NO_2 + HONO, in some time periods, and for NO_2 in others. The data obtained from the 8840 were compared to the appropriate data from each of the NO_2/HONO monitors for each time period.

The NO_2/HONO, ozone, and NO/NO_x monitors were all calibrated in the laboratory before and after the field study. The primary standard for nitrogen oxides was a 49.7 ppm NO standard referenced to the National Institute of Standards and Technology (NIST). This NO standard was used at intervals during the study to establish the concentration of a nominal 50 ppm commercial NO_2 standard, which was used for NO_2 calibration of the monitors. The O_3 monitor was calibrated with a Dasibi 1008-PC Primary Ozone Calibrator. Separate NO_2 calibrations were performed on the two operating modes of the electro-chemical NO_2/HONO monitors. Nitrous acid calibrations were done using a permeation tube of nitric acid (HNO_3). Passing the HNO_3 vapor over a bed of glass beads coated with $NaNO_2$ resulted in complete conversion of HNO_3 to HONO. No calibrations were conducted in the field, but the NO_2/HONO monitors and O_3 and NO/NO_x monitors were zeroed periodically during the field study using high purity air.

The three NO_2/HONO monitors were calibrated with both NO_2 and HONO on November 13, the day before the start of the preliminary field study, and on November 26, after the equipment was set up in the laboratory after the field study. Considerably different results were found in these calibrations, as shown in Table 2. Presented there are the sensitivities (in mV/ppbv) found for NO_2 and HONO in the pre- and post-field study calibrations, and the ratio of post- to pre-study results for each monitor. The NO_2 results in Table 2 show that Monitors 1-3 exhibited only about 50 percent, 70 percent, and 45 percent of their pre-study NO_2 sensitivity, respectively, in the post-study calibrations. However, the HONO results show that the same monitors retained 89 percent, 91 percent, and 77 percent, respectively, of their pre-study HONO sensitivity, i.e., the HONO sensitivity was more stable over time than was the NO_2 sensitivity. This finding is consistent with the previous observation (Appendix A), that the HONO response is also more consistent from one sensor to another than is the NO_2 response. The data in Table 2 also show that each sensor exhibited individual characteristics regarding its response.

TABLE 2. NO_2 AND HONO CALIBRATION RESULTS IMMEDIATELY BEFORE AND AFTER THE PRELIMINARY FIELD TESTS

Calibration Date	Calibration Species	Sensitivity in mV/ppbv					
		Monitor 1		Monitor 2		Monitor 3	
		NO_2 + HONO[a]	NO_2[b]	NO_2 + HONO[a]	NO_2[b]	NO_2 + HONO[a]	NO_2[b]
11/13/97[c]	NO_2	0.897	0.874	0.452	0.441	0.536	0.456
11/26/97[d]	NO_2	0.453	0.419	0.322	0.291	0.244	0.202
Ratio After/Before:		**0.51**	**0.48**	**0.71**	**0.66**	**0.46**	**0.44**
11/13/97[c]	HONO	1.968	---	2.047	---	1.483	
11/26/97[d]	HONO	1.760	---	1.853	---	1.147	
Ratio After/Before:		**0.89**		**0.91**		**0.77**	

a Data taken by bypassing the $CO_3^=$ filter in the monitor
b Data taken through the $CO_3^=$ filter in the monitor
c Before the preliminary field study
d After the preliminary field study

The results in Table 2 indicate poor stability of the NO_2 response, and presented a problem for interpreting the field data. Although difficult field conditions were encountered (such as the excessive indoor temperature on the first night in the research house), and although a difference in the relative response of the monitors was noted during the field study (relative to that seen in the laboratory), there was no clear evidence of a substantial loss of sensitivity or a downward trend in response during the field period. In fact, as shown below, the three monitors exhibited high rather than low response in the field study. Thus, it was impossible to fix a time or date when the apparent sensitivity change might have occurred. As a result, and because of the close proximity in time of the pre-study calibrations to the field data, the pre-study calibration factors were used in reducing the field data.

The process for reduction of the field data from the NO_2/HONO monitors was as follows. First the mV output of the NO_2 channel of each monitor was converted to ppbv NO_2 using the NO_2 calibration factor for that channel. Then for each 10-minute NO_2 measurement period the mV signal corresponding to this level of NO_2 on the NO_2 + HONO channel was calculated, and subtracted from the succeeding 10-minute NO_2 + HONO signal of each monitor, using the NO_2 calibration factor for the NO_2 + HONO channel. This calculation was needed because generally slightly different NO_2 calibration factors were found in the two channels of the monitors. The alternating measurement modes of the monitors required pairing successive measurements in performing this subtraction, since NO_2 and NO_2 + HONO were not determined simultaneously. The remaining analog signal from the NO_2 +HONO channel was then converted to ppbv HONO, using the scale factor for HONO determined in the laboratory.

Obviously erroneous data were occasionally obtained from one or more monitors for brief periods in the field study. These data generally took the form of abrupt and unrealistic changes in reported concentrations. In most cases, these occurrences were traced to problems in data acquisition, and were corrected by improving the common ground connections of all monitors and the data system. In such cases the spurious data were deleted. However, in a few cases no obvious cause was found, and the data were retained in the data set.

Comparisons were made among the three electrochemical monitors, and between the monitors and the 8840 nitrogen oxides monitor, for NO_2, NO_2 + HONO, and HONO concentrations. The HONO concentration could be determined from the conventional NO_x monitor only at those times when the carbonate-coated filter was inserted in, or removed from,

the sample inlet. At those times the step change in instrument response directly indicated the HONO level. HONO was determined in this way at eight times during the field study.

Additional monitoring equipment was operated in the test house for Battelle's tests of hearth products, including continuous monitors for CO, CO_2, SO_2, NO_2, formaldehyde, total hydrocarbons, and polynuclear aromatic hydrocarbons, along with a temperature/dew point sensor. Summary data from those instruments were obtained as needed to characterize the environment in the test house.

3.3. Preliminary Field Schedule

The field tests took place from about 7:00 p.m. on November 14, to about 9:30 a.m. on November 18, 1997. The monitors and other equipment were installed in the research house on the evening of November 14, at a time when a severe hearth product test was being conducted. At that time, a hearth product was being operated overnight at full heat output, and the temperature inside the house was over 95°F. Levels of all pollutants were high, as indicated by the instruments operating for the hearth product tests. As a result, to avoid contamination of the NO_2/HONO sensors at the very start of the field tests, the NO_2/HONO monitors were made to sample outdoor air until the hearth product test had ended the next morning. Thus the overnight period of November 14-15 was a test of operation of the monitors under severe conditions, but not of indoor sampling under such conditions.

From the morning of November 15 until the morning of November 18, all three NO_2/HONO monitors, and other associated equipment, sampled primarily indoor air. Hearth products with and without porous inserts to reduce emissions, a gas range, and a gas oven were all operated at some time during this period. The hearth products were operated for several hours, until steady state contaminant levels were reached in the research house. Sometimes the house was forcefully ventilated after a combustion source was operated, and at other times the house was allowed to air out naturally. Sampling of indoor air was also conducted during periods of several hours when no sources were operating in the house, and outdoor air was also sampled.

Table 3 summarizes the testing activities that were conducted over the four days at the research house, and shows the maximum levels of several air contaminants in each period. The

location of the NO_2/HONO monitors and the type of sampling conducted with them is also shown. Note that the maximum pollutant levels shown in Table 3 are less than or about equal to the maximum levels of these species tested as interferants in the laboratory studies (Appendix A and Section 4). Thus the results of the laboratory tests are fully applicable to the interpretation of the field results.

TABLE 3. SUMMARY OF PRELIMINARY FIELD TESTS

Period	Sources Active	Maximum Values Observed							
		Location of NO_2/HONO Monitors	Air Sampled	CO_2 ppm	CO ppm	NO ppb	NO_2[a] ppb	HCHO ppb	SO_2 ppb
11/14 p.m. to 11/15 a.m.	Maximum heating with unvented hearth product	Living Room	Indoor; Outdoor	6,350	7.7	2,380	925	--	46
11/15 a.m. to 11/16 a.m.	Hearth product on low heat; then on max with porous burner inserts	Living Room	Indoor	6,260	7.2	1,550	1,120	300	31
11/16 a.m. to 11/17 a.m.	Gas range; then no sources overnight	Living Room; Kitchen	Indoor	--	--	1,490	400	--	--
11/17 a.m. to 11/18 a.m.	Gas oven; oven plus range; then hearth product on low with porous insert	Kitchen; Bedroom Hallway	Indoor; Outdoor	4,560	2.8	1,490	620	89	32

(a) NO_2 data are from conventional NO/NO_x monitor.

Outdoor conditions during the preliminary field tests were typical of the Midwest U.S. in early winter: temperatures in the 20's to 40's Fahrenheit, with a few inches of snow on the ground, and light winds. Because of the urban location and associated vehicle traffic, nitrogen oxide levels in outdoor air often exceeded 100 ppbv, predominantly in the form of NO. As a result, outdoor ozone levels were low, and measured indoor ozone levels were zero.

3.4. Preliminary Field Data

The data useful for evaluation of the NO_2/HONO monitors are those from the morning of November 15 to the morning of November 18. Within that period, there were times when the 8840 NO/NO_x monitor determined NO_2, and other periods when it determined NO_2 + HONO. An initial broad view of the field data can be gained by comparing the electrochemical NO_2/HONO monitor results to the 8840 results over the entire field study, for these two complementary data sets.

Figure 4 shows the NO_2 data from the entire field study from all three NO_2/HONO monitors, and from the 8840. The time axis (i.e., x-axis) in Figure 4 extends from about 10:30 a.m. on November 15 to about 9:30 a.m. on November 18. Periods of operation of hearth products are evident in Figure 4 as the highest levels, approaching a steady state over periods of several hours. NO_2 levels dropped sharply as the home was forcefully ventilated after such tests (15:30, November 15) or allowed to air out naturally (06:00, November 16, and 07:00, November 17). On November 16 and 17, periods of indoor air sampling with no sources produced low indoor NO_2 levels. Operation of a gas range and oven took place on the afternoon of both November 16 and 17. Figure 5 shows the same overall pattern of data from the entire field period, for the sum of NO_2 + HONO.

The data from the three electrochemical NO_2/HONO monitors clearly are strongly correlated with the data from the 8840 monitor, for both NO_2 (Figure 4) and NO_2 + HONO (Figure 5). However, the NO_2/HONO monitors do not provide good quantitative agreement, either with the 8840 monitor or with each other. Monitor 1 shows the closest agreement relative to the conventional monitor, and Monitor 2 the poorest. The relative behavior of the three NO_2/HONO monitors appears to be consistent throughout the field study, i.e., there is no apparent drift of one monitor relative to the others or to the 8840 monitor. This is an important point, since as described above,the NO_2 calibration done on all three monitors the day before the field study did not agree well with the calibration done after the field study It was originally expected that some shift in sensitivity had occurred during the field period, but no evidence for that is apparent from the field data.

Figures 4 and 5 show that the response of the NO_2/HONO monitors was the same relative to the conventional NO_x monitor both at high levels (i.e., > 500 ppbv NO_2) and at levels near or below the California one-hour NO_2 standard of 250 ppbv. This observation is consistent with the wide linear range found for the NO_2/HONO monitors (Appendix A). One interesting feature of the data is that the NO_2/HONO monitor response continued to increase somewhat during hearth product operation after the conventional monitor's data had stabilized. This is evident in Figure 4 (after 22:00 on November 17) and Figure 5 (after 18:30 on November 16). However, this behavior may be due to an artifact in the conventional NO_x instrument response, not to an error in the electrochemical monitor response. In these periods, the conventional monitor response actually peaked, and then decreased, at a time when the hearth products were operating

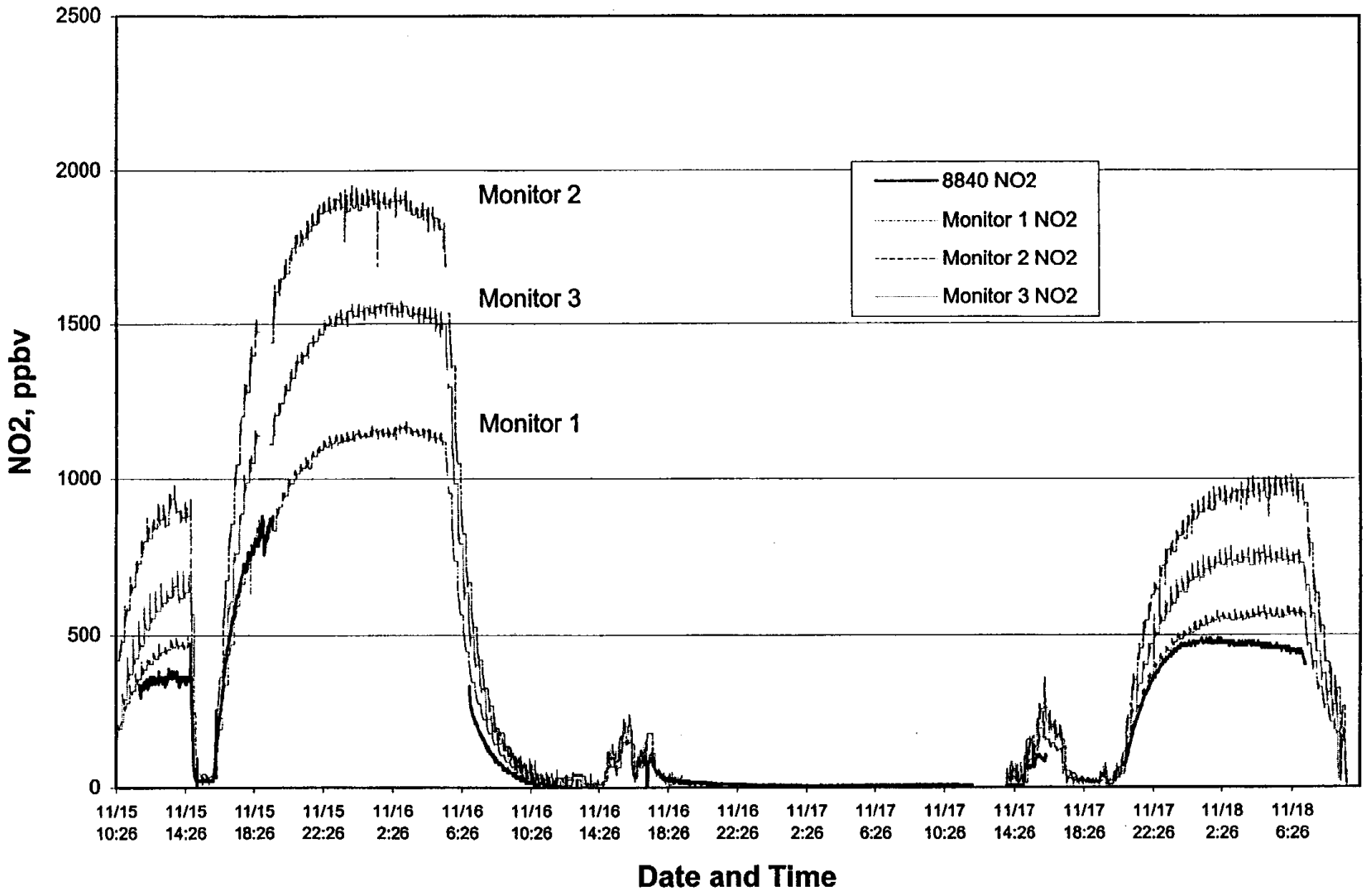


FIGURE 4. NO_2 DATA FROM THE PRELIMINARY FIELD TESTS

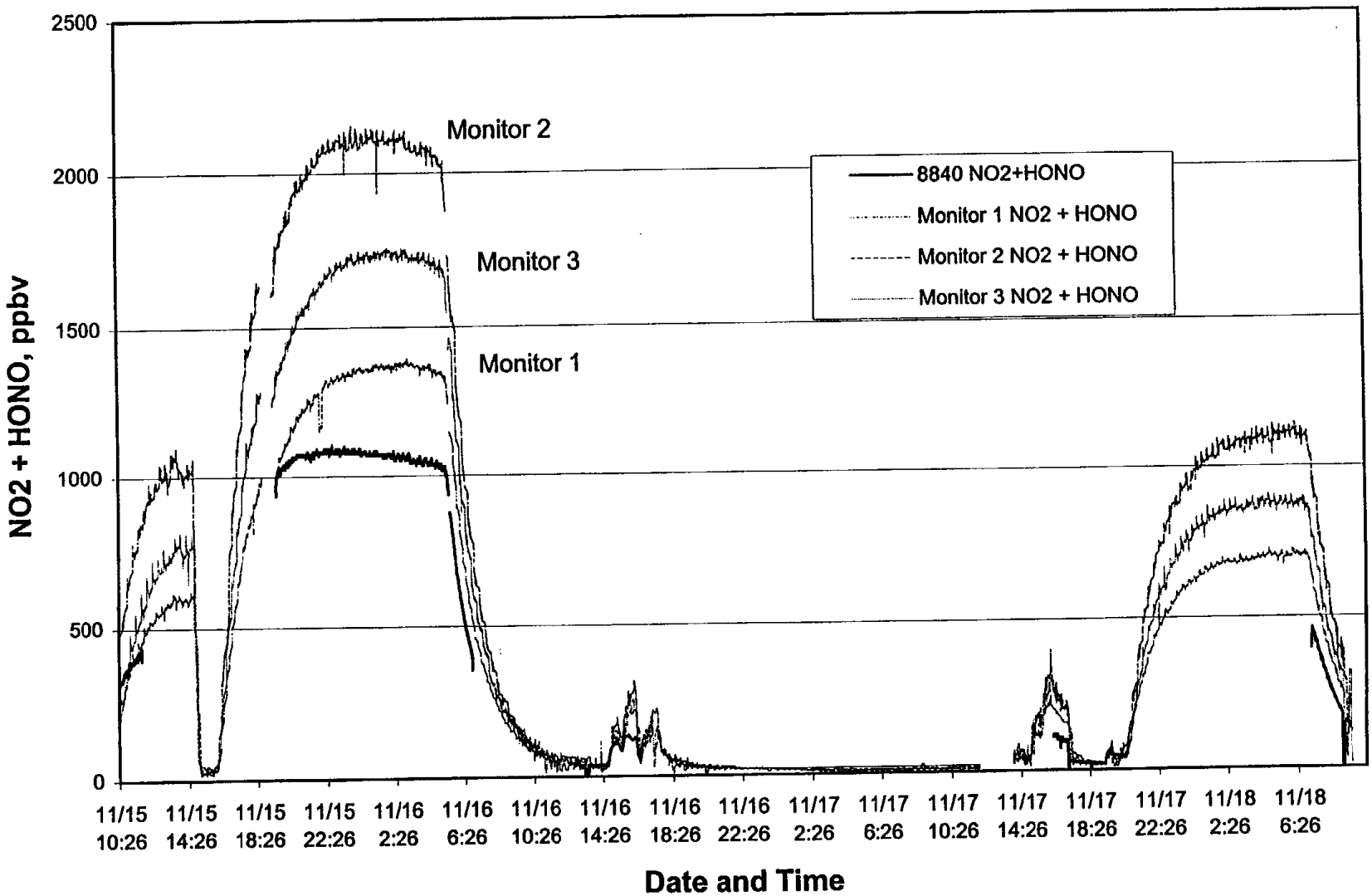


FIGURE 5. NO_2 + HONO DATA FROM THE PRELIMINARY FIELD TESTS

continuously. This may be due to a slight loss of sensitivity of the 8840 NO_x monitor as pollutant levels built up in the research house. It is also possible that other factors (e.g., air exchange rate) changed overnight, altering the steady state conditions. However, the steady decrease in NO_2 or NO_2 + HONO indicated by the conventional monitor appears unrealistic.

A quantitative comparison of the electrochemical and conventional NO_2 data is shown for Monitors 1 through 3, in Figures 6 through 8, respectively. In each of these figures, all of the several thousand data points from the field study are plotted. In each figure, the linear regression line (forced through zero) is shown, with the slope and R^2 value as indicated. Figures 6 through 8 show regression slopes of 1.12, 1.94, and 1.48, for Monitors 1 through 3, respectively, with R^2 values of 0.97. Good correlation over a wide range of NO_2 levels, but differing degrees of quantitative agreement, is clearly indicated.

A hook-shaped feature in the data is evident in Figures 6 through 8, at about conventional NO_2 = 450 ppbv. This is an artifact of the behavior noted above, in which the conventional and electrochemical monitors show different temporal profiles during operation of hearth products. The feature in Figures 6-8 corresponds to the hearth product tested after 20:00 on November 17 (Figure 4). As noted, this artifact may result from the response of the conventional monitor, not from a fault in the NO_2/HONO monitors.

Quantitative comparisons of NO_2 + HONO data are shown for Monitors 1 through 3 in Figures 9-11, respectively. As was the case for the NO_2 data, the NO_2 + HONO data show strong correlations (R^2 = 0.98 to 0.99). However, the regression slopes for NO_2 + HONO are 1.23, 1.93, and 1.56 for Monitors 1 through 3, respectively.

A pronounced hook-shaped feature is also present in the data in Figures 9-11, at about conventional NO_2 = 1,100 ppbv. This feature results from the hearth product testing that began after 15:30 on November 15 (Figure 5). As above, this feature results from the differing time profiles determined for the hearth product emissions by the conventional and electrochemical monitors.

The testing of individual chemical species prior to the field study (Appendix A), and subsequent testing of mixtures of species (Section 4), both indicate that interference from other contaminants present in the field study cannot explain the quantitative differences between the monitor and the 8840, shown in Figures 4-11. The other contaminants (e.g., CO_2, CO, HCHO, SO_2, NO) varied widely during the preliminary field tests, but within the same concentration

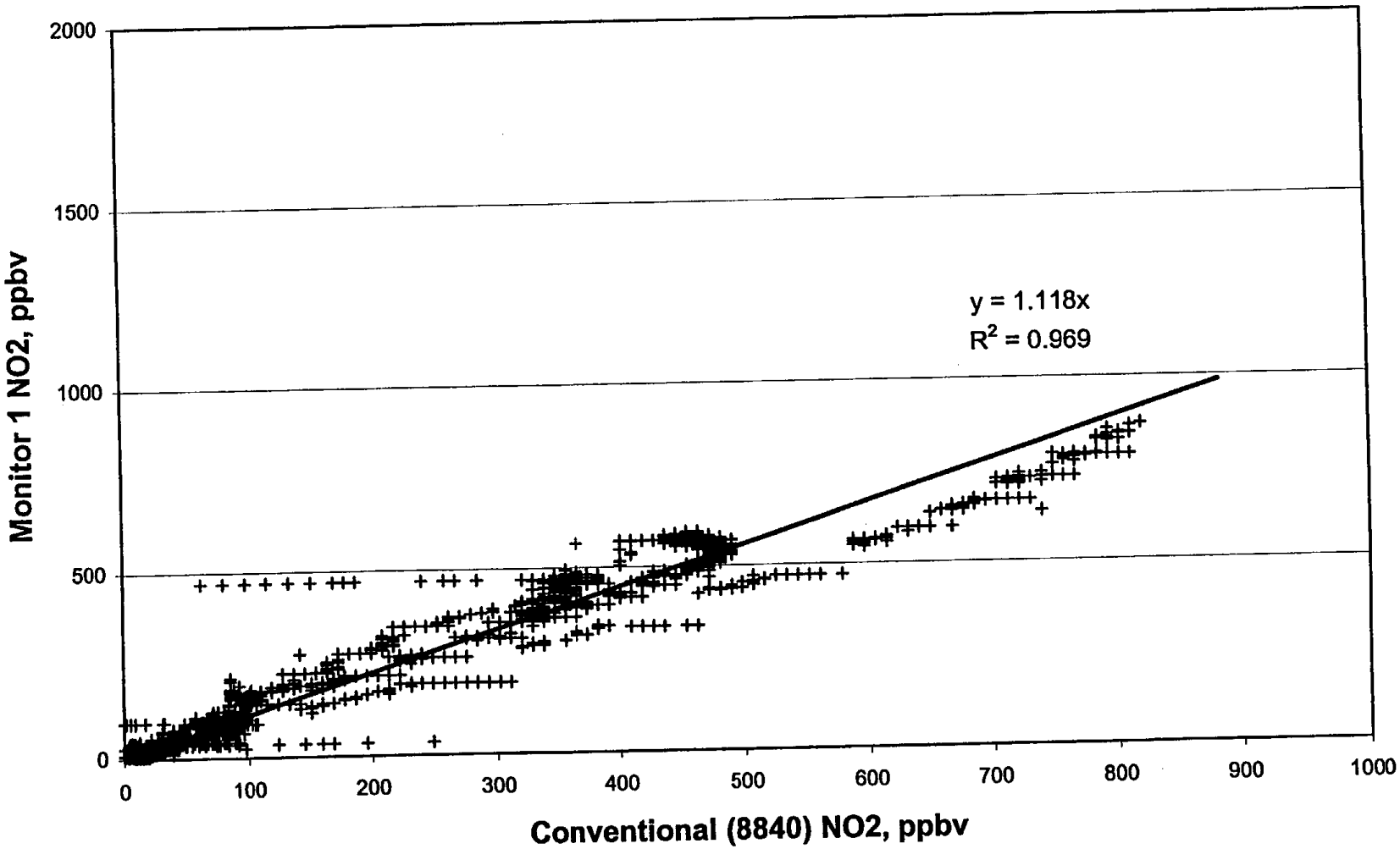


FIGURE 6. COMPARISON OF NO_2 DATA FROM MONITOR 1 AND THE CONVENTIONAL MONITOR

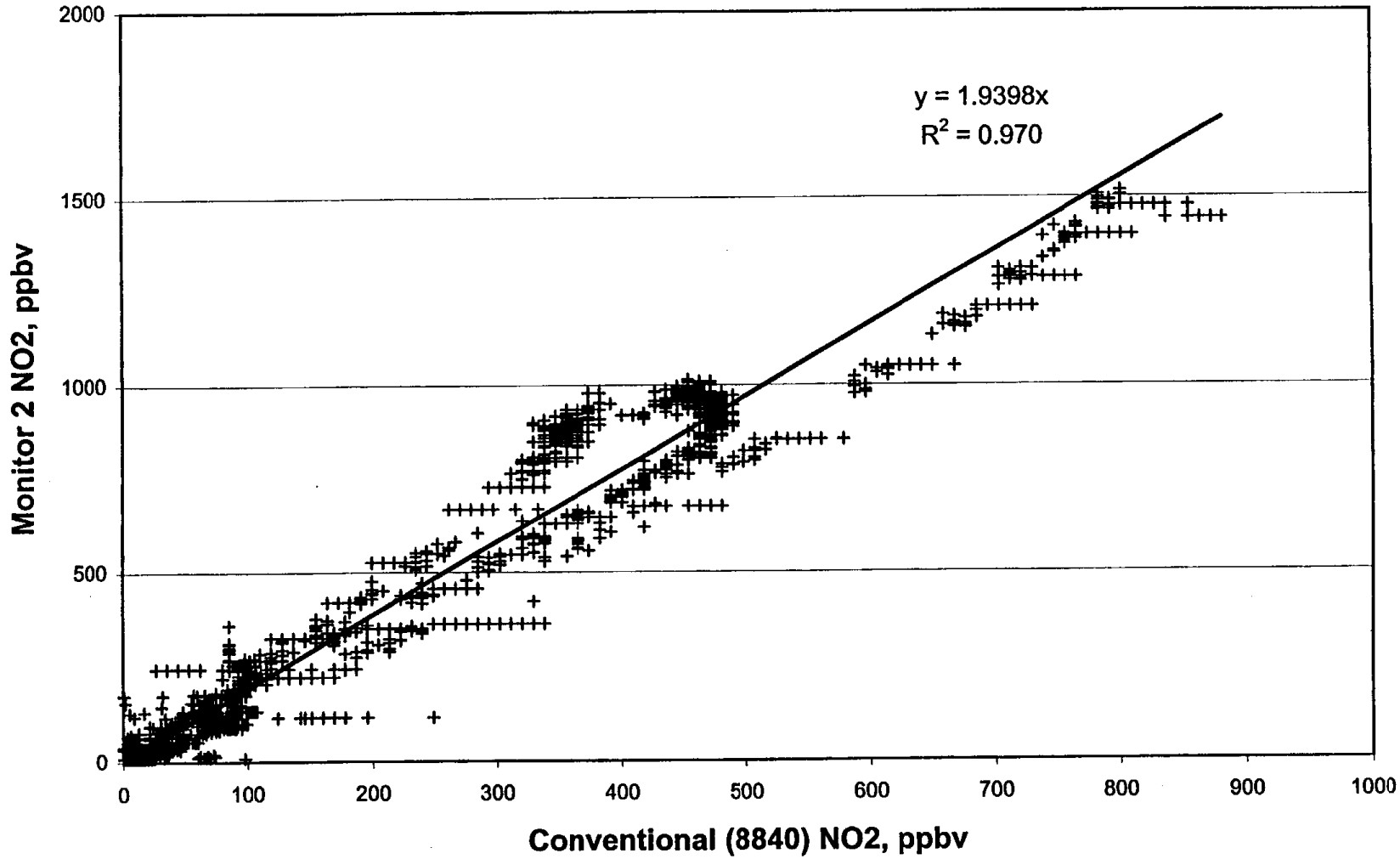


FIGURE 7. COMPARISON OF NO_2 DATA FROM MONITOR 2 AND THE CONVENTIONAL MONITOR

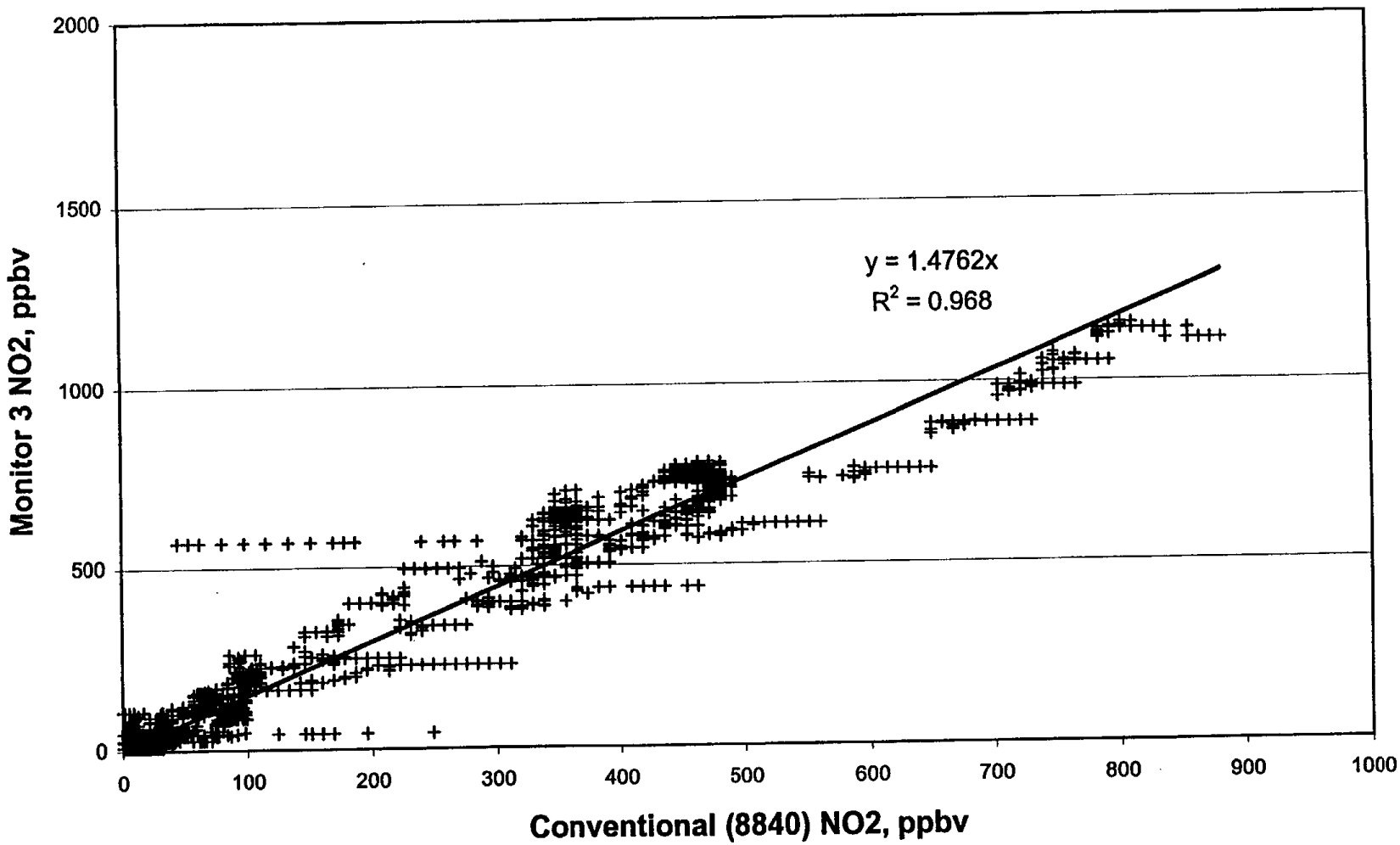


FIGURE 8. COMPARISON OF NO_2 DATA FROM MONITOR 3 AND THE CONVENTIONAL MONITOR

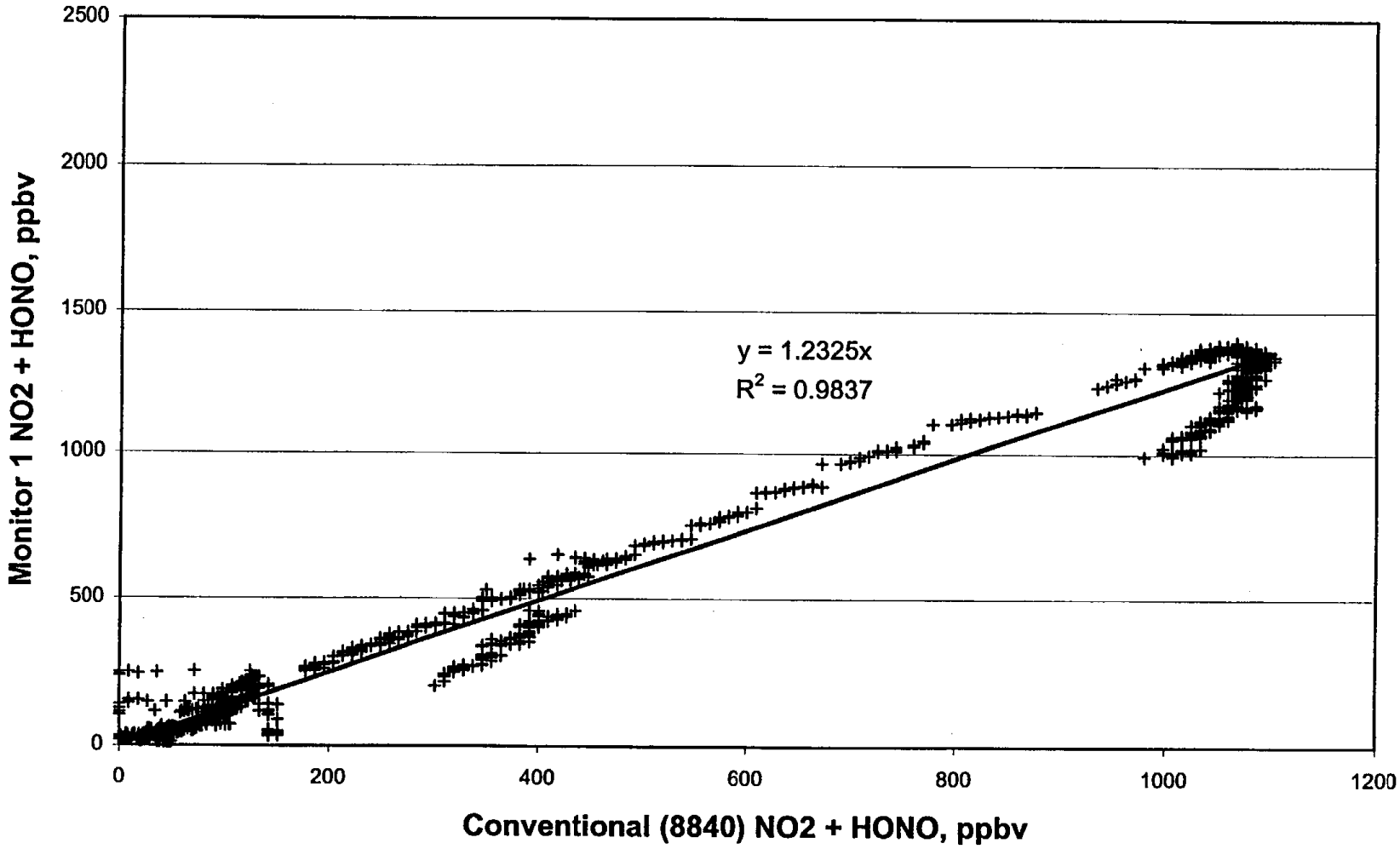


FIGURE 9. COMPARISON OF NO_2 + HONO DATA FROM MONITOR 1 AND THE CONVENTIONAL MONITOR

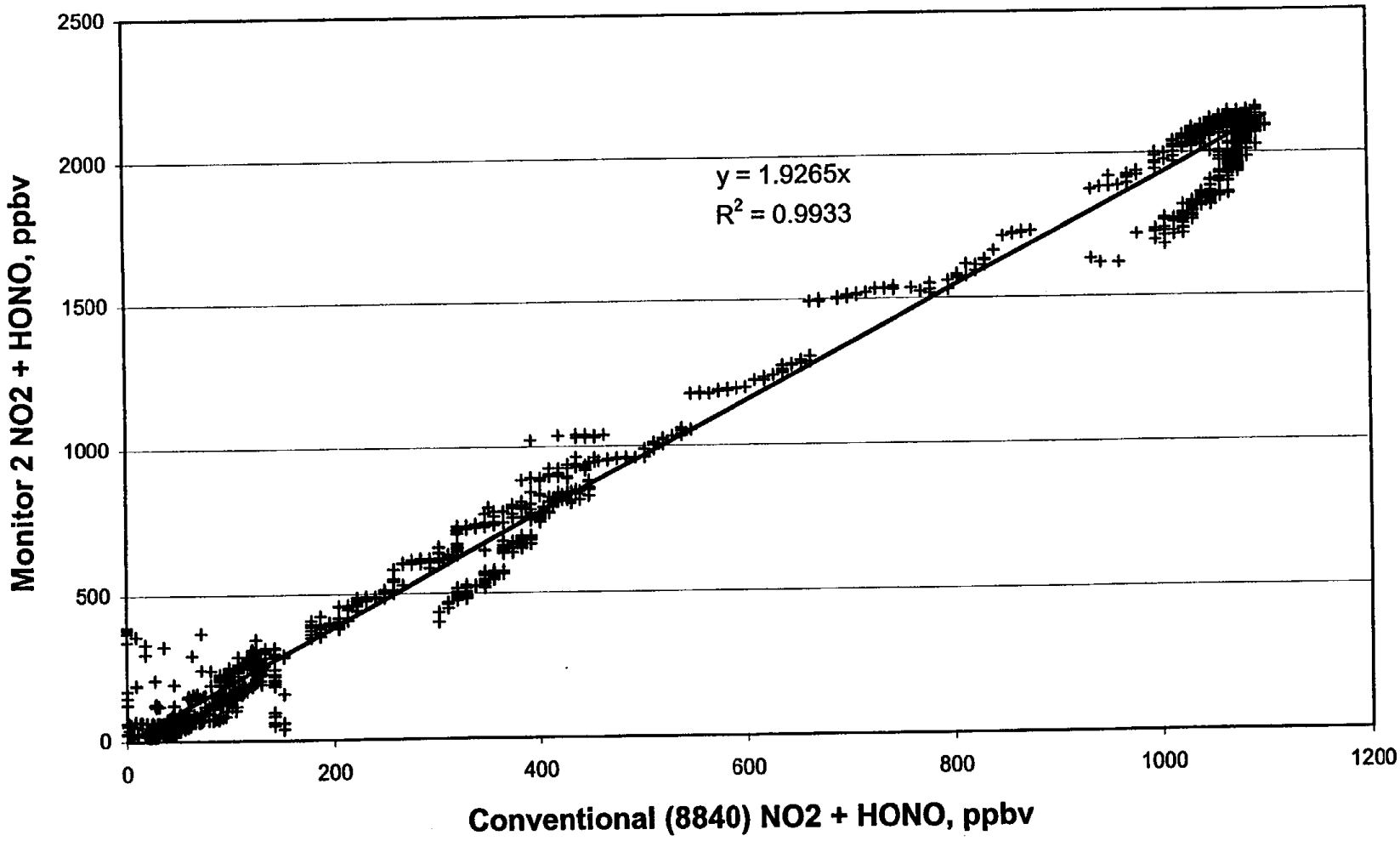


FIGURE 10. COMPARISON OF NO_2 + HONO DATA FROM MONITOR 2 AND THE CONVENTIONAL MONITOR

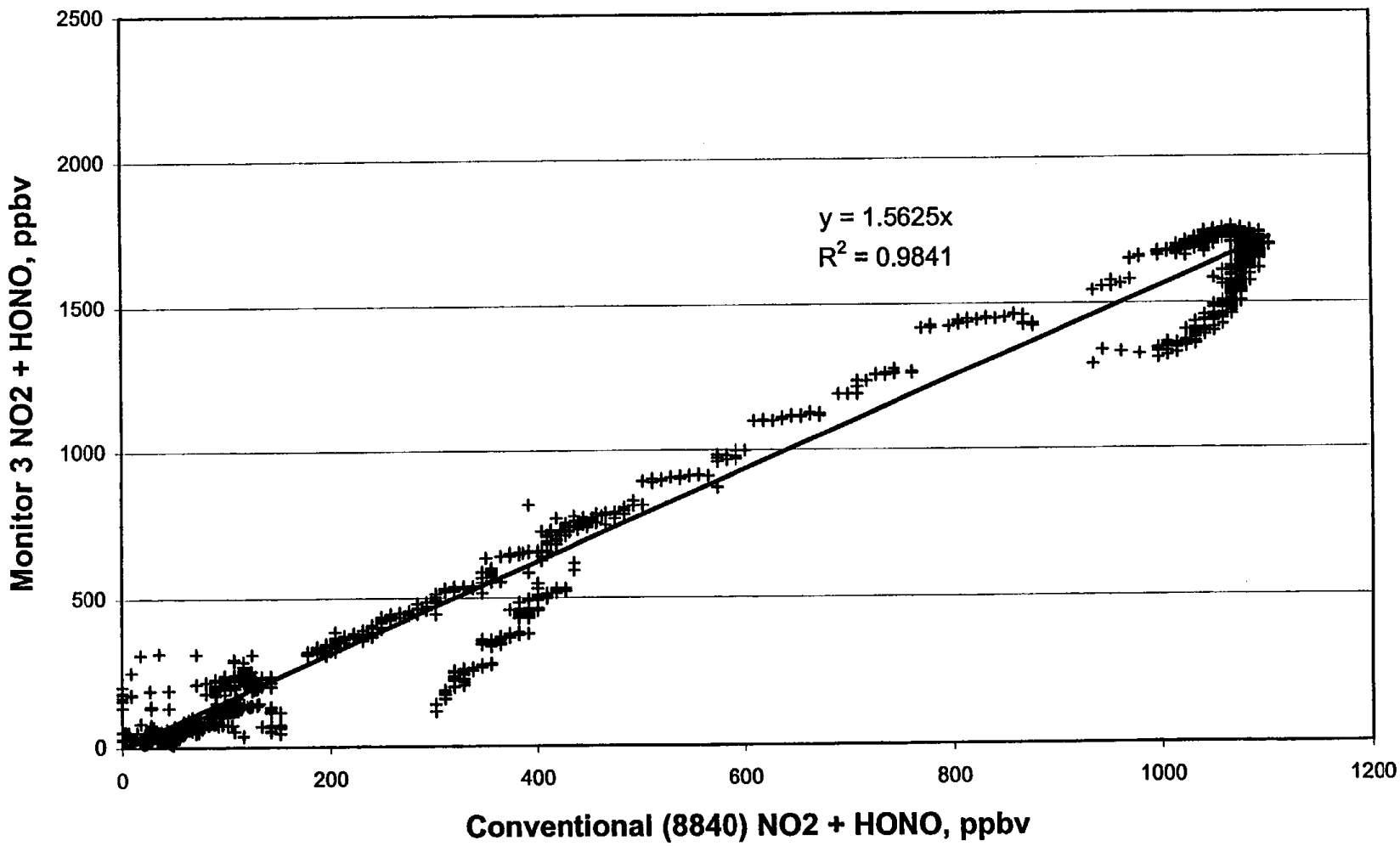


FIGURE 11. COMPARISON OF NO_2 + HONO DATA FROM MONITOR 3 AND THE CONVENTIONAL MONITOR

ranges found to cause negligible interference in the laboratory. Also, chemical interferences would affect all three monitors, and thus cannot explain the differing behavior of the three NO_2/HO monitors. Similarly, temperature effects do not appear to explain the differences. Indoor temperature varied somewhat during the field period, but the relative behavior of the monitors was the same at normal temperature as at elevated temperature, and one monitor (#1) showed relatively good agreement with the conventional monitor throughout the field study. A variety of possible explanations have been considered for the disagreement in NO_2 data from the field study. Basic information on the sensors was reviewed again, the stability of the conventional monitor's calibration was checked, and the path of data reduction was traced all the way back to the raw data files. No calibration problems or other factors were found, and no errors were found in data reduction. The results in Figures 4 to 11 are particularly puzzling, since they indicate greater response (i.e., higher sensitivity) of the NO_2/HONO monitors than expected based on laboratory calibrations. This indication contrasts with the general behavior of the monitors. These observations lead to the conclusion that the quantitative differences seen are due to NO_2 calibration factors that poorly represent the actual sensitivity in the field. However, the actual cause of that disagreement is unknown.

Turning now to the HONO data, a different picture emerges from the preliminary field data. Figure 12 shows the HONO concentration determined by the three monitors throughout the field period. Greater noise exists in the HONO data because of its determination by difference, but the pattern of activities during the study is clearly evident in the HONO data. More importantly, the three NO_2/HONO monitors agree closely in the HONO data. In fact, although the HONO data from all three monitors are plotted in Figure 12, in most cases they are undistinguishable because the traces overlay one another. This close agreement in HONO concentration is striking given that HONO is determined by difference using a calculation that incorporates separate scale factors for NO_2 and HONO. The close agreement shown for HONO in Figure 12 indicates that the monitors' response to HONO was little changed relative to its pre-field study calibrations. This finding confirms the observation made from laboratory calibrations before and after the field study, that the sensitivity of the electrochemical sensors to HONO is more stable than that to NO_2 (see Table 1).

The electrochemical monitors also gave close quantitative agreement for HONO, relative to the conventional nitrogen oxides monitor. Figure 13 shows this result. For clarity, only the

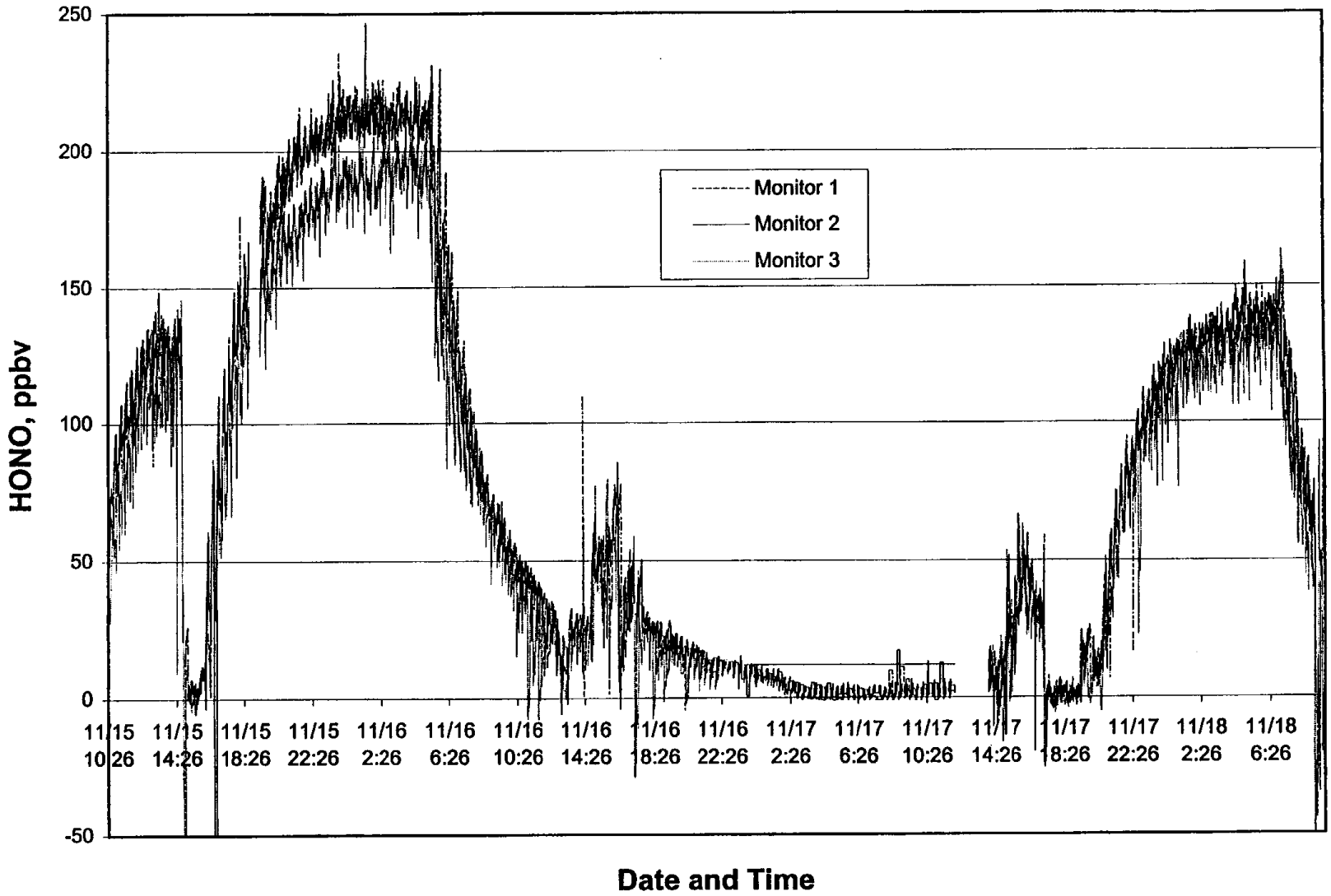


FIGURE 12. HONO CONCENTRATIONS DETERMINED IN THE FIELD STUDY BY MONITORS 1-3

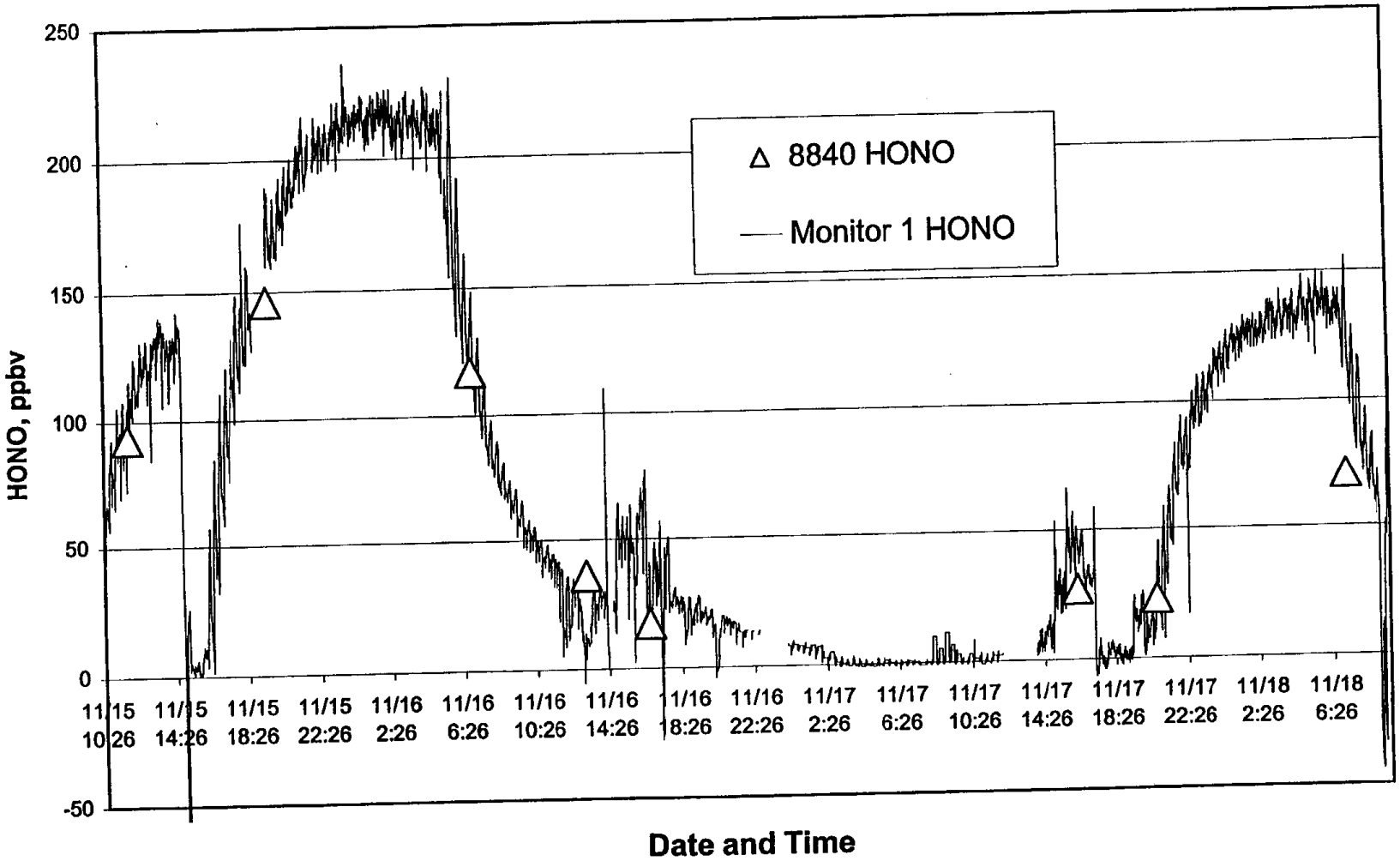


FIGURE 13. COMPARISON OF HONO DETERMINED CONTINUOUSLY BY MONITOR 1 TO HONO DETERMINED AT DISCRETE INTERVALS BY THE 8840 CONVENTIONAL MONITOR

continuous HONO data from Monitor 1 are shown, along with the HONO levels determined at eight times in the field study using the conventional monitor. All of the HONO data from the conventional monitor fall on or near the continuous HONO trace from Monitor 1. These observations show the electrochemical monitors to be sensitive and accurate detectors for HONO indoors.

The maximum HONO levels in the preliminary field tests were about 220 ppbv, associated with an overnight hearth product test. Levels of 50-75 ppbv were determined during operation of the gas range and oven in the research house. Inspection of Figures 4, 12, and 13 shows that the ratio of HONO to NO_2 varied considerably during the various activities in the field study. An example is shown in Figure 14, which shows the ratio of HONO to NO_2, both determined by electrochemical Monitor 1, during the operation of a hearth product overnight on November 15-16. Monitor 1 was chosen for this illustration because it provided the closest agreement with the conventional nitrogen oxides monitor (Figures 4 and 5). Figure 14 shows the NO_2 and HONO levels determined by Monitor 1, and the resulting HONO/NO_2 ratio, during operation of a hearth product from 16:14 on November 15 to about 10:40 on November 16. The hearth product was turned off at about 05:30 on November 16, but the indoor pollutant levels dropped gradually over the next several hours as the home was allowed to air out without any forced ventilation. Figure 14 shows that at the start of the hearth product run and during the run, HONO/NO_2 ratios were low, stabilizing at about 0.2 during operation of the hearth product. Once the hearth product was turned off however, NO_2 levels dropped more rapidly than HONO levels, and the HONO/NO_2 ratio rose to about 1.5 over the next several hours. Figure 14 shows that the low HONO/NO_2 ratio characteristic of the hearth product emissions dominated the indoor air levels as long as the source was operating, but the conversion of a fraction of the NO_2 to HONO became more evident once the source was stopped. Figure 14 also shows the disadvantage of the sequential two-channel approach currently implemented in the HONO/NO_2 monitors: stepwise noise in the NO_2 and HONO data, and in turn greatly exaggerated noise in the HONO/NO_2 ratio, especially during periods of rapidly changing concentrations. Although this effect could be minimized by more sophisticated data processing, that improvement would require greater effort in data reduction.

The preliminary field data also show that the monitors are sensitive enough to determine emissions from residential cooking activities. However, operation in alternating 10-minute

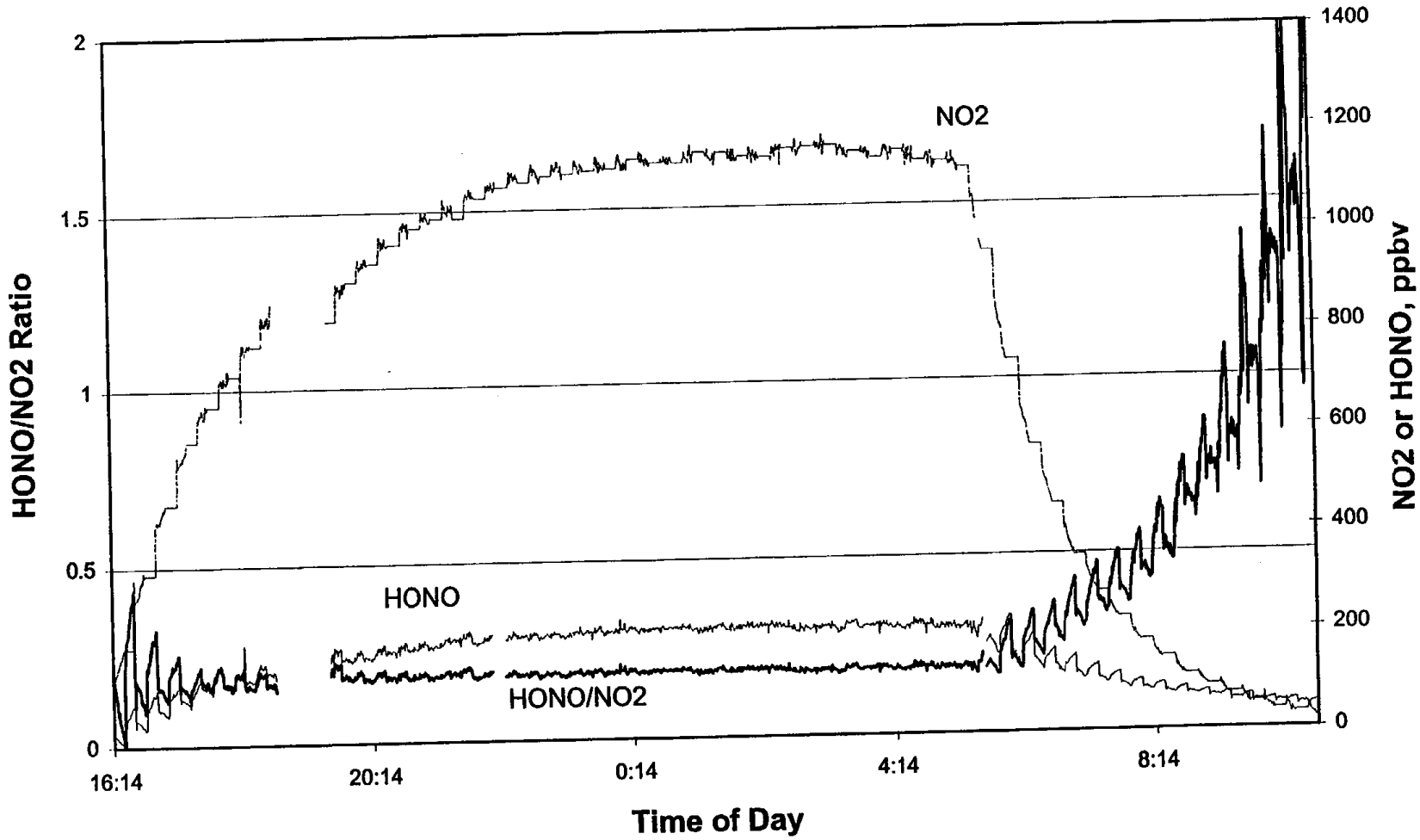


FIGURE 14. NO_2 AND HONO CONCENTRATIONS, AND NO_2/HONO RATIO, FROM MONITOR 1 DURING OPERATION OF A HEARTH PRODUCT

cycles is an obstacle in following short-term processes such as cooking emissions. Figure 15 illustrates these observations, by focusing on a period of operation of the gas range and oven in the research house in the late afternoon of November 17 (see Figures 4 and 5). Figure 15 shows the NO_2 + HONO signal from all three monitors and from the 8840 conventional NO_x monitor, from 14:30 to 19:30 on that day. Simulated cooking activities included operating the oven on "Bake" at 350°F for one hour starting at 14:58; and heating water with two range burners from 15:40 to 16:11. The monitors were located in the kitchen during the simulated cooking activities, and were moved to the bedroom hallway about one hour after the cooking activities ended.

Figure 15 shows that NO_2 + HONO levels of about 150 to 350 ppbv from cooking activities were readily detected by all three monitors, though with the quantitative differences noted above. All three monitors tracked the same emissions profile, although the 10-minute cycle time of the monitors resulted in differing detection of rapid changes in concentration. This effect, which is readily seen in Figure 15 (e.g., at 15:00 and 17:20) is purely an artifact of the alternating 10-minute cycle time. The response time of the monitors is actually about one minute, so the opportunity exists to minimize this response artifact by shortening the cycling time. Figure 15 shows that the emissions from the range burners are clearly detectable when added to the emissions from the oven. The data also show that contaminant concentrations in the kitchen dropped slowly after the appliances were turned off. This implies relatively slow mixing into the rest of the house, which is consistent with the low NO_2 + HONO levels measured in the hallway (Figure 15).

3.5. Operational Performance

The operational aspects of the electrochemical monitors' performance include factors such as ruggedness, ease of use, data completeness, etc. Performance in those areas in the preliminary field tests is discussed below.

The monitors proved to be rugged under difficult field conditions. Indoor temperatures up to 100°F occurred overnight on November 14-15 due to operation of a hearth product. Although the NO_2/HONO monitors sampled outdoor air in this period, they were exposed to the high indoor temperatures, and temperatures inside the monitors' chassis were surely even higher.

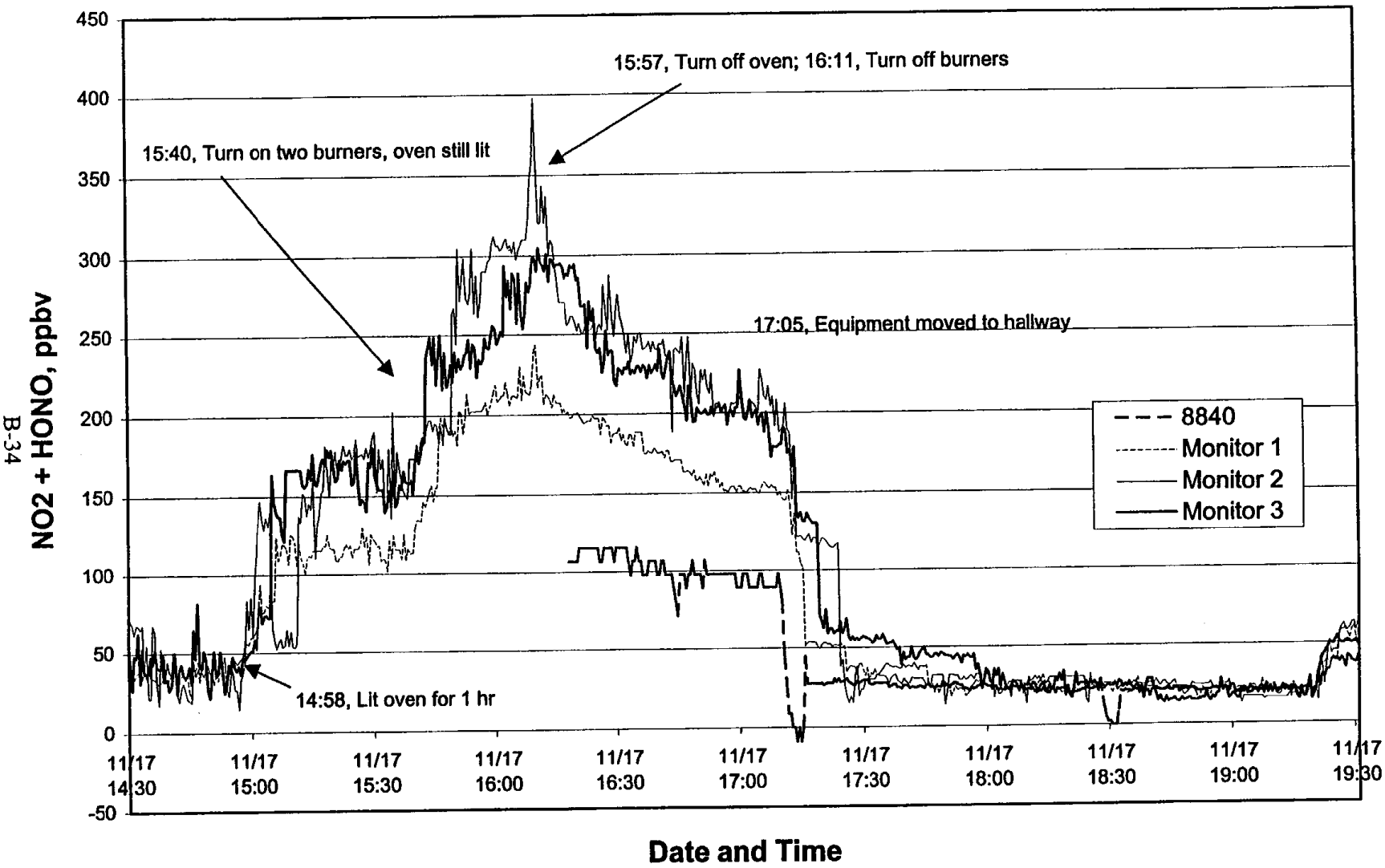


FIGURE 15. NO_2 + HONO LEVELS DETERMINED BY MONITORS 1-3 AND BY THE CONVENTIONAL MONITOR DURING OPERATION OF A GAS OVEN AND RANGE BURNERS

The physical operations of the monitors (i.e., air pumping, valve switching, voltage regulation, etc.) were unaffected by the excessive temperatures, and a review of the data shows that the electrochemical sensors themselves also operated reliably throughout this period. Erratic signals on the morning of November 15, at the end of the hearth product test, were at first thought to be due to overheating of the sensors, but were later found to be caused by problems in data acquisition (see below). Also in the field study, the monitors were transported from room to room, subjected to a variety of high pollutant levels, and operated in a physically crowded and electrically noisy environment. No problems in monitor operation were evident as a result of these factors. The field study also included transporting the monitors between Columbus and Chicago. The monitors stabilized promptly once power was restored in the field. A minor problem was found regarding the construction of the monitors, in that erratic signals sometimes occurred when a monitor's cover was removed or replaced. This was traced to the pinching of electric wires within the chassis between the 12 V DC power supply and the metal case of the monitor. Rerouting of the wires resolved this problem, and minimal loss of data occurred. Use of a non-metallic case or a more rigid chassis should prevent this problem.

As a result of the reliability of the monitors, data completeness was generally not limited by the monitors themselves. However, the data acquisition process did result in some loss of data. As currently assembled, the monitors use electronic circuits designed by TSI to provide a 0-1V analog output proportional to the microampere currents of the electrochemical cell. It was found early in the field study that small AC leakage potentials from the data acquisition system could produce erratic signals from the monitors. In addition, static electricity in the dry indoor environment may have played a role. As a result, it was found necessary to ground all the monitors to one another and to the data acquisition system to avoid electrical disturbances in the data. This approach minimized data acquisition problems for the duration of the field period. The same approach was taken in subsequent laboratory tests, but problems similar to those found in the research house were not observed in the laboratory.

The monitors were easy to use in the field study, because of their small size (4.5 in H x 12 in W x 7 in. D) and weight (about 8 pounds), their self-contained design, and the lack of any consumables. Startup consisted of connecting to AC power, turning on the monitors' front panel switches, and connecting analog outputs to the data system. Both startup and shutdown required approximately 5 minutes. Stabilization of the monitors upon startup required a few hours, only

because the DC bias voltage had been interrupted during transport to Chicago. Over shorter transport times, no such interruption would occur. Operator attention was required only to supply high purity air to the monitors periodically in the field study. On two occasions in the field, minor adjustments were made to the monitors' zero settings to counteract drift that had occurred between zeroing intervals. These activities were minimal, and for the most part the monitors operated unattended.

An important operational performance issue was the impact of the alternating 10-minute measurement modes on data quality. This approach, i.e., alternating 10-minute periods measuring NO_2 and NO_2 + HONO, requires only a single detector in the monitor, and was selected as a compromise between the need for reasonable time response and the need to maximize data collection (as opposed to mode switching and stabilization times). However, this approach caused artificial variations in the final data in periods when actual concentrations were changing rapidly (e.g., see Figure 15), because of the need to determine the difference between non-simultaneous data channels. The alternating channel approach also requires relatively long periods of zeroing (which were not always achieved in the field study), to assure a set of measurements in either mode that represent only zero air. Finally, the alternating mode approach requires a great deal of effort in data reduction. Measurements in one mode must be subtracted from preceding or successive measurements in the other mode. Judgments must be made about the appropriateness of the subtraction process, especially when measured concentrations are changing rapidly. With the present NO_2/HONO monitors, this process was carried out after data acquisition, and required substantial effort to obtain the final data set. Some of the data reduction and subtraction procedures could be automated electronically within the NO_2/HONO monitor, and with a shorter switching time could provide improved data quality. However, some scrutiny of the data would still be needed when monitoring rapidly changing concentrations.

4. FURTHER LABORATORY TESTING

Following the preliminary field tests, laboratory testing of the NO_2/HONO monitors (Task 2) was resumed. In part, these further laboratory tests were to complete testing that was suspended at the time of the field tests. In addition, the further laboratory tests were conducted to explore the uniformity and stability of response of the electrochemical sensors. This aim was prompted by the decreasing sensitivity of the sensors (Appendix A), and the unexplained calibration differences seen before and after the preliminary field tests (Section 3). Laboratory tests were resumed, using the same sensors that were used in the initial laboratory tests and the preliminary field tests. Later, a new set of electrochemical sensors was obtained and installed in the monitors for further evaluation.

4.1. Stability of Response

Using the same electrochemical sensors used in the preliminary field tests, further calibration tests were done to document the long-term sensitivity of the monitors. This activity included the post-field study calibrations conducted upon return from Chicago in November, 1997, and continued with calibrations through January of 1998. Figure 16 shows the results, in terms of the NO_2 sensitivity of each monitor as a function of the time elapsed since the sensors were first put into use. Figure 16 essentially updates Figure 5 of Appendix A by including additional data, but also includes a correction factor for the NO_2 standard concentration. This correction was made necessary by gradual loss of NO_2 in the commercial NO_2 standard used in this study. The basis for this correction is comparisons of that NO_2 standard to a NIST-traceable NO standard at intervals during the program.

Figure 16 shows that prior to the preliminary field studies, the sensitivity of all three monitors decreased at a substantial rate. Linear regressions to the data prior to the field tests are shown in Figure 16, and indicate NO_2 sensitivity losses of about 24 percent, 6 percent, and 33 percent per month, for Monitors 1 through 3, respectively. Only the rate for Monitor 2 is consistent with the 5 percent per month decay stated for these sensors by the manufacturer. Figure 16 also shows the change in sensitivity found after the field period (Day 36) relative to before the field period (Day 25). Surprisingly, the sensitivities of all three monitors apparently

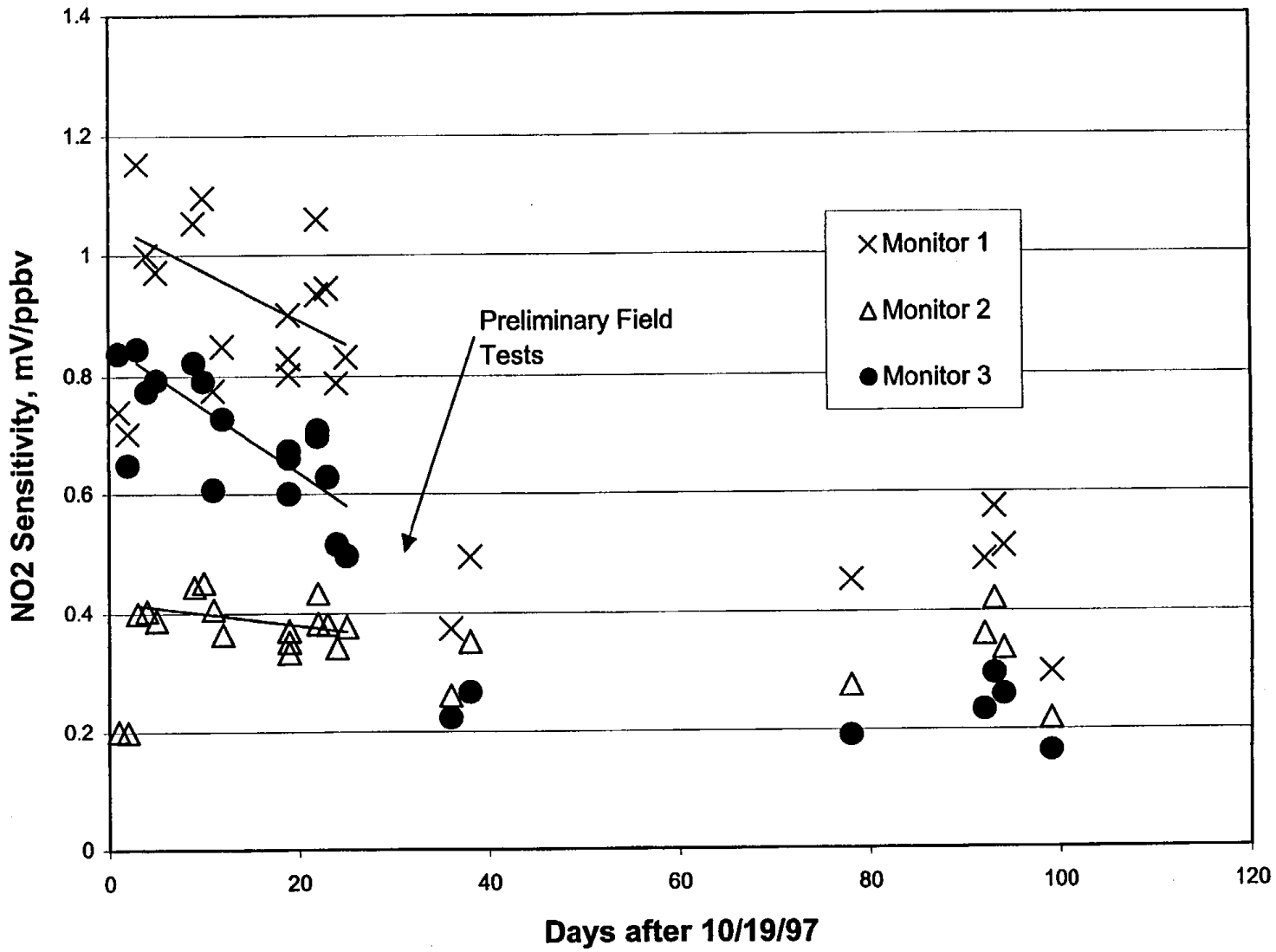


FIGURE 16. LONG-TERM COMPARISON OF NO_2 SENSITIVITY OF MONITORS 1-3

stabilized after that point. Although there is considerable scatter in the individual calibration points after Day 36 (relative standard deviations are about 20 percent for all three monitors), there is no obvious trend in sensitivity between Days 36 and 99. No explanation has been found for the sensitivity shift that apparently occurred after the field study, and none is evident for the relative stability of the monitors beyond that point. Note that although the sensors appear to show stable average response after the field study, the relatively low sensitivities (e.g. 0.2 to 0.4 mV/ppbv for Monitors 2 and 3) and the variability in the calibration data indicate that frequent calibration would still be needed.

4.2. Temperature, Humidity, and Interference Tests

Additional tests of the three prototype monitors in the laboratory included evaluation of temperature and humidity effects, and chamber tests in which multiple target species and contaminants were present simultaneously, rather than separately as in previous tests (Appendix A).

A single-point check of relative humidity (RH) dependence was conducted at room temperature, using 436 ppbv NO_2 prepared in clean air of 45 percent RH, and then of 75 percent RH. Monitors 1 through 3 showed increases in NO_2 response of 22 percent, 22 percent, and 30 percent, respectively, as the RH was increased. This degree of dependence on RH is consistent with previous tests at lower RH values, that are summarized in Appendix A.

A more complete test of temperature and RH dependence was then conducted, by placing the three monitors inside a heated 0.4 m^3 chamber. The monitors sampled humidified calibration mixtures through a Teflon tube extending outside the chamber, while the monitors themselves were maintained at constant chamber temperature. Multipoint NO_2 calibrations were conducted at 21°C (70°F) and 30°C (86°F), and at both low and high relative humidities. The slopes of linear regressions to the calibration data were then compared for each set of test conditions. The results of this test are summarized in Table 4, in terms of the NO_2 response of each monitor relative to that at the lowest temperature and RH conditions. Monitor 3 gave some erratic readings in this test, and the sensor in that unit ultimately failed before completion of the test.

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

Test No.	Temp./RH	Relative NO_2 Response		
		Monitor 1	Monitor 2	Monitor 3[b]
1	21°C/24%	1[a]	1	1
2	21°C/84%	1.49	1.68	2.46
3	30°C/20%	1.31	1.22	1.54
4	30°C/60%	2.03	1.45	--

a: Response normalized to 1 at lowest T and RH.
b: Monitor 3 exhibited erratic readings, and failed prior to last test.

Comparison of the first three test conditions in Table 4 shows that over the ranges tested, the humidity dependence of the sensors is larger than the temperature dependence. For example, Monitors 1 and 2 show a 20 to 30 percent increase in sensitivity as the temperature increases from 21 to 30°C (Tests 1 and 3), but a 50 to 70 percent increase as the relative humidity increases from 24 to 84 percent (Tests 1 and 2). The results found in Test 4, in which both temperature and RH are elevated, are consistent with the combined effects of these separate results for Monitor 1 (i.e., a factor of two relative to the low T, low RH condition). However, the Test 4 result does not appear consistent with the separate results for Monitor 2, and no conclusions can be drawn for Monitor 3. The RH effects shown in Table 4 are consistent with the previous results obtained over narrower RH ranges, noted above. Note that these temperature and RH effects cannot account for the differences in NO_2 determined in the preliminary field tests (Figure 4). In the field tests, RH was relatively low because of the wintertime conditions, and the water produced by operation of the gas combustion appliances was insufficient to raise the indoor RH substantially. Furthermore, the large differences found among Monitors 1-3 in the field tests (Figure 4) cannot simply be attributed to a temperature or RH effect, which should influence all three monitors.

During the course of the T/RH tests, an additional observation was made regarding sensor behavior with RH. After extended exposure to elevated RH (e.g., 80 percent RH at room temperature), all three monitors exhibited a large, slow, upward drift in signal upon being abruptly switched to relatively dry (i.e., RH $\approx$15 percent) room air. This drift reversed itself slowly after resupplying humid air, and was not related to the nitrogen oxides content of the room air. Apparently this behavior is caused by the re-equilibration of the electro-chemical

sensors following the sudden reduction of RH level. In previous evaluations of the RH dependence of baseline signal (Appendix A), a small dependence was found, but abrupt and large changes of RH were not tested. Such large and sudden changes are not likely to occur in any normal indoor use of the NO_2/HONO monitors. However, this behavior may limit the variety of environments in which the monitors are applicable.

Following the T/RH tests described above, the failed sensor in Monitor 3 was replaced. Two final tests were then conducted, in which the three monitors were operated side-by-side in Battelle's 17.3 m^3 chamber, while several target species and potential interferants were injected into the chamber. The purpose of this effort was to observe the response of the monitors to a complex mixture of species, for comparison to previous tests with these species individually. Those tests of individual target species and potential interferants are described in Section 2 and Appendix A.

Each chamber test began with the monitors sampling humidified zero air in the chamber, and continued with successive additions of chemicals. All chemicals except ozone and HONO were introduced into the chamber from compressed gas standards through calibrated mass flow controllers; the flow rate and duration of introduction determined the final chamber concentration. NO from a 1,000 ppm standard was first diluted to about 25 ppm in a flow of high purity N_2, which was then introduced into the chamber. This approach was intended to minimize the formation of NO_2 from the NO/O_2 reaction. HONO was produced by adding 0.3 M $NaNO_2$ solution dropwise with a syringe pump into a Pyrex flask containing 2.5 M H_2SO_4. HONO vapors produced in the flask were then swept into the chamber by a flow of 2 L/min of high purity N_2. Ozone was produced by the brief activation of a high capacity corona discharge ozone generator, through which a few liters per minute of dry air were passed into the chamber. A Monitor Labs Model 8840 nitrogen oxides analyzer and a Thermo Environmental Model 49 ozone monitor sampled from the chamber to document the contaminant levels produced. The chamber air was stirred continuously by an internal fan.

Table 5 summarizes the multicomponent chamber tests, showing the schedule of addition of chemicals and the chamber concentrations prepared. Table 5 shows that the chemicals used in these tests included all the likely interferants tested individually in previous tests (Appendix A), as well as ammonia (NH_3), which had not been tested before. The interferant levels were also in the upper range of those from the previous tests with individual contaminants.

TABLE 5. SUMMARY OF COMPLEX CHEMICAL MIXTURES PREPARED FOR CHAMBER TESTING OF THE NO_2/HONO MONITORS

Date	Species	Time Period of Introduction	Concentration Prepared
2/16/98	NO_2	09:27 to 09:43	630 ppbv
	CO	09:50 to 10:02	116 ppmv
	CO_2	10:10 to 11:07	5,300 ppmv
	HCHO	11:23 to 11:57	400 ppbv
	NO_2	11:59 to 12:03	~600 ppbv
	NO	12:09 to 12:59	1,490 ppbv
	SO_2	13:52 to 13:56	500 ppbv
	NH_3	15:14 to 15:46	580 ppbv
2/20/98	NO_2	09:51 to 10:00	1,130 ppbv
	CO	10:01 to 10:07	105 ppmv
	CO_2	10:09 to 11:04	5,090 ppmv
	HONO	11:44 to 11:48	37 ppbv
	O_3	12:28 to 12:29	500 ppbv
	HONO	13:15 to 13:19	75 ppbv
	NO_2	14:22 to 14:25	540 ppbv

The primary conclusion from these multicomponent tests was that the monitors performed as expected based on previous single-component tests. There was no indication of synergistic interference effects or previously undetected interferences. For example, Figure 17 shows the analog outputs of one of the monitors during the first multicomponent chamber test. The darker trace represents the NO_2 + HONO channel, and the lighter trace the NO_2 channel. The times at which injection of various species began (see Table 5) are indicated in the figure. The sharp increase in response due to NO_2 additions at 09:27 and 11:59 is clearly evident, and the gradual decrease of NO_2 due to dilution and surface losses is apparent after both these points. The brief drop in response at about 11:15 is due to the monitor's air pump being turned off inadvertently. No discernible effect results from addition of large concentrations of CO, CO_2, HCHO, or NH_3. A small increase in response did occur during the addition of NO between 12:09 and 12:59, that is attributed partly to the slight response of the monitors to NO, and partly to formation of some NO_2 as the NO was introduced into the chamber. Also, a very slight suppression of the monitor's response occurred after the addition of SO_2 (Figure 17); this behavior is consistent with previous tests of SO_2 alone (Appendix A). Note that the HONO concentration, indicated by the difference in the two measurement channels, was minimal

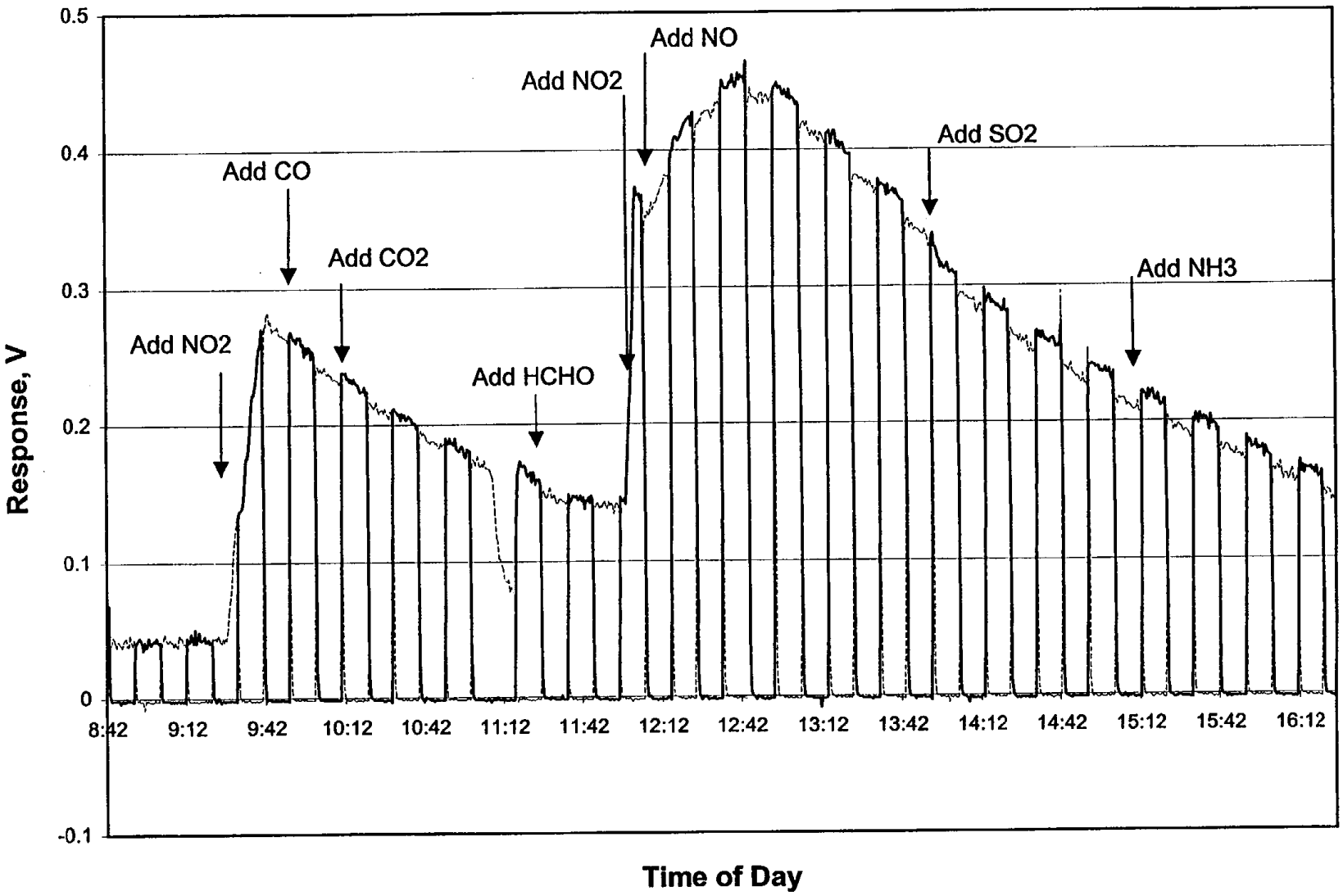


FIGURE 17. RESPONSE OF NO_2/HONO MONITOR IN CHAMBER TEST WITH NO_2, CO, CO_2, HCHO, NO, SO_2, AND NH_3

at the start of the test, but increased significantly as the test continued. This is presumably due to production of a small amount of HONO from NO_2 in the chamber.

Figure 18 shows the corresponding response of one of the monitors during the second multicomponent chamber test. As in Figure 17, both measurement channels are shown, and the times of injection of several chemical species into the chamber are indicated. Data acquisition was lost for about one-half hour late in this test, producing a gap in the data collected. Figure 18 shows that a sharp increase in the response of both measurement channels occurred upon addition of NO_2 after about 09:50. Addition of CO and CO_2 had no effect on the measurements. Two successive additions of HONO caused sharp increases in signal in the unfiltered measurement channel, while that of the $CO_3^{=}$- filtered channel was unaffected. Both channels increased equally upon addition of NO_2 late in the test. All these observations are consistent with the expected behavior of the monitors based on previous tests. However, the injection of O_3 into the test chamber produced no response on the monitor in this test, in contrast to the quantitative positive response seen when O_3 was previously tested alone. The reason for this finding is not clear. Measured O_3 levels in the chamber were still near 100 ppbv nearly two hours after the injection of O_3, so the levels present were ample to produce a response from the monitors. Perhaps the presence of the other species altered the composition of the electrolyte in the electrochemical sensors enough to minimize any O_3 response. In any case, this unexpected behavior indicates that O_3 will be less important as an interferent in a complex air matrix than when present alone.

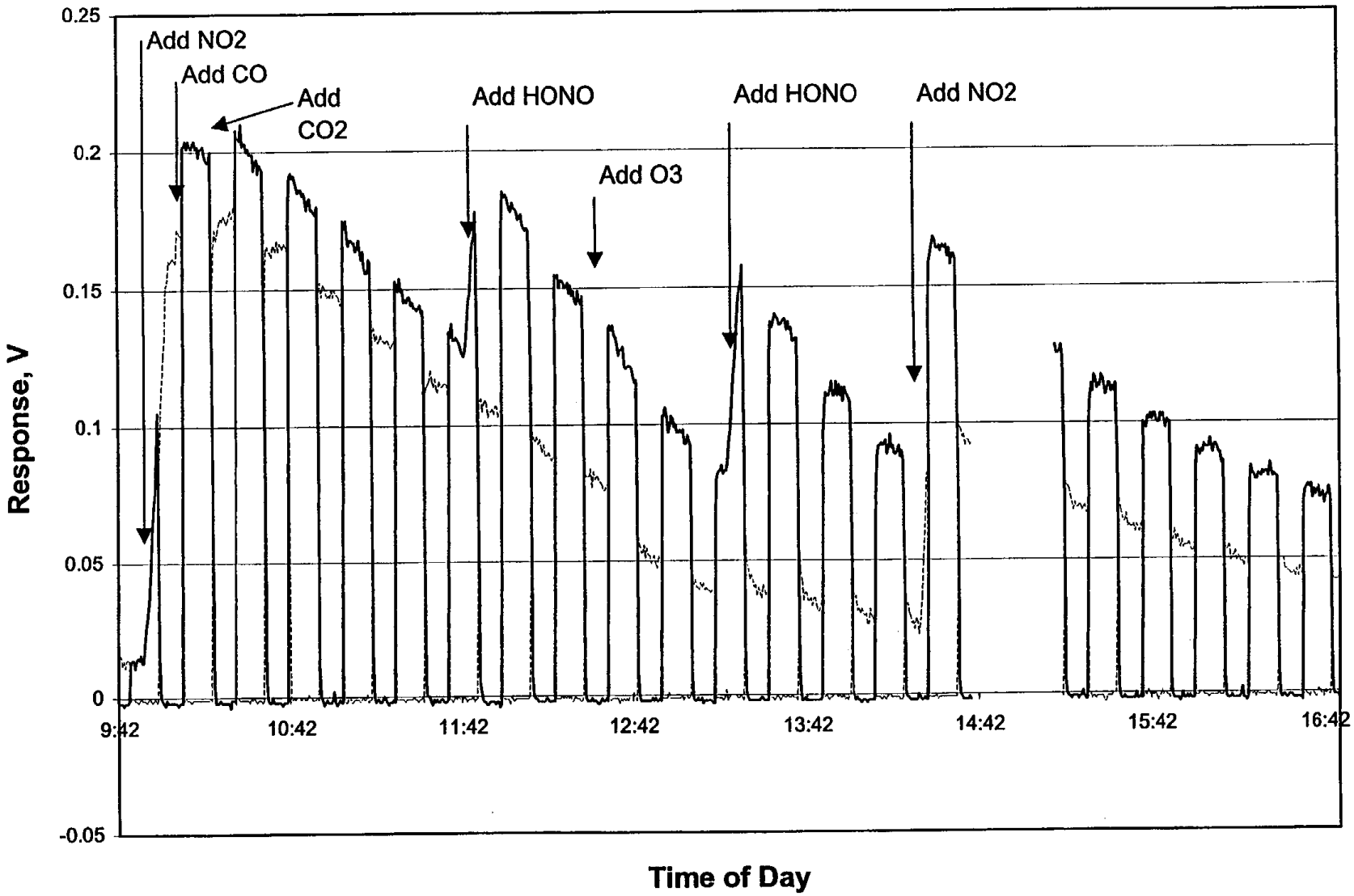


FIGURE 18. RESPONSE OF NO_2/HONO MONITOR IN CHAMBER TEST WITH NO_2, CO, CO_2, HONO, AND O_3

4.3. Testing of New Sensors

For a final set of laboratory tests, four new sensors were purchased from TSI, Inc., with the stated requirement that they be closely matched in NO_2 sensitivity. The sensors were delivered promptly, and had consecutive serial numbers from a single batch of sensors. Three of the new sensors (Serial Numbers 1841, 1842, and 1843) were installed in Monitors 1 through 3 respectively, on March 24, 1998, and the bias voltage in all three monitors was adjusted to exactly –100 mV. After 24 hours of stabilization, they were used in all further laboratory tests.

Initial calibrations of the new sensors showed essentially identical response. For example, Figures 19 through 21 show the results of simultaneous multipoint calibrations of Monitors 1 through 3 on March 27, 1998. The response of all three was linear, and very similar; in fact if plotted together the data overlay one another. The data shown include points taken at high and low concentrations randomly, as well as points taken by successively increasing the NO_2 concentration from zero to 836 ppbv and then stepping back down to zero air. No difference was seen between the stepped and randomized data. The regression results shown in Figures 19-21 show excellent correlations, and slopes (i.e., sensitivities) that differ by no more than 3 percent. The precision of the monitors with the new sensors was also excellent: at the 290 ppbv point the relative standard deviation of the three replicate points was 5.3 percent for Monitor 1; 2.5 percent for Monitor 2; and 0.9 percent for Monitor 3. The baseline noise on zero air indicated a detection limit of less than 10 ppbv. These results show that uniformity of response, and high sensitivity, can be obtained with new sensors.

The stability of response of the new sensors was then evaluated by repeated NO_2 calibrations over several weeks. The results of those calibrations are shown in Figure 22, which plots monitor sensitivity versus the number of days after the new sensors were installed on March 24, 1998. For consistency, the data shown are based on the response to a 290 ppbv NO_2 standard, prepared using identically the same dilution flow settings on each test day. Figure 22 shows the individual calibration results for each monitor over a seven-week period, along with a trend line for each monitor. The trend lines have the form:

Monitor 1 Sensitivity = 0.852 mV/ppbv – 0.00643 mV/ppbv/day x (Days)
Monitor 2 Sensitivity = 0.817 mV/ppbv – 0.00655 mV/ppbv/day x (Days)
Monitor 3 Sensitivity = 0.816 mV/ppbv – 0.00828 mV/ppbv/day x (Days).

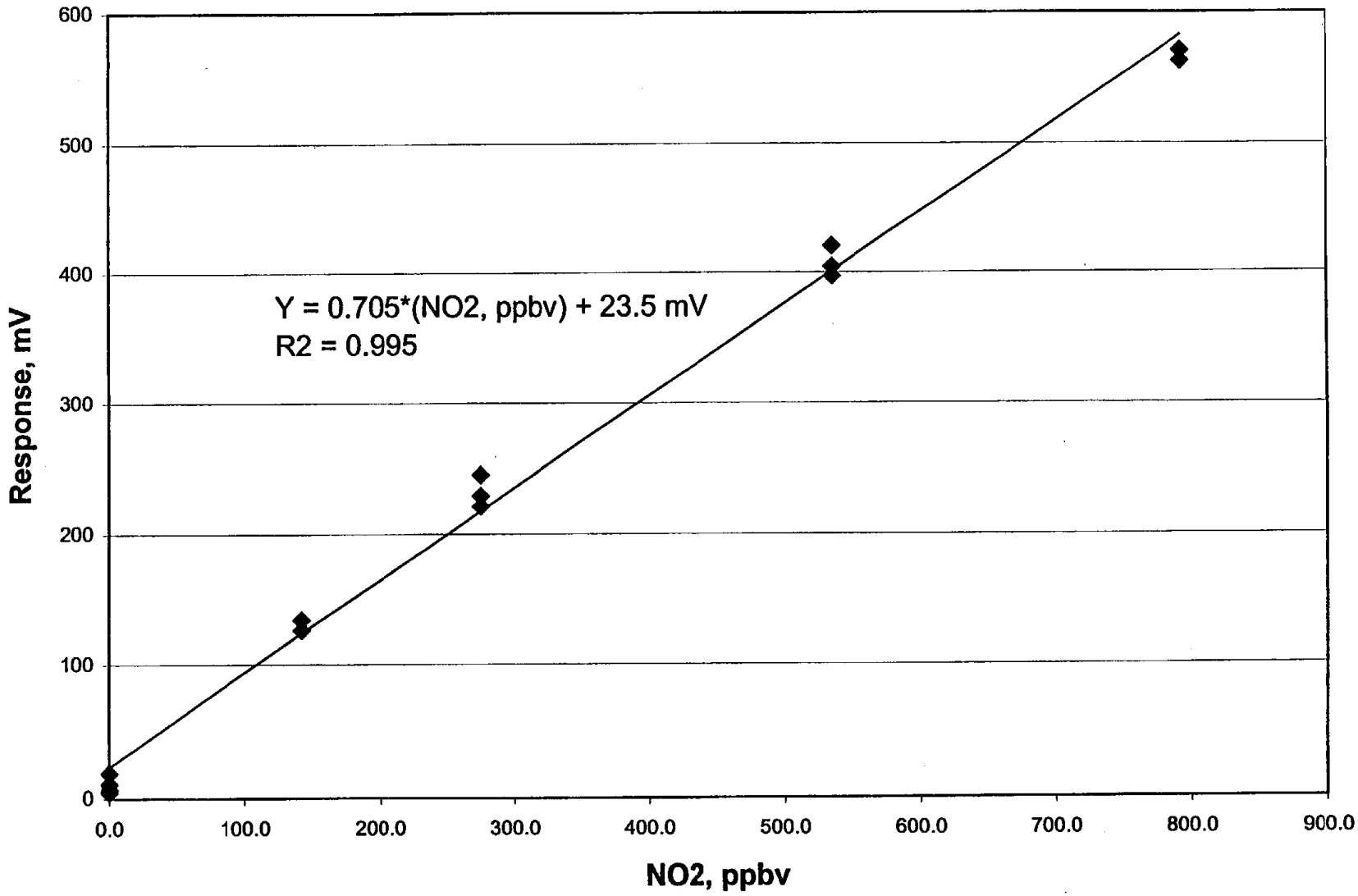


FIGURE 19. MULTIPOINT NO_2 CALIBRATION OF MONITOR 1 WITH NEW ELECTROCHEMICAL SENSOR

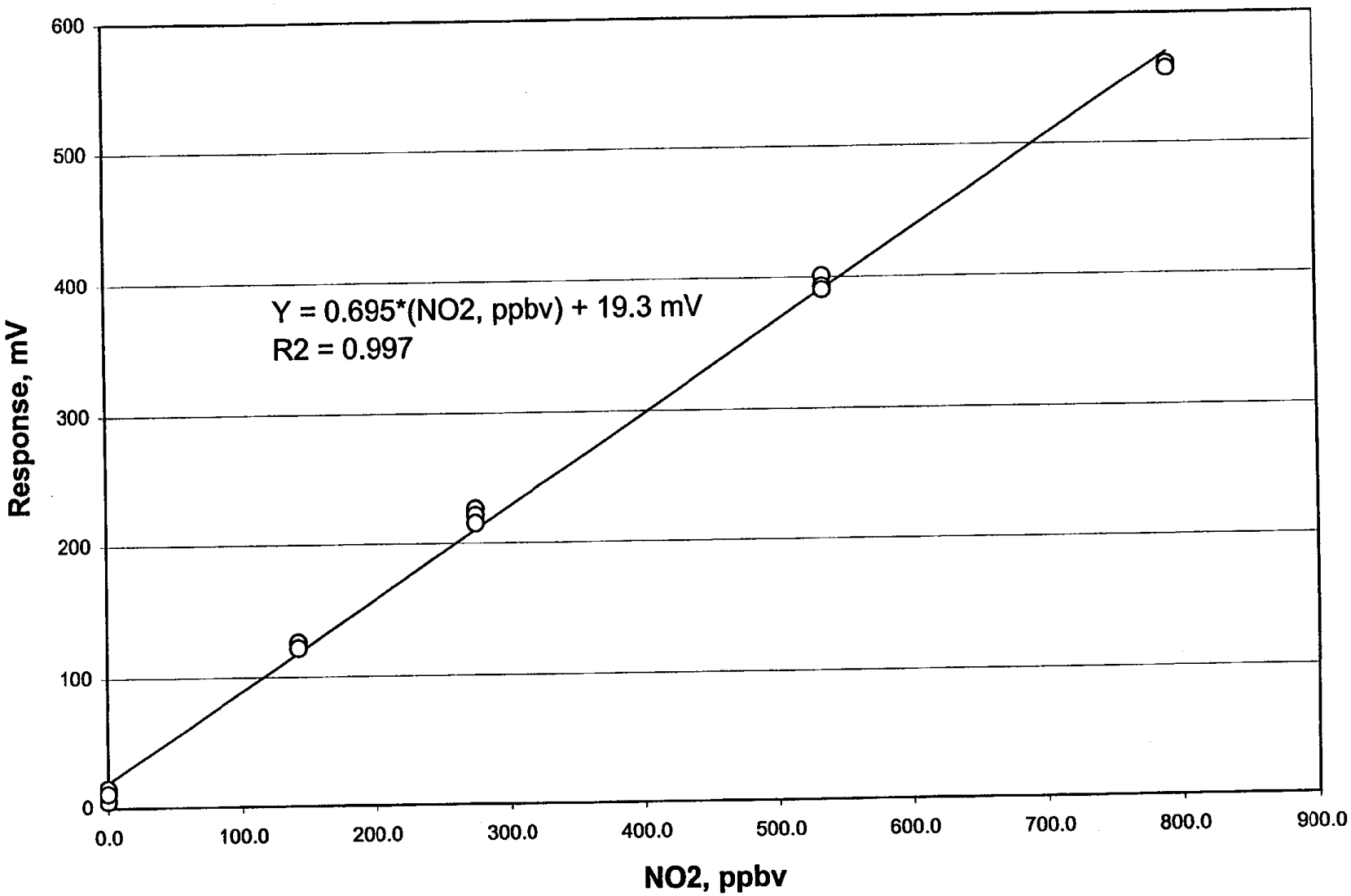


FIGURE 20. RESPONSE OF NO_2/HONO MONITOR 2 IN CHAMBER TEST WITH NO_2, CO, CO_2, HCHO, NO, SO_2, AND NH_3

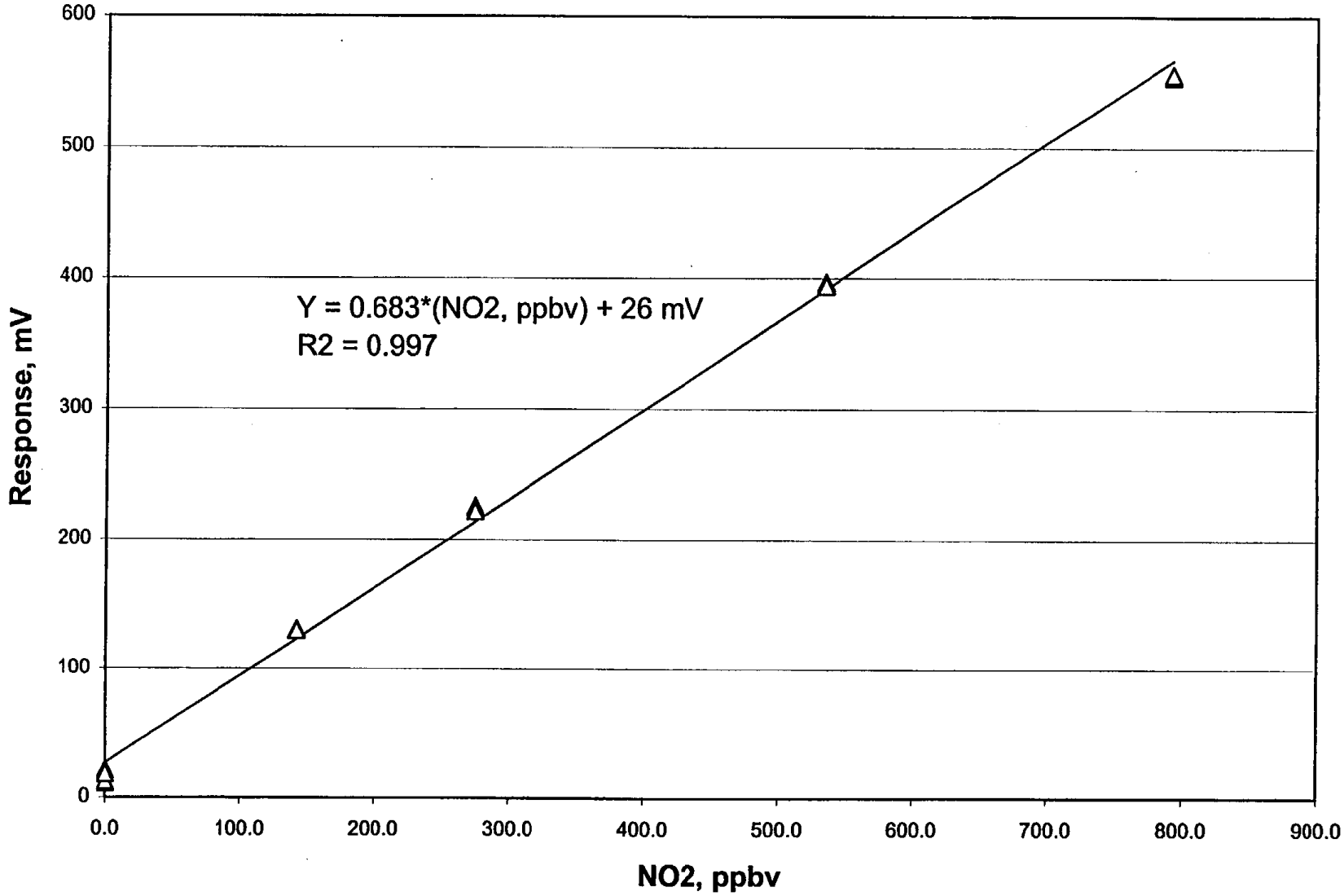


FIGURE 21. RESPONSE OF NO_2/HONO MONITOR 3 IN CHAMBER TEST WITH NO_2, CO, CO_2, HCHO, NO, SO_2, AND NH_3

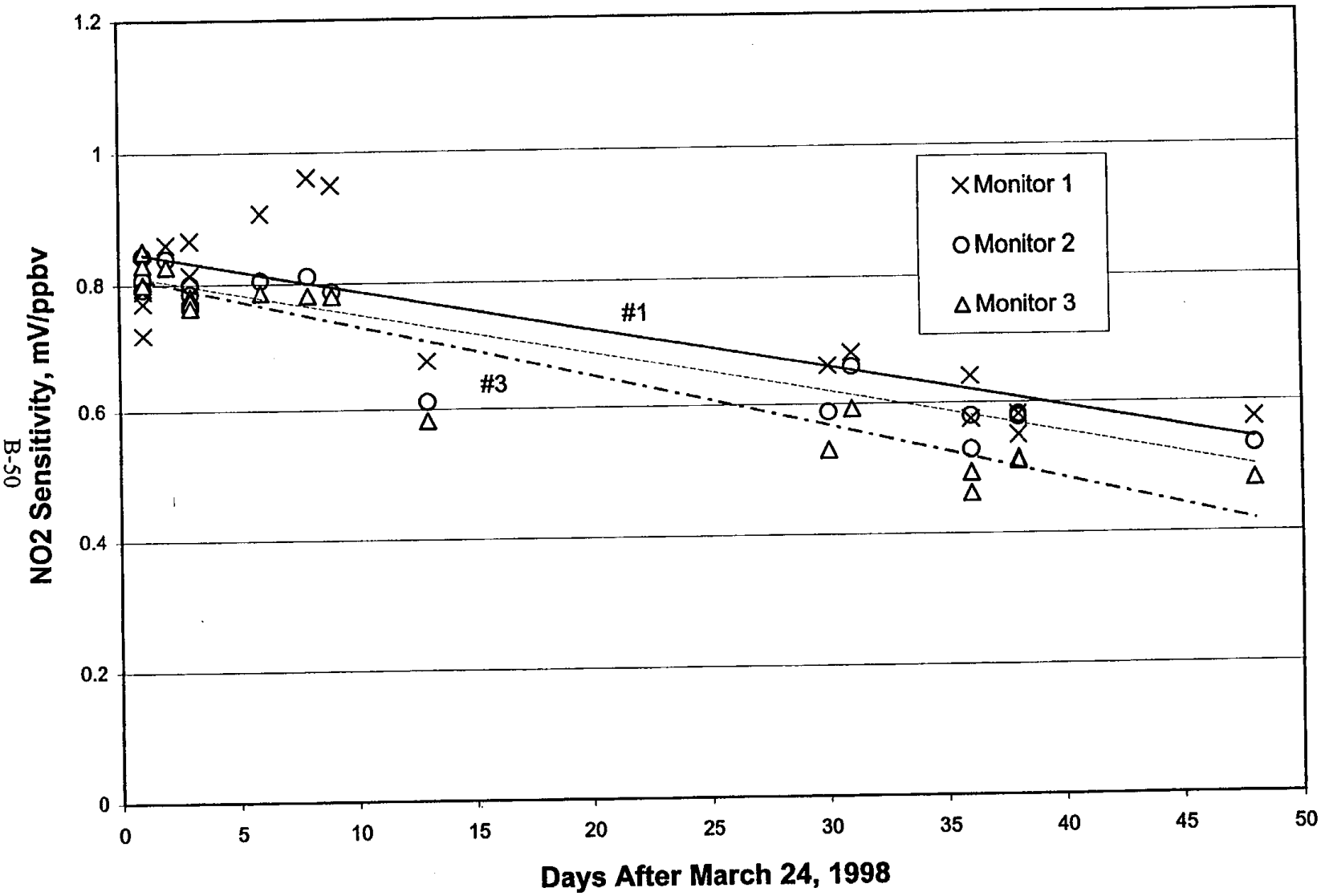


FIGURE 22. NO_2 CALIBRATION RESULTS OVER A 7-WEEK PERIOD FOR MONITORS WITH NEW ELECTROCHEMICAL SENSORS

The data points in Figure 22 show that the sensitivities of Monitors 2 and 3 were stable, and that of Monitor 1 increased somewhat, during the first 10 days of operation. After that the sensitivity of all three monitors decreased substantially. Over the seven-week period documented in Figure 22, the trend lines indicate that Monitors 1 to 3 lost sensitivity at an average rate of 19 percent, 20 percent, and 25 percent per month, respectively. This rate of change is similar to that observed previously with a less closely matched set of sensors, as discussed in Section 4.1. The rate of sensitivity loss is quite similar among the new sensors, perhaps reflecting the greater uniformity of these sensors relative to those tested earlier.

The cause of the loss of sensitivity by the new sensors is not known. Throughout the time period covered by these calibrations, the monitors were operated in a laboratory with normal temperatures, and sampled only filtered room air or clean humidified air. No excessive temperatures, air contaminant levels, particulate matter levels, or extremely dry air were encountered at any time. Thus the conditions were always well within the allowable range recommended by the manufacturer. In some periods the monitors were turned off overnight, with bias voltage maintained on the sensors but no air flow or other functions operating. At other times the monitors sampled calibration mixtures or filtered room air, while cycling automatically between measurement modes, for a few days at a time. Thus, the operating modes of the monitors were typical of what would be expected in indoor survey measurements. The NO_2 standard used for calibration was also checked against a NIST-traceable NO standard at the start and end of this seven-week period, and was found constant within 1.5 percent. It should be noted that the final sensitivities shown in Figure 22, after nearly seven weeks of operation, are still more than sufficient for indoor NO_2 measurements. However, the instability shown could limit the usefulness of the monitors in routine use by relatively unskilled operators, because of the need for relatively frequent calibrations to document the response characteristics of the monitor.

Discussions have been held with representatives of TSI, Inc., and with William Penrose of Custom Sensor Solutions, Inc., the original developer of the sensitive NO_2 sensor, on the issue of loss of response. TSI staff were unable to suggest possible causes for the sensitivity loss, other than those related to particulate matter, excessive temperature, or sampling of dry air. Mr. Penrose inquired about how the sensors are used in the monitors, and raised the question whether the bias voltage supplied to the sensors could be disturbed by operations such as turning the air

pump or AC power on and off, or the switching of the relay and three-way valve in the monitor. According to Mr. Penrose, any electrical disturbance that shifts the bias voltage by a few hundred mV (from the set bias of –100mV) could result in oxidation of the electrode surface and loss of sensitivity. He also was not surprised to hear that HONO response was more stable than NO_2 response, but offered no explanation for that phenomenon. Although bias voltage supplied to the sensors has always been extremely stable whenever checked, specific tests were done in response to Mr. Penrose's comments. In those tests, the bias voltage of each sensor was monitored while all the other electrical operations of the monitor were exercised. No disturbance of the bias voltage could be detected in any of the monitors with any operation. These results indicate that the design of the NO_2/HONO monitors is not likely to be the cause of the sensitivity losses observed with the monitors.

A final test conducted with the new sensors in the NO_2/HONO monitors was to recheck the humidity dependence seen in previous tests (Table 4). This test was conducted by supplying approximately 250 ppbv NO_2 to the monitors at normal room temperature in air of varying relative humidities. Table 6 shows the results, in terms of the response of each sensor relative to that at the lowest RH level. Table 6 shows that the response of all three monitors increased with increasing RH, though to a smaller extent than was found in earlier tests. This may indicate lower RH sensitivity with newer (i.e., less used) sensors, or improvements in manufacturing of the sensors since the program started. Table 6 shows that Monitors 1 and 3 showed very similar RH dependencies, whereas Monitor 2 showed about twice as large a dependence on RH. This non-uniformity of RH dependence from one sensor to another was also seen in earlier tests (Table 4), and is consistent with the general finding in this program that each sensor exhibits individual characteristics.

The RH test also included a check of the RH effect on the monitors' response to ozone. For this test about 60 ppbv of ozone was supplied to all three monitors in air of varying RH at room temperature. All three monitors showed a positive response to O_3 that was approximately equal to that for an equal concentration of NO_2. The RH results are shown in Table 7, which indicates that the RH dependence of ozone response was closely similar on all three monitors. However, the RH effect on O_3 response was greater than that on NO_2 response (compare Tables 6 and 7), especially considering that the RH range covered in O_3 testing was less than in NO_2

testing. This finding means that removal of ozone will be important in any environment where the ozone level is a substantial fraction of the NO_2 level, and particularly in humid environments.

TABLE 6. SUMMARY OF HUMIDITY DEPENDENCE OF NO_2/HONO MONITORS WITH NEW ELECTROCHEMICAL SENSORS

RH	Relative Response to NO_2		
	Monitor 1	Monitor 2	Monitor 3
19%	1[a]	1	1
58%	1.12	1.25	1.13
74%	1.19	1.43	1.21

a: Response normalized to 1 at lowest RH. Test conducted with 250 ppbv NO_2.

TABLE 7. SUMMARY OF HUMIDITY DEPENDENCE OF OZONE INTERFERENCE WITH NO_2/HONO MONITORS

RH	Relative Response to O_3		
	Monitor 1	Monitor 2	Monitor 3
23%	1[a]	1	1
42%	1.15	1.24	1.15
57%	1.38	1.35	1.38

a. Response normalized to 1 at lowest RH. Test conducted with 60 ppbv O_3.

5. SUMMARY

Based on the test results described above, and the hands-on experience gained with the prototype NO_2/HONO monitors in field and laboratory studies, the positive and negative aspects of the prototypes can be stated. The purpose of this exercise is to define further improvements that can be implemented, and to establish the practical limitations of the approach. These aspects are summarized below as Advantages and Disadvantages of the electrochemical monitors. As will be noted from the following discussion, some features fall into both categories. Also discussed below are a few research topics that may need further attention, depending on the direction of further development of the monitors.

5.1 Advantages

Among the main advantages of the electrochemical approach to NO_2 measurement are the small size, weight, power consumption, and cost of the electrochemical sensors themselves. The sensors each cost less than $200, and contribute a negligible portion of the size, weight, and power consumption of the prototype monitors. As a result, the prototypes are portable and easy to use. The greatest contributors to the size and weight of the prototypes are the internal 24 V DC power supply, the valve switching timer and relay, the air pump, and the filter holder. The greatest contributor to power consumption is the air pump, followed by the valve timer, relay, and the valve itself. The sensor bias voltage supply and amplification electronics require minimal power consumption. The prototype monitors also have the advantage of requiring no consumables other than electrical power. The total cost of the separate components of each prototype monitor is about $1,500. The Teflon housings in which the sensors are mounted were made at Battelle, and cost about $500 each; this price could drop significantly if more than a few were made, or if an alternative material were used. The prototypes have operated reliably in the laboratory and under field conditions.

The detection characteristics of the electrochemical sensors are another advantage. The sensors provide a speed of response that is more than adequate for determination of NO_2 over one-hour periods, for comparison to the 250 ppbv California standard. In fact, the response is fast enough to observe short-term changes due to emission sources, such as gas combustion for

cooking, even at NO_2 levels below the 250 ppbv standard. The response is also essentially linear over the entire range of NO_2 concentrations of interest, and interferences from other common air pollutants are minimal, even at greatly elevated levels such as occur indoors. The noise-limited NO_2 detection limit of the sensors is a few ppbv, though in long term operation drift of the background signal may also determine the detection limit. The only significant interferant appears to be ozone though that interference may be minimized in the presence of other pollutants, and in any case ozone is likely to be negligible in any indoor environment where NO_2 exposures are a concern. Ozone would be a concern if the monitor were used in outdoor air, but initial results in this study indicate that selective removal of ozone from the sample air is feasible.

The response of the electrochemical sensors to HONO is an advantage because of the importance of this compound in human toxic exposures indoors. The greater sensitivity found for HONO allows determination of HONO even in the presence of much larger quantities of NO_2, as the preliminary field studies demonstrated. This capability is an advantage over other methods that may not detect HONO at all, or that may at best have equal sensitivity for NO_2 and HONO.

5.2 Disadvantages

The greatest disadvantage of the electrochemical approach appears to be the instability and/or uncertainty of the sensitivity to NO_2. Although the sensitivity of the monitors is sufficient for indoor measurements over many months, the gradual decay of sensitivity with time would require frequent calibration to assure accurate measurements. There is some evidence that average sensitivity may ultimately stabilize, but at a relatively low level and with considerable variation around the average value. The uncertainty in the NO_2 response is best exemplified by the unexplained quantitative disagreement in NO_2 measurements in the preliminary field study. These factors would be serious limitations if the monitors are to be used as off-the-shelf monitoring tools by relatively unskilled operators.

The lack of uniformity of the sensors is another disadvantage. This factor refers to the individual nature of each sensor, in terms of sensitivity, stability, temperature and humidity dependence, etc. Each of the sensors used in this study exhibited some individual behavior, including those especially selected to have equal initial sensitivity. This factor would mean that

the behavior of one monitor could not predict the behavior of another monitor. In use of the monitors off-the-shelf for survey operations this could be an important drawback, and at least would require calibration of each monitor individually.

The response to HONO, which is an important advantage of the monitors, is also a disadvantage in that separate determination of the NO_2 and HONO levels requires a two-channel mode of operation, in which HONO is determined by difference. In this sense, HONO is an interferant in NO_2 determination, rather than another target species. As currently implemented with a single sensor, the two-channel mode of operation requires extensive manipulation of the raw data to derive concentrations, and introduces artifacts into the data because of the non-simultaneous nature of the two channels. These problems could be minimized by operating with a much shorter cycling time between channels, e.g., 2 to 3 minutes, but simultaneous data would still not be obtained. The two-channel approach could be implemented using two sensors in each monitor, thereby providing truly real-time simultaneous data. However, that option might merely double the concerns about sensor stability and uniformity. Another approach might be to operate with a single sensor measuring only NO_2 (by always sampling through a carbonate filter). Bypassing the filter for brief periods could be used to obtain spot measurements of the HONO concentration, without routine two-channel operation. A third approach could be to operate as in the present monitor, but with sophisticated on-board electronics, to perform signal averaging and storage, and subtraction of one channel from the other. This approach would work best if used with a short cycle time, as suggested above.

The humidity dependence, and to a lesser extent the temperature dependence, of the sensors is a disadvantage. The temperature dependence does not appear to be large, and in any case is reduced by operation of the sensor in the warm, enclosed instrument chassis. The humidity dependence is not so easily accounted for. Control of sample humidity, without alteration of the sample composition, would be required to address this issue.

A disadvantage of the present prototype monitors is that they require an external data acquisition system, thereby defeating the purpose of a small, portable indoor monitor. A self-contained data storage device built into the monitor would be preferable.

Finally, the construction of the prototype monitors themselves is an area for improvement. A more rigid, non-metallic chassis would impart greater physical strength to the monitor, and aid in electrically isolating the various components. Rearrangement of some

components may make the design more efficient, and improved placement of electrical wiring is needed, to eliminate spurious signals such as those seen in the preliminary field study. Some components could also be improved. For example, the timers that control the switching between measurement channels are not sensitive enough to allow fine adjustment of the switching times, or to allow synchronization of the switching in different monitors.

5.3 Unfinished Investigations

The research program described here has followed a path somewhat different from the one originally planned. The behavior of the sensors, and the scheduling of the preliminary field tests, resulted in changes in the order and type of tests conducted. In addition, the effort devoted to issues such as sensor stability diverted attention from some planned activities. Although the behavior of the sensors themselves is the most critical issue in this study, it is worthwhile to document those other issues as well.

The development of an ozone scrubber, capable of removing ozone from the sample air while leaving NO_2 and HONO untouched, was begun early in the program. Natural rubber tubing showed promise for this application in laboratory tests, but effort in this area was postponed when the sensor stability issue surfaced. Completion of this effort would require optimization of the tubing size and length for ozone removal and NO_2/HONO transmission, and determination of the capacity and/or lifetime of the scrubber. However, the development of an ozone scrubber may be a relatively low priority item, since ozone is likely to be a negligible interferant in indoor environments where NO_2 exposures are a concern.

Further assessment of the carbonate filter approach for separation of HONO from NO_2 may also be needed. Although there has been ample demonstration of this approach in previous studies, determination of the (presumably large) capacity of the carbonate filters for HONO was not completed in this study. Also, adoption of a carbonate denuder, rather than a filter, may be preferable to minimize pressure drop effects in the two channel system.

Little attention has been paid to date in developing a dedicated zeroing trap for the NO_2/HONO monitors. High purity air has simply been supplied to the monitors for zeroing. This issue may not be difficult to address, since a charcoal trap or other sorbent should readily remove both of the target species from the sample air. In light of the minimal interferences

observed from air contaminants other than ozone, and assuming the presence of an ozone scrubber, a zeroing device should be quite feasible.

The issue of humidity control of the sample air also merits further consideration. Some information gathering, but no testing, was conducted on this issue early in the study. However, other more critical issues pushed this topic aside. This issue will not be easy to address, especially if measurements of both NO_2 and HONO are desired.

Finally, the topic of internal storage of monitoring data was discussed at the start of the program. It was decided to postpone consideration of this issue until the basic approach had been established. Assuming that some form of the electrochemical monitor is to be developed further, internal data storage will be needed to free the monitor from an external data system.

6. RECOMMENDATIONS

The prototype NO_2/HONO monitors evaluated in this study exhibit some puzzling characteristics, but also some highly attractive features. The monitors are capable of accurate fast-response measurements of NO_2 and HONO in homes, businesses, and public buildings, provided that calibration factors for the field measurements are fully established by appropriate QC efforts. In this regard, they can provide data of value to CARB, whether or not they are capable of the routine, off-the-shelf, indoor survey operations envisioned by CARB and embodied in the RFP. As a result, we strongly recommend that further development and field use of the monitors be conducted. Listed below are specific tasks that we recommend for the further development of the monitors. These are listed approximately in the order of their importance, from highest to lowest.

1. Modification of the Monitors – We recommend that a simpler mode of operation be adopted, and that the components of the monitors be repackaged in a stronger chassis. Rather than continuously cycling between two separate measurement modes, with separate analog signals, we suggest that the monitor be operated as an NO_2 detector, with provision for manually or automatically switching to NO_2 + HONO mode only for brief periods. The revised monitor will have a single analog output, and operate normally with a carbonate filter in the sampling line so that only NO_2 is measured. Measurements of HONO will be made by switching the filter out of line, manually or by a delay timer, for brief periods. The single analog output thus will represent the continuous NO_2 level, with step changes at those times when a spot measurement of HONO is made. This approach will greatly simplify the data reduction process, yet allow measurement of both the primary (NO_2) and secondary (HONO) target species.

   The three existing monitors will be repackaged into a more rigid chassis, and a fourth monitor will be assembled. The repackaging of the monitors will include reorganization of wiring and rearrangement or substitution of components to save space.

2. Data Acquisition Capability – We recommend that on-board data storage be added to the NO2/HONO monitors, in the form of small card-sized magnetic storage devices, which are

commercially available. When operated with a single data channel, collecting data at (e.g.) 30-second to 1-minute intervals, such devices have ample capacity for indoor survey measurements with the monitors. The monitors' data can then be dumped to an electronic file using a PC and appropriate software in the laboratory after the field period.

3. Field Measurements – Operation of the monitors in realistic conditions in a variety of California buildings is strongly recommended. This effort will allow further evaluation of the monitors, while also providing valuable data on indoor NO_2 and HONO levels in representative California locations. We recommend that testing be carried out essentially as originally proposed, i.e., in residential settings, businesses, and in public buildings, with conventional nitrogen oxides monitoring conducted for comparison. In order to save program resources, we suggest that Battelle's subcontractor Valley Research Corporation will play a somewhat different role in this effort than originally proposed. The detailed research effort by VRC to identify appropriate buildings will be reduced, and more of VRC's effort will be devoted to assisting Battelle staff in the field study.

4. Humidity Correction – Other than the apparently inherent instability of the NO_2 response, the humidity dependence of the electrochemical sensors is the greatest factor to be accounted for in ambient measurements. We recommend that a means to minimize this effect be investigated. At least, a search for information on ways to control or reduce humidity in the sample air should be conducted. The findings from this search can then be used to decide whether an approach exists that could be added to the monitors.

5. Zero Trap and Ozone Scrubber – Effort in these subject areas was reduced because of the need to assess the characteristics of the sensors themselves. We recommend development of a zeroing trap (probably charcoal-based) as a valuable activity. Development of an ozone scrubber trap is probably a lower priority, given the intended indoor use of these monitors, but could readily be resumed based on the previous tests with natural rubber. We do not recommend further evaluation of the carbonate filter approach at this stage of the program. That approach has been evaluated previously and has apparently worked well in the NO_2/HONO monitors.

APPENDIX C

INDEPENDENT ASSESSMENT REPORT PREPARED BY
VALLEY RESEARCH CORPORATION

Valley Research Corporation
10223 Monogram Avenue, North Hills, California 91343 Ph/Fx (818) 363-5614

FEB 05 1999

February 1, 1999

Dr. Tom Kelly
Battelle, Rm 6134
505 King Ave.
Columbus, OH 43201-2693

Re: CARB Project No. 96-312, "Development of Short-Averaging-Time Indoor NO_2 Monitor."

Dear Tom,

Please find enclosed a copy of the Task 1 report, "Familiarization with the NO_2/HONO Monitor." The report, as specified by Battelle, describes Valley Research Corporation familiarization activities and recommendations concerning the indoor air monitoring system. Please feel free to contact me at (818)363-5614 or (310)575-1170 with any questions. We look forward to working with you on the second stage of this interesting project.

Sincerely,

Craig Tranby
Research Associate

Task I Report
Familiarization with the NO_2/HONO Monitor

Prepared by

Valley Research Corporation
10223 Monogram Avenue
North Hills, California 91343
(818) 363-5614

Prepared for

Battelle
505 King Avenue
Columbus, Ohio 43201-2693

February 1, 1999

- Task I Report -
Familiarization with the NO_2/HONO Monitor

For this task, Battelle sent Valley Research Corporation (VRC) a package containing one of the newly developed monitors, data acquisition and analysis software, a data transfer shuttle, cables, and instructions on monitor operations and procedures for data acquisition. VRC familiarized itself with these operations in realistic conditions including monitor start-up, shuttle launching, clean air calibration, data downloading to shuttle and a personal computer. This brief report describes the results of the five steps required under this task and provides comments and suggestions as to problems or improvements to the system for uninitiated users. Required task work included:

1. Read the operating instructions provided with the $N0_2$/HONO monitor.

2. Install the data acquisition software on a personal computer.

3. Operate the monitor in an office or laboratory setting to become familiar with its operation and with procedures for acquiring and downloading data.

4. Let the monitor operate for at least 24 hours continuously in the kitchen of a private residence where a gas range is used for cooking. Record the periods when the range or other combustion source is operating.

5. Download the monitoring data and prepare brief report stating any observations and recommendations on the monitor, including its physical construction) reliability, ease of use, data collection procedures, clarity and completeness of instruction, etc.

This document fulfills the reporting requirements described in Subtask 5. VRC completed subtasks 1 through 4 over the period Jan. 7-22. Report writing occurred concurrently and until Jan. 29. The report is divided into two primary sections: 1) description of testing and familiarization activities and 2) observations and recommendations.

Testing and Familiarization Activities

VRC staff spent several days familiarizing itself with the layout and operations of the monitor and shuttle, including: installation and testing of the Boxcar software, clean air sampling using the charcoal trap, test downloads to shuttle and a personal computer, one twelve-hour test in the kitchen of a residence, and one 24-hour test in the kitchen of another residence.

Initially, staff thoroughly reviewed enclosed literature, identified different components included with the system, and load the Boxcar software onto a PC. Then, following instruction of the manual, staff: made available a PC serial port, plugged in and switched on the monitor components, conducted trial clean-air sampling, conducted several Shuttle downloads and PC offloads, and tested exporting of data from Boxcar to Excel formats.

12-Hour Test Description

VRC attempted to maximize the value of the initial testing and familiarization stage of the project by conducting a nondesignated 12-hour test in addition to the required 24-hour test. This allowed the accumulation of experience and observations from separate settings and users. Table 1 shows the activity schedule of the test as well as some readings observed from the monitor's visual display. The 12-hour test specifications:

Location:	Kitchen at 11025 National Blvd., Los Angeles
Monitor Elevation:	Floor level
Appliances: (distance from)	Range (4'), oven (4'), fireplace pilot (20'), no gas heat source in building.
Air Inlet Direction:	90° from range/oven for first hour, 180° thereafter.
Filter Setting:	Automatic for entire period.
Ventilation:	Nearby small window and sliding glass door closed for entire period.

Table 1. 12-Hour Test Activities and Readings

Time	Activity	Reading (ppbv)
4:00p	Begin test/clean air sampling	22
4:40p	End clean air sampling/Adjust potentiometer	45/14
5:00p	Rotated monitor 90°	140
5:40p	One stove burner on for 10 minutes	90
5:50p	Oven on for 1½ hours	
6:15p		350
7:05p	Two stove burners on for 15 minutes	
7:15p		520
8:15p		330
10:15p		260
3:30a	Pump turned off	180

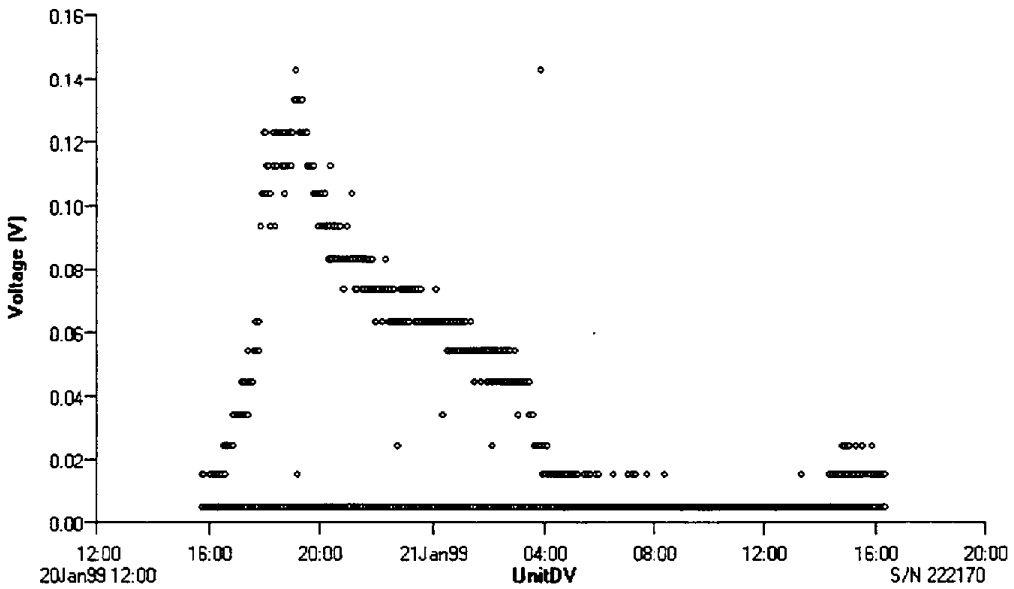


Figure 1. Voltage Readout from 12-Hour Test

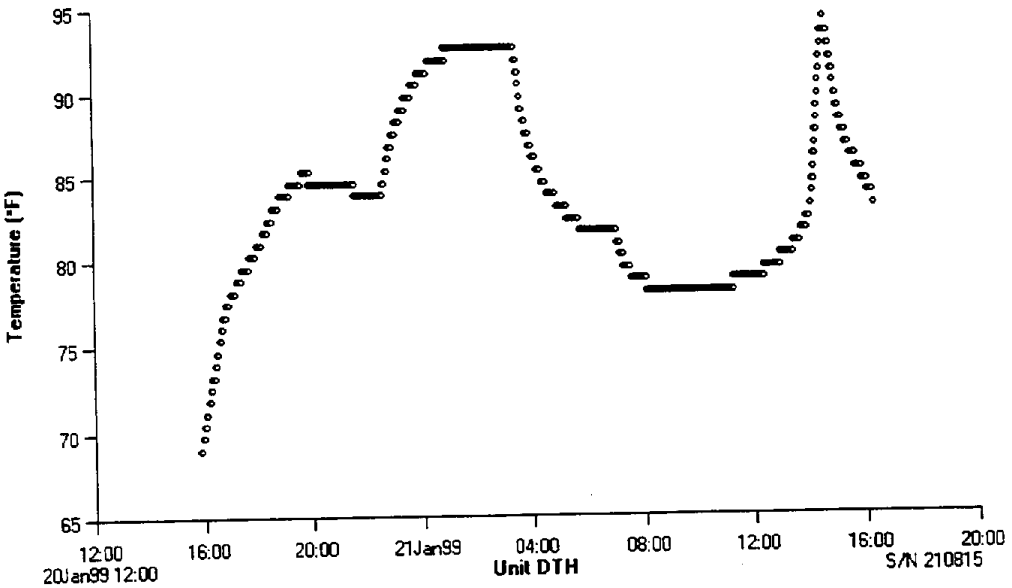


Figure 2. Temperature Readout from 12-Hour Test

24-Hour Test Description

VRC followed up its 12-hour test with a 24-hour test at a different location. VRC opted to not record visual readings during this test. Table 2 shows the activity schedule of the test. The 24-hour test specifications:

Dates:	1/21/99-1/22/99
Location:	Kitchen at 1515 Arapahoe Street, Los Angeles
Monitor Elevation:	3 feet
Appliances:	Range (4'), oven (4'), local gas heating unit in next room (10')
(distance from)	
Air Inlet Direction:	90° from range/oven.
Filter Setting:	Automatic for first 20 hours, manual for 1 hour, auto for final 3 hours.
Ventilation:	Nearby small window opened for brief period. Kitchen door both open and closed.

Table 2. 24-Hour Test Activities

Time	Activity
7:55p	Begin test/clean air sampling. Heater on.
8:19p	End clean air sampling/Potentiometer needs no adjustment.
8:54p	One stove burner on for 6 minutes.
9:05p	Opened kitchen window for 1½ hours.
9:25p	Closed kitchen door for 7¼ hours.
3:55a	Opened kitchen window for rest of period.
4:19a	Opened kitchen door for rest of period.
4:21a	Heater off.
4:22a	One stove burner on for 4 minutes.
5:22a	Heater on for 3¾ hrs., closed kitchen door.
4:00p	Switch to manual filter mode. Filter off.
4:49p	Filter on.
5:07p	Switch back to automatic filter mode.
5:33p	One stove burner on for 8 minutes.
7:25p	Heater off for rest of period.
7:50p	Pump off.

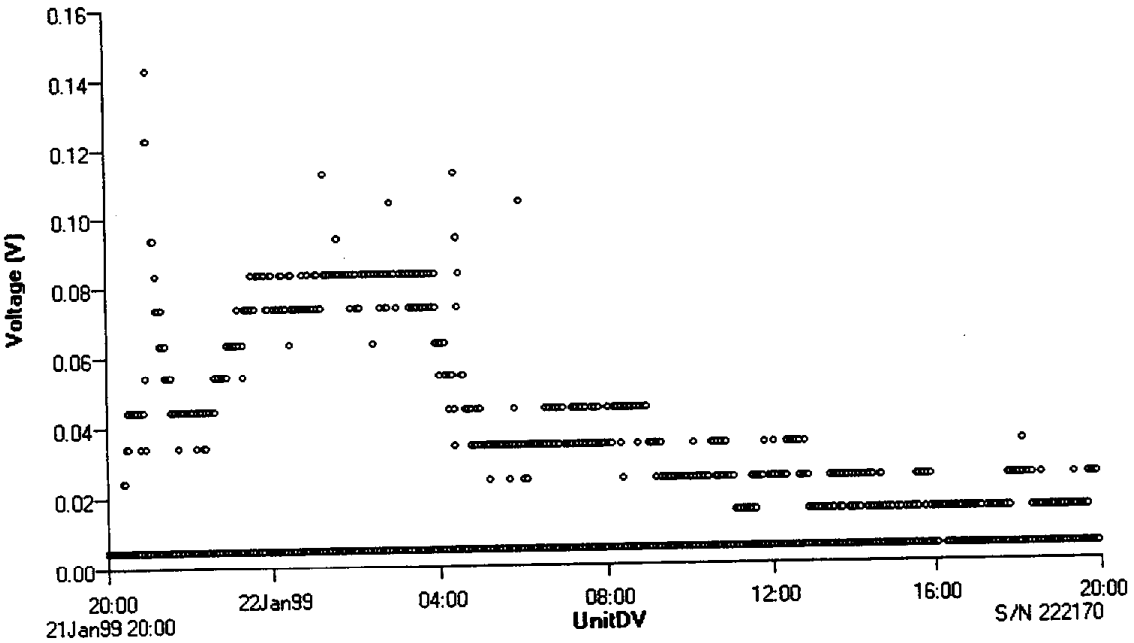


Figure 3. Voltage Readout from 24-Hour Test

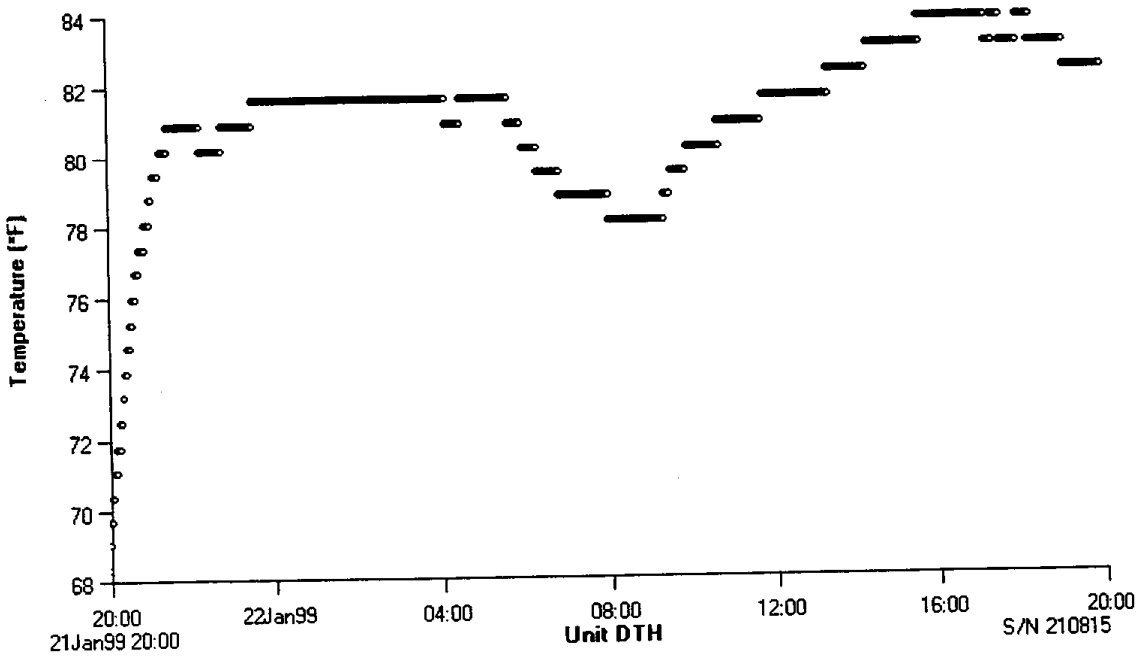


Figure 4. Temperature Readout from 24-Hour Test

Observations and Recommendations

Overall, the monitor appeared to perform as intended. VRC required a minimal amount of guidance from Battelle staff, most of which concerned the recommended positioning of the monitor during the tests. The simple compact layout of the monitor allowed for easy transport and manipulation. Battelle provided fairly clear and concise instructions as to monitor, shuttle and software use. VRC encountered no significant mechanical difficulties or delays in using all aspects of the system provided.

The monitor system appears to be generally ready for the field testing stage of the project. However, in keeping with the purpose of this exercise, this section details the mostly minor questions raised, aspects of concern, and remedies recommended resulting from VRC testing. Most of these concerns relate to improving convenience and ease of use for laypersons. The remainder of the section organizes these issues by area of concern.

Noise - The loud humming of the monitor pump presents one potentially significant problem. During both the 12-hour and 24-hour tests at different residences, the noise from the monitor was found to be grating while in the same room and still audible while in other rooms. In real-world situations, occupants of the buildings being tested will already have enough other reservations about allowing monitoring before introducing considerable noise as a factor. We recommend that Battelle reconfigure the monitor case and pump housing to provide dampening of noise and vibration. This should not require major design changes, merely insulating materials in the pump mount and casing.

Hardware/Connections – A few minor improvements could be made in terms of hardware and connections:

- The data shuttle to PC connection requires a stereo cable (provided) and a free serial port.
- Some users may have difficulty identifying or freeing up the appropriate port. It would be helpful if the instructions provided a little background on PC port connections.
- Also, the stereo cable could be a bit longer and including a 25- to 9-pin adapter would also add convenience to the system.

- An additional piece of included equipment to enable ready use of the system would be a small screwdriver tool for adjusting the zero potentiometer.
- Since many components and accessories comprise the system, Battelle should consider creating a single case carrying for the entire system, or possibly provide ways to attach accessories to the monitor. This will help avoid the loss or breaking of smaller components.
- On a very minor note, the air flow meter is somewhat dark and difficult to view.

Instructions – A few minor clarifications or additions to the instructions would enable easier orientation for new users:

- The system currently requires the user to review two separate sets of instructions: one for the monitor operation and one for the Shuttle. This unnecessarily creates an possibility of losing one of the sets and the inconvenience of referring back and forth. VRC found the cursory stepwise procedure on Shuttle use provided by Battelle to be quite helpful and convenient in operating the system. VRC recommends incorporating additional information from the Hobo Shuttle instructions into the primary manual so as to eliminate the need for a separate set of instructions.
- On a more general note, the inclusion of connection diagrams and possibly others in the consolidated manual would facilitate successful use by the user.
- It may make it easier for some users if the manual provided certain up front information. As discussed, a connection diagram showing monitor, shuttle, PC and cables would be very useful.
- A brief general explanation of how the components work together (some users may not be familiar with the idea of a data shuttle, in particular).
- Some indication that certain features do not apply (i.e., the analog ports) to typical users would help speed orientation with the system.
- The sentence in Step 3 on the last page of the manual, "Once the green "successful" light flashes, push the button on the shuttle to complete the operation," appears unnecessary.
- It doesn't seem that pump activation has any impact on the Shuttle offloading procedure, and should be noted as such.
- No instruction was provided for interpreting or translating the raw voltage data displayed in the BoxCar program into NO2/HONO concentrations. Data interpretation in general

warrants a brief discussion in the manual.

Charcoal Trap – VRC had two primary concerns regarding connection and use of the charcoal trap.

- Instructions should be provided as to the proper connection of the charcoal trap, particularly since the sensor is sensitive to changes in air pressure. Improper connection of the trap could damage the sensor.
- Positioning the trap during the 20-plus minute calibration period was awkward since resting the trap caused a twisting of the connection tube (a thick book was used to alleviate this twisting during the tests). Some instruction should be provided as to its proper positioning.

Monitor Location - No information was provided in terms of positioning the monitor during testing. This could have a significant effect on the levels of NO2 and HONO detected. Aspects to consider include: height off floor, distance from appliances, and direction of air inlet.

- The manual should provide clear guidance as to the appropriate height above floor level for monitor positioning. The ability of locating the monitor at the optimal level may be limited at some locations. However, avoiding floor level and the likely increased concentrations found there would be recommended.
- In terms of the distance from appliances, the user should find a neutral location, evenly positioned among any gas combustion appliances in the room.
- The direction of the air inlet should also be neutrally oriented, if possible among nearby appliances.

Ventilation - No information was initially provided regarding ventilation near the monitor. Battelle subsequently told VRC to control ventilation by keeping doors and windows closed. The proximity to forced air sources might also be considered. As with the monitor location, Battelle should develop protocols for ventilation, possibly consulting with CARB staff.

Temperature Readings - VRC has some concern about the temperature reading depicted in Figures 2 and 4. The temperatures recorded by the monitor were consistently above likely ambient room temperatures. The figures also show greater than expected temperature

fluctuations, some of which seem dependent on the functioning of the monitor itself. VRC staff was not able to fully corroborate external activities and resultant temperatures with temperature data recorded by the monitor. Perhaps, as in the case of the voltage readings, some additional interpretive discussion should be provided in the instructions.

APPENDIX D

REVISED OPERATING MANUAL FOR THE NO_2/HONO MONITORS

OPERATING MANUAL FOR THE BATTELLE NO2/HONO MONITOR

Prepared December 8, 1998

PLEASE READ ENTIRE MANUAL CAREFULLY BEFORE OPERATING THE MONITOR

Introduction

This document is the operator's manual for the instrument that Battelle has developed to continuously monitor nitrogen dioxide (NO2) and nitrous acid (HONO). This document describes the purpose, design, and operation of the monitor, and includes instructions for starting up and shutting down the monitor, initiating data collection, transferring data to a personal computer, and converting data to Excel or Lotus spreadsheets.

The NO2/HONO monitor was developed for the California Air Resources Board, under contract 96-312, for the purpose of conducting screening measurements of NO2 levels in California homes. A one-hour average NO2 standard of 250 ppbv exists in California to protect the health of residents. Previous indoor NO2 measurements, typically averaged over periods of 48 to 168 hours, have suggested that one-hour average NO2 levels are very likely to exceed that 250 ppbv standard in homes with unvented combustion appliances used for cooking or heating. The development of the NO2/HONO monitor thus was motivated by the need for a rapid, portable, inexpensive, and fast means of determining NO2 in homes. Capability for HONO monitoring, while not the primary goal of the development effort, was included because of the greater toxicity of HONO relative to NO2, and the known production of HONO from NO2 indoors.

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

Detection Principle

The NO2/HONO monitor is based upon a sensitive commercial electrochemical sensor (NO2-SNL, TSI, Inc., St. Paul, Minn.). The sensor includes a proprietary electrode design that produces very low background current, allowing detection of NO2 at levels below 10 ppbv. In addition, the sensor responds to HONO with a sensitivity 3 to 5 times that to NO2. As a result, HONO can readily be detected by difference in the presence of an excess of NO2, using a chemically treated filter to selectively remove HONO from air containing NO2. In practice, the monitor functions as an automatic two-channel analyzer, using a three-way valve to switch the sample air flow alternately around or through the treated filter. These two modes of operation thus

measure (NO2 + HONO) and NO2, respectively. Accounting for the different sensitivities to NO2 and HONO allows both species to be determined from the alternating operating modes. The sensor current is converted and amplified to a 0 – 2 V DC output, which is directed to rear panel analog terminals and recorded by an internal data logger. Only one of the two alternating measurement modes provides signal at any time, the other going to zero.

Instrument Schematic

The NO2/HONO monitor consists of a single chassis about 12 in. by 9 in. by 8 in. The lower part of the chassis encloses the power supplies and battery charger for the electrochemical sensor, and the upper part encloses the monitor itself, consisting of the air pump, rotameter, valve, filter holder, sensor housing, valve timer and relay, and associated electronics and plumbing. The monitor requires 120 VAC power, however all electrical connections within the upper part of the chassis are of low voltage (12 V DC maximum) for safety. Sample air is drawn through a port on the rear panel of the instrument by an internal pump, and is expelled inside the chassis. Data acquisition is accomplished by two miniature dataloggers inside the instrument, connected to plug-in jacks for data startup and downloading on the back panel. Analog outputs for the two measurement modes are also mounted on the back panel. A schematic of the components in the upper chassis of the monitor is shown in Figure 1.

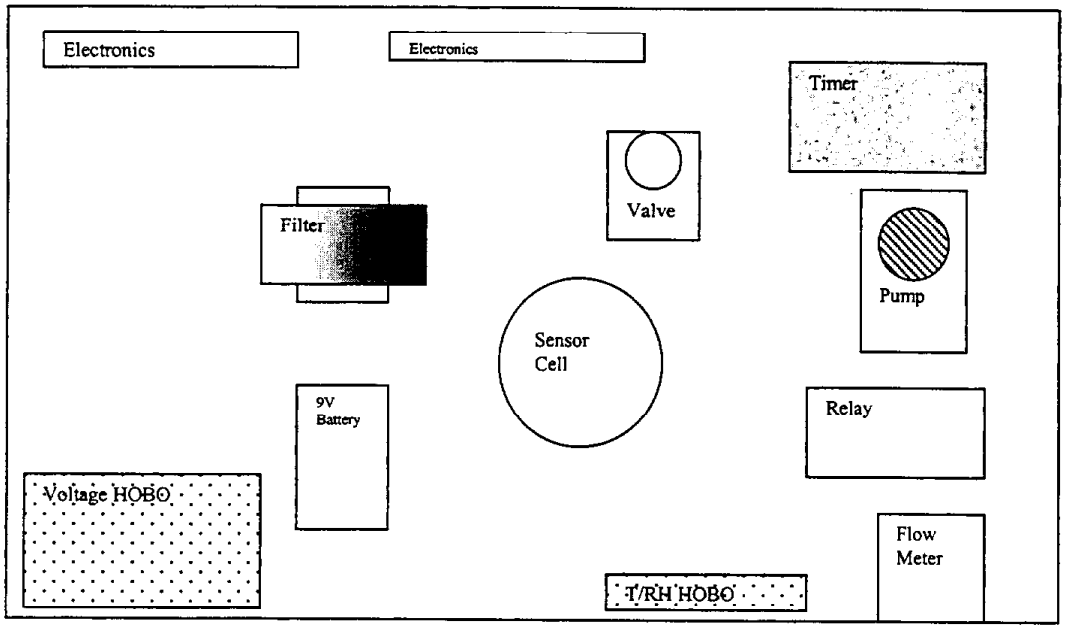


Figure 1. Schematic showing top level of monitor.

Things Not to Do

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

1. Do not plug the air inlet on the back of the analyzer, with a finger or any other object; the sensor does not like being under vacuum.
2. Do not pressurize the air inlet, e.g., by connecting it to a pressurized gas supply; the sensor also doesn't like being under elevated pressure.
3. Do not operate the analyzer for long periods on dry (< 20 % RH) or hot (> 90 °F) air.

Front Panel Features

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

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

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

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

Filter – when the **Manual/Auto** switch is in the Auto position, this switch is inactive. When the **Manual/Auto** switch is in the Manual position, this switch allows selection of either the filtered (i.e., NO2) or unfiltered (i.e., NO2 + HONO) modes of operation. **On/Off** – one or the other of these lights will be lit in either Automatic or Manual operation, indicating which measurement mode the monitor is currently in.

Digital Display – This display shows the approximate sample NO2 level in ppbv. This display is based on the assumptions that the sensor response is due entirely to NO2, with no HONO present, and that the monitor reads exactly zero when sampling clean air. This display is intended solely as a visual indicator of sampling conditions, and not as a quantitative readout.

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

Back Panel Features

The following are the features on the back panel of the NO2/HONO monitor, listed as they are labeled on the monitor:

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

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

Filter Out/Filter In. – these two sets of analog terminals carry the 0 –2 V analog signal from the monitor. The Filter Out terminal gives an analog signal for the instrument running in unfiltered mode, while the Filter In terminal gives a signal for the filtered mode. Only one set of terminals will have a positive analog signal at any time, the other being zero. In Automatic operation the analog output will switch from one set of terminals to the other every three minutes.

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

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

Bias – these plugs allow the bias voltage applied to the electrochemical sensor to be checked. When properly functioning, this should read 100 mV.

Instrument Start-Up

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

2. Switch on the front panel Power switch.

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

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

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

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

Data Acquisition

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

The HOBOs have been set up to collect data once per minute, and have a capacity of about 11 days of data collection at that rate with two channels of data collected. Each HOBO is powered by its own battery, and has its own internal clock. Whenever the Shuttle is used to start data acquisition or download data, the HOBO's clock is reset to match the clock in the PC running the Boxcar software. Instructions and illustrations provided by the manufacturer of the HOBO

dataloggers accompany this document, and should be consulted for the details of use of the HOBOs.

The following is a general stepwise procedure:

1. With the Boxcar software running on the PC, connect the Shuttle to the PC using the stereo cable provided. Select "Logger" from the main menu, and then "HOBO Shuttle Readout" from the dropdown menu that appears, and download any data files from the shuttle. This resets the Shuttle clock to match the PC clock.

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

   Note: Initial download may take 10 – 15 minutes since the HOBO is likely to be fully loaded with superfluous data; the HOBO runs continuously after downloading.

3. To transfer the collected data from the Shuttle to the PC, connect the Shuttle to the PC using the stereo cable provided, choose "Logger" from the menu, and then "HOBO Shuttle Readout" from the dropdown menu that appears. This selection will initiate the transfer from the Shuttle to the PC. When the transfer is complete, the program will prompt the user to input the file name under which the information will be stored.