# PASSIVE MONITORING FOR NITROUS OXIDE

NIOSH Technical Report

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**16. Abstract (Limit: 200 words)**

A commercial passive nitrous-oxide (10102440) monitor was evaluated. The monitor, developed and marketed by Solid State Sensor Company, Lisle, Illinois, depended on molecular diffusion of the analyte to the collection medium. Precision and accuracy were determined by exposing the monitor to 12.5 to 100 parts per million nitrous-oxide for up to 6 hours at relative humidities of 0 to 90 percent. The samples were stored for up to 2 weeks before analysis. Samples were thermally desorbed and analyzed by infrared spectrophotometry. Monitors were spiked with 20 micrograms of nitrous-oxide, stored for 1 week, and the percent recovery was determined. Field samples were collected in hospitals and dental offices. In the laboratory and field tests, the monitors over sampled for short exposure times and under sampled for long exposure times. Precision of monitors analyzed on the day of exposure ranged from 9 to 22 percent relative standard deviation; precision of monitors stored for 2 weeks was 20 to 30 percent RSD. Average percent of recovery of the spiked samples was 54 to 60 percent. None of the results were affected by humidity changes. The authors conclude that the performance of the monitor is unsatisfactory.

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## I. INTRODUCTION

In the field of industrial hygiene monitoring, a sampler that is small and lightweight, requires no mechanical pump and can be easily worn on the lapel is ideal. When such a sampler is available for monitoring a substance for which the only viable sampling method is collection in air bags, it is extremely attractive. The sampling device is a passive monitor or diffusive sampler and the substance is nitrous oxide.

The administration of inhalation anesthetics and analgesics in hospital and dental operations inevitably results in the exposure of operatory personnel to these agents. Although the benefits of anesthetics and analgesics are obvious to the patient, the hazards to occupationally exposed personnel have just recently been reported (1). The major adverse health effects of these agents, of which nitrous oxide ($N_2O$) is by far the most common, include: increased incidences of spontaneous abortion in exposed female workers and the wives of exposed male workers, congenital abnormalities among the children of exposed workers, and liver, kidney, and central nervous system effects (1,2). Based on these health effects, NIOSH recommends that occupational exposures to $N_2O$, the most frequently used analgesic agent be limited to 25 parts per million (ppm) during the period of administration when used in combination with a halogenated anesthetic, and 50 ppm when used by itself (1).

Until recently, worker acceptable personal monitoring devices for $N_2O$ were not available. Nitrous oxide determinations were limited to either gas bag collection followed by infrared spectrophotometric (IR) or gas chromatographic analysis or direct area monitoring by IR (1,2,3). Since area monitoring does not provide personal exposure data and bag/sampling pump arrangements are bulky and cumbersome (and often refused to be worn by doctors, nurses and dentists), a more acceptable means for determining individual exposures was necessary.

A passive monitor, which relies on molecular diffusion instead of a mechanical pump for movement of the analyte to the collection medium, for $N_2O$ was developed and marketed by Solid State Sensors Co. (Lisle, Illinois). The passive monitor is approximately 2.2 cm in diameter, 4.5 cm long, and weighs approximately 20 grams. It is vastly superior to a sampling pump/air bag arrangement from a worker acceptability standpoint. These passive monitors, provided they meet certain performance criteria, should aid considerably in the determination of personal exposures to $N_2O$. Additionally, passive monitors have been used as sampling systems for several other gasses and vapors (4-9).

The purpose of this work was to evaluate this commercially available passive monitor, for performance and reliability in determining personal exposures to $N_2O$.

## II. EXPERIMENTAL

### Apparatus

### Exposure Chamber

Atmospheres of nitrous oxide were generated in a recirculating exposure chamber as shown in Figure 1. The chamber walls are 1/2-in. polymethylmethacrylate sheet, measuring two feet on each side. The top and bottom sections taper to join 1-ft. diameter galvanized duct work. Circulation of chamber air is accomplished with an 11 5/8-in. Dayton centrifugal blower powered by a 1/2-h.p. electric motor.

To control air flow, two plates, one stationary and one moveable, with 1-in. diameter openings are located at the top of the chamber. The total open area of the plates was equivalent to the cross sectional area of the duct work. From the stationary plate is suspended a 1/2-in. thick plastic grating on which rests a 1/4-in. open-cell urethane foam pad and three layers of 1/16-in. mesh nylon screening. The chamber contains 18 sampling ports (Fig. 2) constructed of 1/4-in. stainless steel tubing with brass fittings at which passive monitors may be hung or active samplers may be attached via quick-connects to sampling pumps. The ports are arranged five inches apart since this distance has been shown to be sufficient to prevent starvation of the atmosphere around the passive devices (9).

At the bottom of the chamber is a 40-foot coil of 1/4-in. stainless steel tubing which can be connected to a temperature control unit (constant temperature bath). A 1/4-in. thick aluminum mesh screen and two 1/16-in. mesh nylon sreens rest on the coil. On the side of the chamber is an access port through which samplers may be passed without disturbing the chamber atmosphere. Six openings are located on the side of the chamber to permit use of a hot wire anemometer probe to monitor face velocities at each sampling port. The openings are threaded and are closed with 5/16-in. Teflon$^R$ coated bolts with Neoprene$^R$ gaskets when not in use. On the front of the chamber are two 8-in. diameter openings with polymethylmethacrylate flanges to which 30-in. sleeve gloves are attached. In the duct work immediately above the blower is a plate containing two quick-connect fittings and a septum for introducing gasses and water into the system. On the back of the duct work above the blower is a sleeve for connection to an exhaust system for clearing the chamber. The volume of the exposure chamber is calculated to be 523 liters.

### Operational Ranges

The final air flow design, using the foam pad and screens at the top of the chamber and aluminum mesh and screens at the bottom, provided enough pressure drop to reduce the air flow variance to 9.5% at 200 fpm. A face velocity range of 25-200 fpm was achieved by changing the pulley on the electric motor operating the blower.

A 4 1/2-in. pulley wheel was used for 200 fpm and a 2-in. pulley for 25 fpm. The port-to-port variation in analyte concentration was better than or equal to the precision of the IR (ca. 3%) used.

After the chamber had been conditioned with high concentrations of $N_2O$ to fill any active sites on the surfaces, the analyte stability was excellent. Nitrous oxide loss with time was approximately 5 ppm/hr. By adding $N_2O$ from compressed gas cylinder of certified concentrations of $N_2O$ in $N_2$, through mass flow controllers, the analyte variation in concentration during an exposure up to 8 hours was better than approximately $\pm 3\%$. The time required to completely clear the chamber of analyte by attaching the 2 1/2-in. exhaust hood snorkel was 15 minutes with the recirculating blower operating, and 5 minutes when the blower was not used.

The relative humidity range was 0-90%. Humidity was reduced by placing mesh bags containing calcium sulfate in the chamber until the proper humidity level was reached. An increase in humidity was achieved by injecting water with a syringe through the septum above the blower.

A temperature range of 15-45 °C was achieved by circulating a solution of ethylene glycol and water from a constant temperature bath through the coil at the bottom of the exposure chamber. By insulating the duct work and the blower with 3/4-in. polyurethane foam, the temperature stability was maintained at ±1 °C.

## Instrumentation

A Wilks-Miran Model 80 Infrared Spectrophotometer (IR) was used to continuously monitor the chamber concentration of $N_2O$ and to analyze the samples. This instrument has a 5.75-L gas cell and a variable pathlength (0.75-21.75 m). To keep the calibration curve within the linear range, a pathlength of 20.25 m was used for concentrations less than 50 ppm and for high concentrations (greater than 50 ppm) a 3.75-m pathlength was used.

Chamber air was circulated through the IR cell by means of a DuPont P4000 sampling pump set at approximately 4 Lpm. The inlet of the IR cell was connected to the chamber with 3-mm ID Teflon$^R$ tubing using quick-connects. The outlet of the IR was connected to the pump inlet, and the outlet of the pump returned to the chamber.

The IR was calibrated by means of a closed-loop circulating system (Figure 3). The IN and OUT valves of the IR were connected to the DuPont P4000 pump with Teflon$^R$ tubing (3-mm ID). A septum was placed in-line to allow for injection of pure nitrous oxide to the circulating system (10). Standards prepared in this manner compared favorably to standards prepared in air bags.

Temperature and humidity were monitored with a Humitemp$^R$ Digital Humidity-Temperature Reader (Phys-Chemical Research Corporation). The analyte was metered into the chamber from cylinders of certified $N_2O$ concentrations in nitrogen with a Tylan Mass Flow Controller (Tylan Corp.).

Samples were thermally desorbed using the apparatus shown in Figure 4. The desorption unit consisted of a quartz tube wrapped with 18 gauge nichrome wire. A variable transformer was used to control the current to produce a temperature of 300 $^oC$ within the quartz tube. Plugs of quartz wool were used to hold the sorbent in place. The tube inlet was connected to a cylinder of compressed nitrogen through a dry test meter (Singer, model DTM-115) for monitoring the volume of gas used in desorption. The other end was connected to an air bag for collecting the desorbed $N_2O$.

## Samplers

The object of this study was to evaluate diffusive samplers for their accuracy in monitoring nitrous oxide. At the time of this study the only commercially available $N_2O$ monitor was that marketed by Solid State Sensors Co. In this monitor (Figure 5) a dessicant section precedes the sorbent section. The monitors, as received from the manufacturer, were individually heat sealed in 3-in. X 5-in. aluminized Mylar$^R$ bags. One end of the bag was cut open, the monitor removed and exposed for the sampling period, then returned to the bag. The open end of the bag was folded over twice and sealed with vinyl backed tape. The monitor-containing bags were then placed in a shipping carton and returned to the manufacturer for analysis.

Alternate samplers used in this study were air bags (Calibrated Instruments, Inc.), molecular sieve collection tubes (SKC Inc. 226-40-02), and silica gel collection tubes (prepared according to reference 11). The air sampling bags are constructed of a 5-layer laminated material and have a self-sealing septum and an on/off valve tubing connector. When sampling, these bags were connected with Tygon$^R$ tubing to duPont P200 sampling pumps set at flow rates of 50-100 cc/min. The molecular sieve and silica gel tubes were also connected to the P200 pumps at 175-200 cc/min flow rate for sampling.

## Analytical Procedure

Nitrous oxide was thermally desorbed from the passive monitors. Since commercial thermal desorbers used in GC work did not have the capacity to hold the volume of sorbent from a monitor, the desorption unit (Figure 4) described earlier was assembled.

## Thermal Desorption Procedure

The sorbent from a monitor was transferred to the quartz tube containing a plug of quartz wool at the tapered section (Figure 4). Another plug of quartz was added to hold the sorbent in place. The tapered end of the tube was attached to an air bag with Tygon$^R$ tubing, and the opposite end was connected to the dry test meter. Approximately 0.5 L of $N_2$ was metered through the system to insure that the sorbent was blanketed by $N_2$. The sorbent was then heated to 300 $^oC$ for 20 minutes after which additional $N_2$ was passed through the sorbent into the air bag to provide a final voume of 6-L (14). This procedure allows for any backflow of $N_2O$ from the thermal desorption to be collected in the air bag. The air bag valve was then turned to the off position before detaching it from the desorption unit.

## Infrared Spectrophotometer Analysis

The Wilks-Miran Model 80 IR spectrophotometer can be calibrated by the closed-loop system (Figure 3) or by using standards prepared in air bags. The volume of the gas cell plus the tubing, and the pump was determined to be 5.76 L. For closed-loop calibration, appropriate volumes of pure $N_2O$ were injected into the system through the septum with a syringe and absorbance readings recorded. A calibration curve was drawn plotting absorbance against concentration (Figure 6). Using a 20.25-m pathlength the calibration curve was linear to approximately 50 ppm. For higher concentrations a shorter pathlength was used. At a 3.75-m pathlength, the curve was linear from 150-400 ppm. This pathlenth was used when monitoring the chamber concentration at 300 ppm and when analyzing air bag samples from these runs. Concentrations of monitors desorbed into 6 L of $N_2$ were consistently less than 10 ppm, therefore, the longer pathlength was used for analysis of diffusively collected samples.

To analyze the contents of the air bags, the inlet valve of the IR cell was closed. The in/out valve was opened and connected with Tygon$^R$ tubing to a vacum pump. The cell was evacuated (28-in. Hg) and the in/out valve closed. The tubing from the pump was disconnected and the air bag was attached to the valve with Tygon$^R$ tubing. The valve on the air bag was opened and then the valve on the IR was slowly opened, filling the IR cell with the contents of the air bag. Absorbance readings were recorded, and concentration determined from the calibration curve.

## Passive Monitor Laboratory Evaluation

The nitrous oxide passive monitors were evaluated in the laboratory first with a screening test designed to determine the significant variables and then with a more sophisticated statistical test designed to determine the interaction of these variables. Additional experiments were conducted to determine precision and accuracy, sampling rate variation with time, stability and temperature effects.

A Plackett-Burman screening (12) design which uses high and low extremes in variables was employed to evaluate seven variables in twelve trials (experiments). The variables were relative humidity at 10 and 80%, face velocity at 25 and 200 fpm, concentration on $N_2O$ at 10 and 300 ppm, exposure time at 1 and 8 hours and three potential chemical interferants. The potential interferants, chosen because of their probability of being present in hospital operatories or dental offices, were isopropanol, carbon dioxide and halothane, an anesthetic agent widely used in combination with $N_2O$. The concentrations used correspond to approximately one-half and two times the Occupational Safety and Health Standard (13) for these substances. Humidity levels were chosen to bracket the expected levels encountered while sampling. The face velocity levels were the minimum and maximum levels that could be satisfactorily reproduced in the exposure chamber. The sampling times were chosen as being the probable minimum and maximum times at which persons would be occupationally exposed to $N_2O$. The low level $N_2O$ concentration corresponds to approximately one-half the NIOSH recommended exposure level (1) and the high concentration approximates levels typically encountered in hospital and dental operatories (1,2,14).

The significant variables determined from the Plackett-Burman screening design were investigated in more detail with a Box-Behnken response surface experimental design (12). This experimental design provides information on the linear, interaction and curvature effects of the variables. The data obtained with the Plackett-Burman and Box-Behnken experimental designs were evaluated, the significant variables determined, and contour plots drawn with the Statistical Analysis System (SAS) computer software.

The uniformity of sampling rate was determined by exposing 18 monitors to approximately 50 ppm $N_2O$ and removing two monitors at 0.5, 1.0, 1.5, 2.5, 3.5, 4.5, 5.5, 6.5 and 7.5 hours. One monitor from each set was analyzed by the investigators and the other returned to the manufacturer for analysis.

The stability of $N_2O$ collected by these monitors was investigated by several different experimental schemes. First, for storage studies, monitors were exposed to $N_2O$ at high and low relative humidities and stored for two weeks before analysis. Second, in an experiment designed to determine the effect of exposure to variable concentrations of $N_2O$ (high dose/no dose), eight monitors were exposed to a high $N_2O$ concentration and a high relative humidity level for two hours. Following this exposure, four of the monitors were removed from the chamber and analyzed and the remainder were returned to the exposure chamber after it was cleared of $N_2O$ and exposed to a high humidity environment for an additional four hours. Third, in order to determine if $N_2O$ was "off-gassing" from the monitors during the time delay between sampling and analysis, eight monitors were first spiked with 20 ug $N_2O$. Four of the monitors had been exposed to a humid (80% R.H.) and $N_2O$ free atmosphere for four hours before being spiked with $N_2O$. After spiking, the monitors were capped and sealed in a gas sampling bag to which 6.0 liters of nitrogen were added. The four samplers that had not been exposed to the humid environment were placed in a second bag. Following one week's equilibration at room temperature, the contents of the bags were analyzed for $N_2O$.

Precision and accuracy determinations were conducted at approximately 0.5, 1.0, and 2.0 times the NIOSH recommended exposure limit of 25 ppm. Six monitors were exposed at each of the three concentration levels for six hours. Precision was the relative standard deviation of the analysis of these monitors and accuracy was determined by comparison with the independent sampling method (air bags). In most cases, a sufficient number of monitors were exposed so that analysis could be conducted both in our laboratory and by the manufacturer.

Temperature effects were investigated by comparing the diffusive flux (uptake rate) obtained for monitors exposed at various temperatures. The temperatures used were approximately 15, 25 and 40 °C.

### Field Samples

Field samples were collected in hospital operating rooms and dental offices. Sixteen pairs of samples (one air bag and one passive monitor) were collected in a total of three operating rooms. Five air bags with two passive monitors per air bag were collected in a total of three dental treatment rooms. The passive monitors were placed within six to eight inches of the air bag pump inlet during sampling. It was not possible to collect additional air bags in the dental offices because of the small size of the rooms. Two passive monitors were also placed on each the dentist and dental hygienist.

## III. RESULTS AND DISCUSSION

### Principles Used in Diffusive Sampling

Diffusive sampling across a "dead-air" space (quiescent zone) is governed by Fick's first law (6) which states that the flux J, the quantity of substance diffusing per unit time through a unit area, of a substance through a perpendicular to the direction of diffusion is directly proportional to the concentration gradient:

$$J = -D \frac{dc}{dx} \qquad \text{(A)}$$

where D is the diffusion coefficient, C is the concentration of diffusing gas, and X is the distance in the direction of diffusion.

For a passive monitor (diffusive sampler) Fick's law can be integrated and simplified to:

$$Q = \frac{DA}{L} C_A t \qquad (B)$$

where Q is the quantity of substance collected, A and L are the cross-sectional area and length of the diffusion path, $C_A$ is the concentration of analyte in the air being sampled and t is the sampling time. The simplification of Fick's law assumes the passive monitor sorbent is an efficient collection medium for the analyte.

Since the DA/L term can be defined as the effective sampling rate (K) and is constant for monitors where A and L do not change during sampling, Equation B therefore becomes:

$$Q = K C_A t \qquad (C)$$

This equation may be reorganized to calculate the sampling rate when the quantity of analyte collected on the monitor (Q), the analyte concentration in the atmosphere sampled ($C_A$), and sampling time (t) are known:

$$K = \frac{Q}{C_A t} \qquad (D)$$

For this study, Q was equal to the concentration of $N_2O$ in the air bag ($C_B$) following desorption, times the dilution volume (V) used for desorption, times a factor for converting L to mL, that is:

$$K = \frac{C_B V \ (1000 \text{ mL/L})}{C_A t} \qquad (E)$$

Where K has the units of mL/min and $C_A$ is the analyte concentration (ppm) in the atmosphere sampled.

Reorganizing this equation to determine the time weighted average concentration in the sampled atmosphere results in:

$$C_A = \frac{C_B V \ (1000 \text{ mL/L})}{Kt} \qquad (F)$$

An "analyte permeable membrane" is sometimes used instead of a "dead-air" space in diffusive sampling. The permeation flux (F) of a vapor through a membrane can be expressed (5) as the product of the diffusion constant (D) of the vapor, the area (A) of the membrane and the partial vapor pressures ($P_1$ and $P_2$) of the vapor on the two sides of the membrane, divided by the thickness of the membrane (S):

$$F = DA \ (P_1 - P_2) \ /S \qquad (G)$$

For an efficient vapor (analyte) sorbent in the monitor, the vapor pressure of the analyte within the monitor can be assumed to be zero (5). When the outside of the membrane is exposed to the atmosphere to be sampled, the vapor pressure on that side of the membrane is due to the analyte concentration in the atmosphere. Under these circumstances the quantity of analyte collected (Q) can be expressed as the product of a constant, K, incorporating the diffusion of the analyte and the size of the membrane, the concentration of analyte in the atmosphere ($C_A$) being sampled, and the length of the sampling period (t):

$$Q = K \ C_A \ t \qquad (H)$$

This equation (H) is the same as that representing diffusion across a quiescent zone (C) and consequently suffices for both permeation and diffusion controlled samplers.

## Passive Monitors Laboratory Evaluation

### Screening Designs

The Plackett-Burman screening design was established as shown in Table I. The trials (experiments) were conducted in random order according to the assigned run number. The values shown are nominal values. The actual humidities varied from 7.6 to 17.2% for the low levels and 73.0 to 87.0% for high levels. The face velocity varied from 25-35 fpm and 180-210 fpm for the low and high levels, respectively. The desired concentrations of the potential chemical interferants were obtained by spiking the appropriate volume of the interferant into the exposure chamber. Analyte ($N_2O$) concentrations were established by collecting an air bag sample during the course of each rum and analyzing this with the IR. The analyte concentration determined in this manner was in agreement with the $N_2O$ concentration observed with the continuous monitor (IR) used during each run and concentration obtained by dividing the quantity of $N_2O$ spiked into the chamber by the chamber volume.

Table II shows the actual $N_2O$ concentrations determined in the exposure chamber and the concentrations, precisions and recoveries determined with the passive monitors. As can be seen from the data, in most cases the precision and accuracy were very poor. Statistical analysis at the 90% confidence level of the data, expressed as percent recovery, for each monitor location in the chamber indicated that both nitrous oxide concentration and exposure time were significant variables over the range investigated (Table III). The positive signs (+) indicate the high level and the negative signs (-) indicate the low level of each parameter range. When the mean of the recoveries was used in the calculation to determine significant effects, only the sampling time was a significant variable. The "dummy" variables have no experimental parameter assigned to them and consequently provide an estimate of the experimental error. From the size of this experimental error, the minimum significant factor effect [MIN] is computed. Any factor effect whose absolute value is greater than the [Min] is established as statistically significant. The magnitude of the number indicates the degree of effect for that variable (i.e. the larger the number, the greater the effect due to that variable). Relative humidity was determined not to be a significant effect; however, in most cases it did produce a larger effect than any of the other variables (except time and $N_2O$ concentration).

These three variables (exposure time, $N_2O$ concentration and humidity) were further investigated using the Box-Behnken response surface design. The recoveries obtained with this experimental design are shown in Table IV. Plots of the recoveries versus each of the three variables (Figures 7,8 and 9) showed that a positive bias, greater than 100% recovery, occurred for low exposure times (1 hr) and low $N_2O$ concentrations (10 ppm). The high variability of the results, which was noted with the Plackett-Burman screening design, was obvious again.

The geometry of a Box-Behnken design for three variables is shown in Figure 10. It is difficult to visualize from this plot the regions where acceptable recoveries (100%) occur. Consequently the Box-Behnken data and the Plackett-Burman data were computer evaluated (SAS software) and a mathematical model obtained. A contour plot was drawn from this model and is shown in Figure 11. A plane is shown in the plot at 100% recovery. The shaded regions of the plot represent less than 100% recovery and the unshaded regions depict greater than 100% recovery. As was noted earlier, very high recoveries occurred for short exposure times and low concentrations, while low recoveries occurred with long sampling times (8 hours) and with high $N_2O$ concentrations.

A possible explanation for this apparent oversampling for short exposure times and undersampling for long exposure times is that the diffusional path (L) could be changing as the monitor samples $N_2O$. If the $N_2O$ is absorbed first on the top layer of sorbent, then the next layer, then the next, and so forth, then the diffusion pathlength will be changing as a function of quantity of $N_2O$ collected. For this case, the sampling rate (K) will be changing continuously as $N_2O$ is absorbed by the monitor.

A second possible explanation for the high recoveries for short exposure times and low recoveries for long exposure times is that during the time between exposure and analysis (2 weeks), the $N_2O$ is not completey retained by the sorbent (i.e. off-gasses) and escapes from or permeates through the individual monitor packages. The more lightly loaded monitors then "sample" the environment in the shipping package. Consequently, after the exchange in the shipping package, the less heavily loaded samples appeared to have oversampled while the more heavily loaded samples appeared to have undersampled.

## Passive Monitor Uptake Rate

Eighteen passive monitors were exposed to 41 ppm $N_2O$ and removed from the chamber in pairs, at different time intervals. One monitor from each pair was analyzed in our laboratory and the other returned to the manufacturer for analysis. The temperature and humidity in the exposure chamber were maintained at $23.0 \pm 0.5$ °C and $34 \pm 4\%$ RH, respectively. The monitors to be analyzed in-house were thermally desorbed and the quantity of $N_2O$ on each monitor determined. This quantity was plotted against the exposure time (Figure 12). The dashed lines indicate ±25% of the experimental line drawn through the data. The trend in the data indicates that the sampling rate of the monitors decreases after five hours and that the determination at 7.5 hours was erroneously high. The decrease in sampling may be caused by the capacity of the sorbent being approached, by the possibility of the dessicant "caking" and inhibiting diffusion, or by a changing diffusion path length (L) in the monitor. An erroneously high sampling rate may be caused by a poor seal between the membrane and the monitor housing or a puncture in the membrane, provided this membrane is a permeation membrane and is consequently the rate limiting step in the collection of $N_2O$ by the monitor. Effective sampling rates (uptake rates) were calculated for each of the monitors using equation E and were determined to be $1.45 \pm 0.34$ mL/min (Figure 13). The relative standard deviation was 23.4%. This effective sampling rate was subsequently used to determine air concentrations of $N_2O$ based on the monitor loading and sampling time according to equation F.

This equation and sampling rate was used to calculate the air concentrations and, subsequently, the recoveries of the monitors exposed over different time intervals. These recoveries were plotted with the recoveries obtained by the manufacturer and are shown in Figure 14. The dashed lines represented 25% error. The majority of the samples analyzed in-house are within 98 - 115% recovery, the exceptions being an exceptionally high recovery of 134% at 2.5 hours and low recoveries at 5.5 and 6.5 hours, 56 and 66%, respectively. Manufacurer's analyses exhibited high recoveries, 145% for sampling times of less than or equal to one hour and low recoveries, 45% for sampling times of greater than four hours. This supports the theory presented above that "off-gassing" of $N_2O$ occur in the shipping carton and that the less heavily loaded monitors then collect some of this $N_2O$.

## Stability, Precision, and Accuracy

In the high dose/no dose experiment eight passive monitors were exposed to 202 ppm $N_2O$ at $80 \pm 2\%$ R.H. for two hours. The monitors were removed and capped. Then the chamber was cleared of $N_2O$, the humidity was adjusted to $80 \pm 2\%$, four of the monitors were returned to the chamber and "exposed" for an additional four hours to an $N_2O$-free atmosphere. The monitors exposed for two hours only contained 18± 1 mg $N_2O$ (n=2), and the monitors exposed an additional four hours to an $N_2O$-free atmosphere contained 23 ± 7 ug $N_2O$ (n=4). The difference in these data is not statistically significant. The apparent gain may be partially explained by the number of analysis in each set. Analytical data were determined for two of four monitors exposed only for two hours. One monitor which had taken a torn membrane resulting in a very high sample loading was excluded from the data. The other sample was lost during desorption because of a faulty air bag valve.

An additional experiment was conducted to determine if "off-gassing" of analyte from the monitor was occurring and whether humidity level was a factor in this process. Four monitors exposed to high humidity, and four "unexposed" monitors were spiked with $N_2O$. Each group of four monitors was sealed in a separate air bag and six liters of nitrogen were added to each bag. The atmosphere in each of the two bags was analyzed after 12 days and determined to contain $N_2O$. The monitors were then removed from the bags and analyzed. The average recovery from the monitors not exposed to the high humidity was 54± 29% while the average recovery for the monitors that had been exposed to the high humidity levels was 60 ± 38%. This experiment substantiated the earlier findings that $N_2O$ did "off-gas" from the monitors during storage, and showed that humidity had no significant effects on this loss.

The precision, accuracy and storage sudies results are shown in Table V. As can be seen, high (80%) and low (13%) relative humidities during the exposure had little effect on the monitor's performance. Storage of the monitors after exposure was shown to have a pronounced effect on the analyte recovery. A bias of up to -58% for two weeks storage was observed. Refrigeration of the samples during storage only slightly improved the recoveries. Also, monitors exposed to low concentrations of $N_2O$ and analyzed on the day of exposure were determined to have high recoveries. The precision of the monitors analyzed on the day of exposure ranged from 9 to 22% relative standard deviation (%RSD) while the precision of the monitors stored for two weeks ranged from 20 to 30% RSD.

Temperature studies with the passive monitors (Table VI) gave the expected results of high recoveries at high exposure temperatures and low recoveries at low exposure temperatures due to the fact that diffusion to the sorbent is temperature dependent. An increase of 20 $^{o}$C resulted in a bias of +6% while a decrease of 8 $^{o}$C resulted in a bias of -11%. These biases are slightly larger than that predicted by diffusional theory (4); however, they are within the precision of the sampling device. Additionally, if the membrane at the open end of the monitor is the rate-limiting step (permeation controlled sampling), this will also be affected by temperature.

### Alternate Samplers

In addition to the passive monitors, some other sampling systems were investigated during this study. The collection of $N_2O$ in air sampling bags (with subsequent analysis by IR) has been described by others (1,3), and was determined to be the best alternate air sample collection system. Air bag sampling provides a representative time weighted average sample over the collection period; however, the bags are bulky and not well suited to personal sampling methods. Silica gel and molecular sieve "active" (i.e. a mechanical pump is required) sampling tubes were also investigated for their ability to monitor exposures to $N_2O$. These devices are considerably less bulky and restrictive than air sampling bags. However, when challenged with a concentration of 236 ppm $N_2O$ and sampled at 200 cc/min, breakthrough occurred on both the silica gel and the molecular sieve tubes in less than one minute. This corresponds to a sampling volume of less than 0.2 liters. Consequently, the silica gel and molecular sieve "active" sampling tubes were not satisfactory for $N_2O$ exposure monitoring.

### Field Samples

Field samples were collected to determine the monitors utility in "real" sampling environments. The results of the field samples, hospital operatories shown in Table VII and Figure 15, and dental offices shown in Table VIII and Figure 16, exhibited the same trends noted earlier. That is, the more heavily loaded samples (longer exposure time and/or exposure to high $N_2O$ concentrations) had the lowest recoveries while the less heavily loaded samples exhibited high recoveries. The large standard deviations found in the monitor to air bag ratios for OR 2 and OR 5 (Table VII) make the differences in these data not statistically significant. Also, as was observed earlier, heavily loaded samples exhibited a high degree of variability. This is further evidenced by the pairs of samples worn by the dentist and the dental hygienist. The two samples worn by the dentist, one on each lapel approximately six inches apart, exhibited time weighted average (TWA) concentrations of 143 and 20 ppm. The pair of samplers worn by the hygienist exhibited TWA concentrations of 98 and 157 ppm. Statistical analysis of this data (SAS software) could not detect a significant difference between the passive monitor and air sampling bag results, due primarily to the large relative standard deviation of the passive monitors.

## IV. Conclusions and Recommendations

This evaluation indicates that the performance of the Solid State Sensors passive monitor for $N_2O$, in its present form, is unsatisfactory. It falls far short of the criteria required by NIOSH for a general sampling and analytical method and, therefore, could not be used for any compliance monitoring.

One major problem of the monitor was loss of $N_2O$ during storage. This was particularly troublesome when monitors were returned to the manufacturer for analysis. An equilibration appeared to take place within the shipping container. This resulted in an apparent oversampling of monitors exposed to low $N_2O$ concentrations or exposed for short sampling periods and apparent undersampling of monitors that were exposed for long periods or to high $N_2O$ concentrations. This problem could be eliminated or at least minimized by using a tight fitting monitor cap to contain the $N_2O$ in the monitor and using foil laminate, or other material not permeated by $N_2O$, bags in which to seal the monitors for returning to the manufacturer for analysis. The monitor bags should be designed and used in such a manner that there is a minimum of headspace into which the $N_2O$ may diffuse. However, the basic need is to find a sorbent that has a great affinity for $N_2O$.

The precision was very poor ($>$20% RSD) in several cases. This was probably due in part to a poor seal between the plastic screen on top of the monitor, the diffusional membrane and the monitor and also to imperfections (tears or lack of uniformity) in the membrane. The poor precision was also attributed to the partial, non-reproducible, loss of analyte during storage.

An additional problem not addressed by the manufacturers' analysis of samples is that of sample blanks. Nitrous oxide was found on all of the passive monitors used as blanks in this case study. Consequently, erroneously high values would have been reported had the blanks not been subtracted. Results will be considerably more accurate, particularly for low exposures, if the manufacturer requires that sample blanks be submitted with exposed samples and the appropriate adjustment made.

When this study was approximately 70% complete, Solid State Sensors, Inc. was purchased by another corporation. The monitors marketed by the new manufacturer will have some modifications designed to improve the reliability of the product. Included in these modifications are the use of a foil laminate bag in which to seal the monitor after exposure, and making the screen on the open end of the monitor an integral part of the monitor case. These modifications should help improve the performance of the sampling device.

The manufacturer considers all aspects of the monitor proprietary, including the composition of the sorbent, the dessicant, and the membrane, as well as its principle of operation. One may only speculate as to whether the monitor is a diffusive or a permeation sampler; therefore, both theories have been presented. The reasons for poor performance and their possible remedies are also matters of conjecture.

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Table I

Plackett-Burman Screening Design

| Trial No. | Run No. | Humidity (Δ R.H.) | Face Velocity (fpm) | $N_2O$ (ppm) | Time (hr) | Halothane (ppm) | Isopropanol (ppm) | $CO_2$ (ppm) |
|---|---|---|---|---|---|---|---|---|
| 1 | 10 | 80 | 25 | 300 | 8 | 5 | 200 | 2500 |
| 2 | 3 | 10 | 200 | 10 | 8 | 5 | 200 | 10,000 |
| 3 | 4 | 80 | 200 | 10 | 8 | 5 | 800 | 2500 |
| 4 | 8 | 80 | 25 | 10 | 1 | 5 | 200 | 10,000 |
| 5 | 2 | 80 | 200 | 300 | 1 | 1 | 200 | 10,000 |
| 6 | 1 | 10 | 25 | 10 | 1 | 1 | 200 | 2500 |
| 7 | 11 | 80 | 25 | 300 | 8 | 1 | 800 | 10,000 |
| 8 | 5 | 80 | 200 | 10 | 1 | 1 | 800 | 2500 |
| 9 | 7 | 10 | 200 | 300 | 1 | 5 | 800 | 10,000 |
| 10 | 9 | 10 | 25 | 300 | 1 | 5 | 800 | 2500 |
| 11 | 6 | 10 | 200 | 300 | 8 | 1 | 200 | 2500 |
| 12 | 12 | 10 | 25 | 10 | 8 | 1 | 800 | 10,000 |

# Table II

## Plackett-Burman Data

| Trial No. | $N_2O$ Chamber Concentration (ppm) | Passive Monitor Determinations (ppm) | | | | Relative Standard Deviation (% RSD) | Percent Recovery | | | | Average %Recovery |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | a | b | c | d | | a | b | c | d | |
| 1 | 6.3 | < 5 | < 5 | 6 | 5 | a | a | a | 96 | 80 | 76[b] |
| 2 | 325 | 30 | 32 | 33 | 55 | 10 | 10 | 10 | 10 | 17 | 12 |
| 3 | 300 | 55 | 25 | 74 | 98 | 49 | 18 | 8 | 25 | 33 | 21 |
| 4 | 274 | 31 | C | 27 | 190 | >100 | 11 | C | 10 | 70 | 25 |
| 5 | 7.5 | 29 | 29 | 17 | 33 | 26 | 390 | 390 | 225 | 440 | 360 |
| 6 | 18 | 78 | 45 | 61 | 50 | 25 | 450 | 250 | 350 | 450 | 318 |
| 7 | 14 | < 5 | < 5 | < 5 | < 5 | a | <35 | <35 | <35 | <35 | 29[b] |
| 8 | 350 | 115 | 57 | 158 | 119 | 37 | 33 | 16 | 45 | 33 | 32 |
| 9 | 8.0 | C | 4 | C | C | a | C | 50 | C | C | 50 |
| 10 | 300 | 53 | 84 | 116 | 55 | 38 | 18 | 28 | 39 | 18 | 25 |
| 11 | 325 | 162 | 76 | 53 | 95 | 49 | 50 | 23 | 16 | 29 | 30 |
| 12 | 6.2 | 15 | 13 | 15 | 14 | 7 | 240 | 210 | 240 | 215 | 230 |

a Insufficient data for calculation

b For calculating the average recovery a concentration of 4 ppm was assumed for the monitors marked < 5ppm.

C Sample lost in mail

**TABLE III**

| | RH | FACE VEL. | CONC. | TIME | HALOTHANE | ISOPROPANOL | $CO_2$ | EXP. ERROR | | | | RESULTS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Run | $X_1$ | $X_2$ | $X_3$ | $X_4$ | $X_5$ | $X_6$ | $X_7$ | $X_8$ | $X_9$ | $X_{10}$ | $X_{11}$ | $y$ |
| 1 | + | + | − | + | + | + | − | − | − | + | − | 64 |
| 2 | + | − | + | + | + | − | − | − | + | − | + | 9 |
| 3 | − | + | + | + | − | − | − | + | − | + | + | 18 |
| 4 | + | + | + | − | − | − | + | − | + | + | − | 11 |
| 5 | + | + | − | − | − | + | − | + | + | − | + | 387 |
| 6 | + | − | − | − | + | − | + | + | − | + | + | 424 |
| 7 | − | − | − | + | − | + | + | − | + | + | + | 29 |
| 8 | − | − | + | − | + | + | − | + | + | + | − | 32 |
| 9 | − | + | − | + | + | − | + | + | + | − | − | 50 |
| 10 | + | − | + | + | − | + | + | + | − | − | − | 17 |
| 11 | − | + | + | − | + | + | + | − | − | − | + | 50 |
| 12 | − | − | − | − | − | − | − | − | − | − | − | 242 |
| SUM + | 912 | 580 | 137 | 187 | 629 | 579 | 581 | 928 | 518 | 178 | 917 | $\boxed{[MIN] = 142}$ |
| SUM − | 421 | 753 | 1196 | 1146 | 704 | 754 | 752 | 405 | 815 | 755 | 416 | |
| DIFFERENCE | 491 | -173 | -1059 | -959 | -75 | -175 | -171 | 523 | -297 | -577 | -501 | |
| EFFECT | 82 | -29 | $\boxed{-176}$ | $\boxed{-160}$ | -12 | -29 | -28 | 87 | -50 | 96 | 84 | |

## Table IV

### Box-Behnken Data

| Trial No. | Run No. | Time (hr) | Humidity (% RH) | Chamber Concentration[a] (ppm) | Average Recovery (%) | Relative Standard Deviation (%RSD) |
|---|---|---|---|---|---|---|
| 1 | 1 | 8 | 50 | 296 | 48 | 4.8 |
| 2 | 2 | 1 | 50 | 284 | 174 | 3.9 |
| 3 | 7 | 8 | 50 | 7.5 | 131 | 21 |
| 4 | 8 | 1 | 50 | 7.2 | 722 | 35 |
| 5 | 3 | 4.5 | 80 | 288 | 65 | 45 |
| 6 | 4 | 4.5 | 10 | 301 | 80 | 16 |
| 7 | 14 | 4.5 | 80 | 10 | 263 | 7.9 |
| 8 | 9 | 4.5 | 10 | 5.5 | 321 | 12 |
| 9 | 12 | 8 | 80 | 146 | 91 | 5.1 |
| 10 | 10 | 8 | 10 | 139 | 99 | 6.5 |
| 11 | 13 | 1 | 80 | 139 | 210 | 9.3 |
| 12 | 11 | 1 | 10 | 142 | 192 | 8.3 |
| 13 | 5 | 4.5 | 50 | 158 | 110 | 2.3 |
| 14 | 6 | 4.5 | 50 | 146 | 102 | 15 |
| 15 | 15 | 4.5 | 50 | 152 | 142 | 7.3 |

[a] Determined by air bag analysis

## TABLE V

## PRECISION, ACCURACY AND STORAGE

| NOMINAL CONCENTRATION (ppm) | HUMIDITY (%RH) | MEAN RECOVERY (%) | RSD (%) | STORAGE (days) | ANALYSIS |
|---|---|---|---|---|---|
| 50 | 80 | 95 | 9 | 0 | I |
| | | 45 | 21 | 14 | M |
| 50 | 13 | 94 | 22 | 0 | I |
| | | 60 | 30 | 14* | I |
| | | 42 | 29 | 14 | M |
| 25 | 42 | 100 | 24 | 2 | I |
| 12.5 | 45 | 167 | 10 | 0 | I |
| | | 78 | 20 | 14 | M |

*REFRIGERATED DURING STORAGE

## TABLE VI

## TEMPERATURE EFFECTS ON MONITORS

| TEMPERATURE (°C) | 43.5° ±1° | 23.0° ±0.5° | 15.0° ±1° |
|---|---|---|---|
| SAMPLE MEAN (ppm) | 35 | 22 | 40 |
| STANDARD DEVIATION | 5.2 | 5.3 | 4.0 |
| % RSD | 14.9 | 24.1 | 10.0 |
| AVERAGE BIAS | +6% | 0% | −11% |

**TABLE VII**

## HOSPITAL OPERATORY FIELD SAMPLES

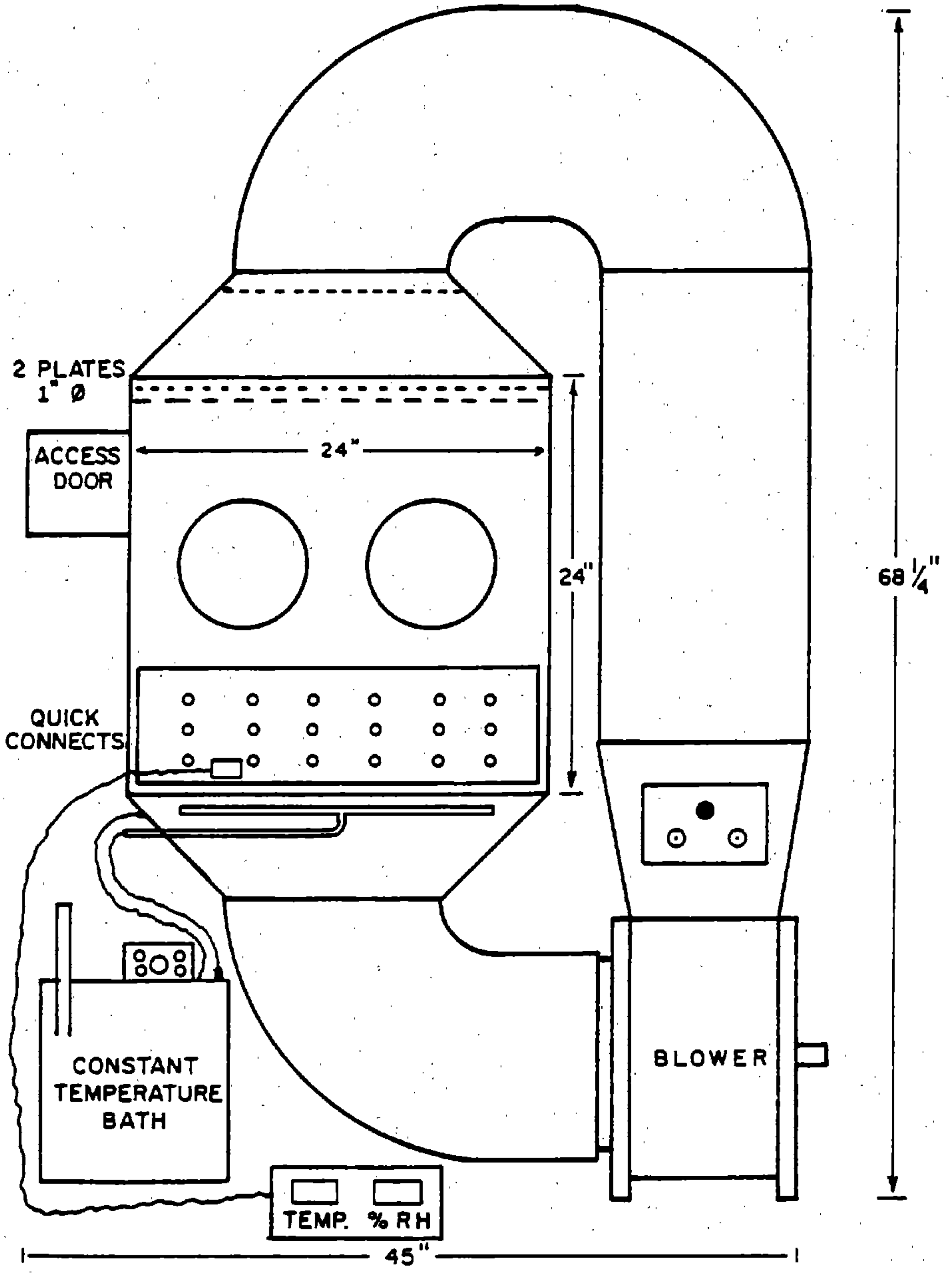
| OPERATING ROOM NO. | SAMPLING TIME | PASSIVE MONITOR | AIR BAGS | RATIO |
|---|---|---|---|---|
| | (hrs) | (ppm) | (ppm) | (M/B) |
| 3 | 4.6 | 10 | 32 | .31 |
| | | 15 | 29 | .52 |
| | | 16 | 32 | .50 |
| 2 | 3.0 | 13 | 20 | .65 |
| | | 10 | 15 | .67 |
| | | 10 | 15 | .67 |
| 5 | 2.3 | 43 | 45 | .96 |
| | | 33 | 26 | 1.3 |
| | | 30 | 30 | 1.0 |

**TABLE VIII**

## DENTAL OFFICE FIELD SAMPLES

| SAMPLING TIME | PASSIVE MONITORS A | PASSIVE MONITORS B | AIR BAG RESULTS | RATIO A | RATIO B |
|---|---|---|---|---|---|
| hrs | ppm | ppm | ppm | M/B | M/B |
| 3.0 | 106 | 96 | 241 | .44 | .40 |
| 2.3 | 169 | 127 | 437 | .39 | .29 |
| 2.8 | 21 | 223 | 296 | .07 | .75 |
| 2.7 | 126 | 68 | 217 | .58 | .31 |
| 2.4 | 73 | 44 | 400 | .18 | .11 |

# EXPOSURE CHAMBER

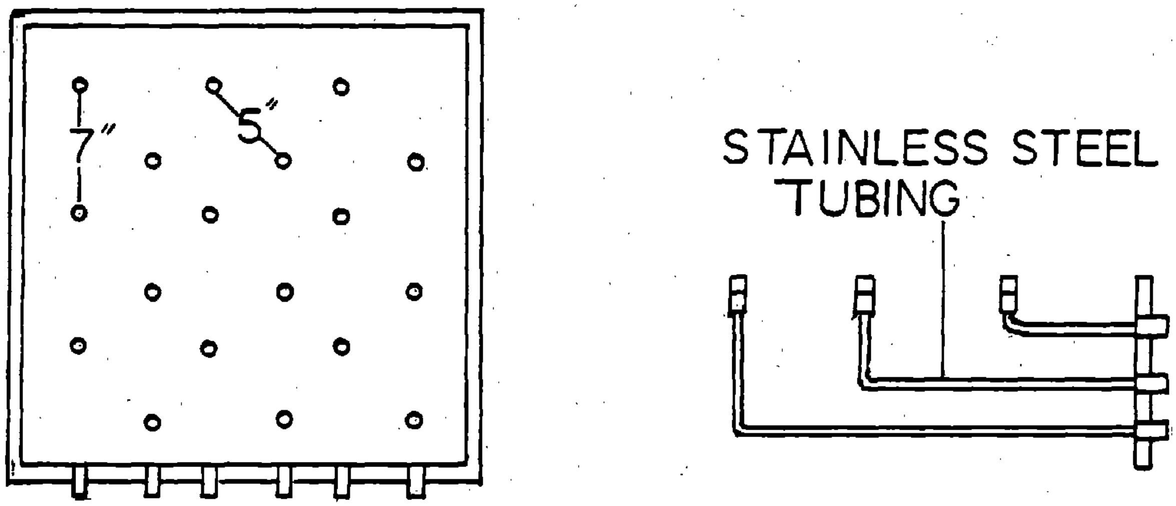


FRONT VIEW

**FIGURE 1**

25

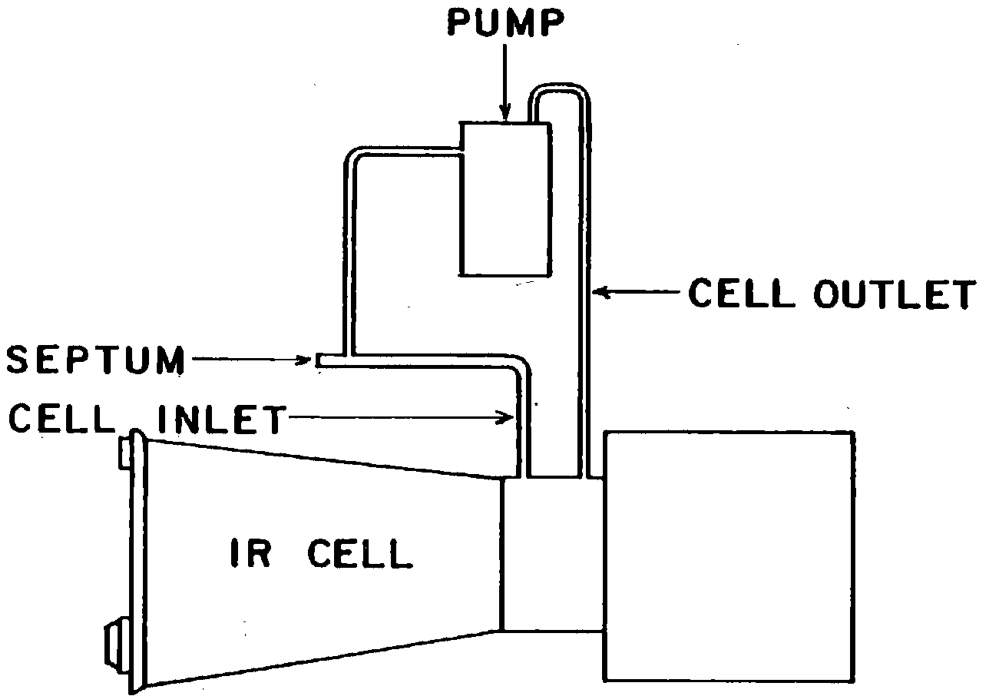
# SAMPLING PORTS



TOP VIEW

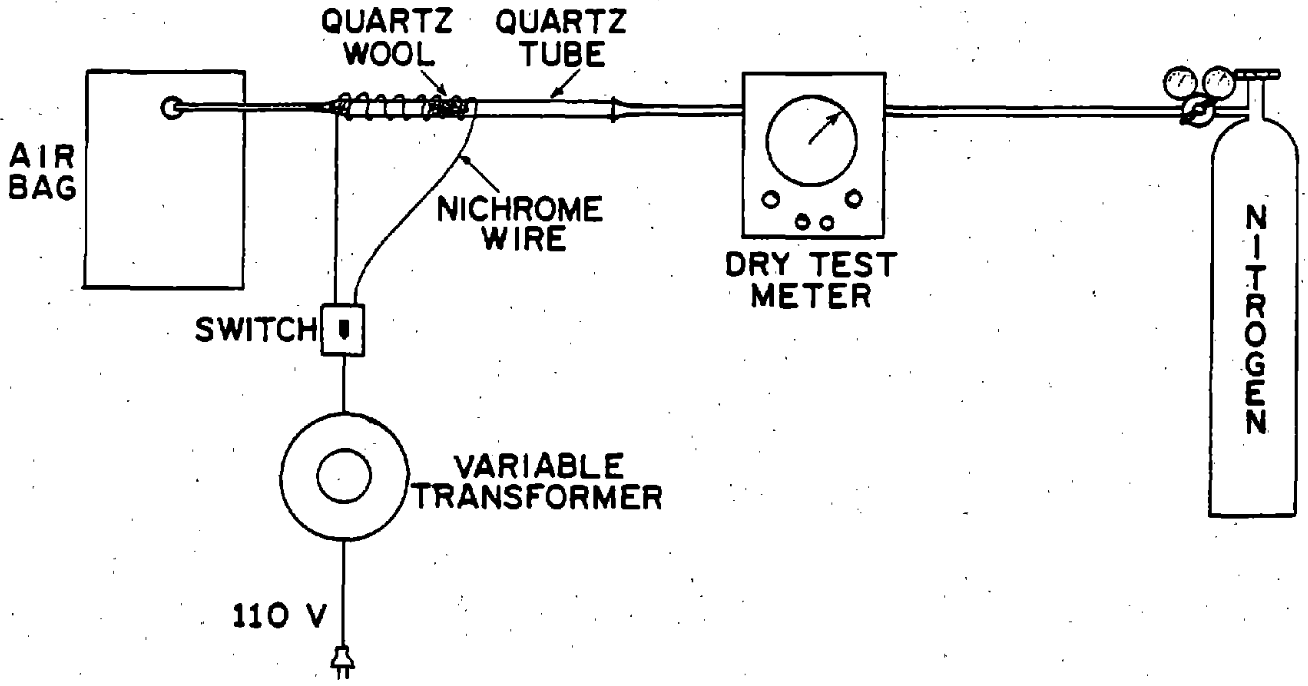
SIDE VIEW

**FIGURE 2**



CLOSED-LOOP CALIBRATION SYSTEM

FIGURE 3



THERMAL DESORPTION UNIT

**FIGURE 4**

# $N_2O$ Monitor

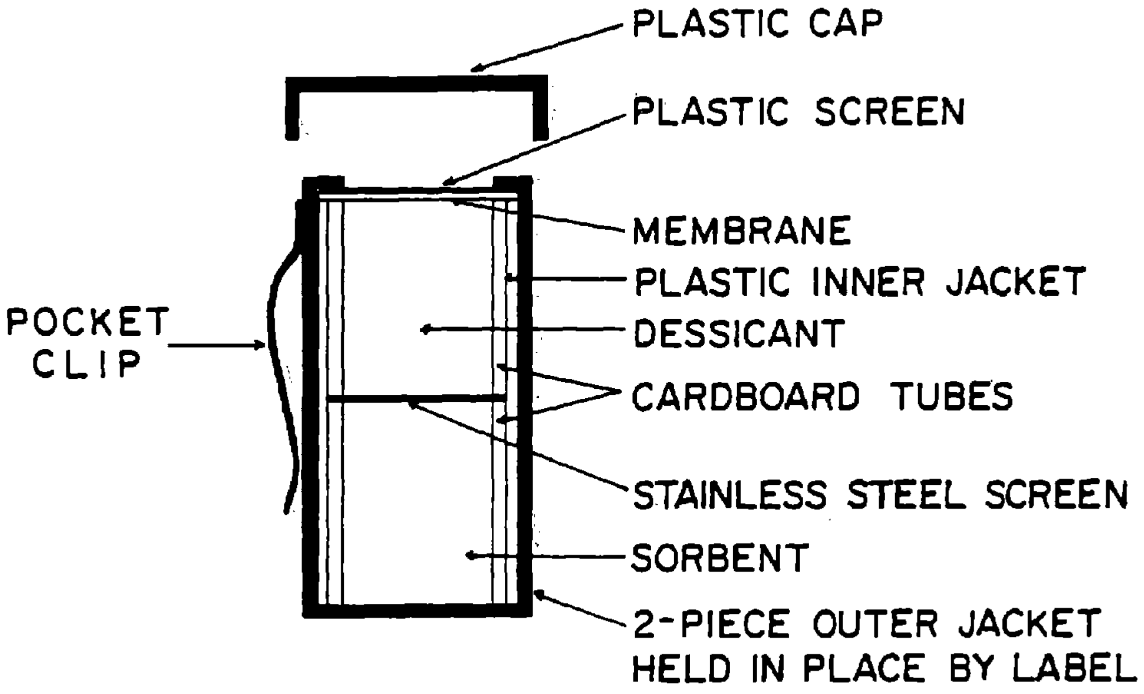


**FIGURE 5**

## FIGURE 6

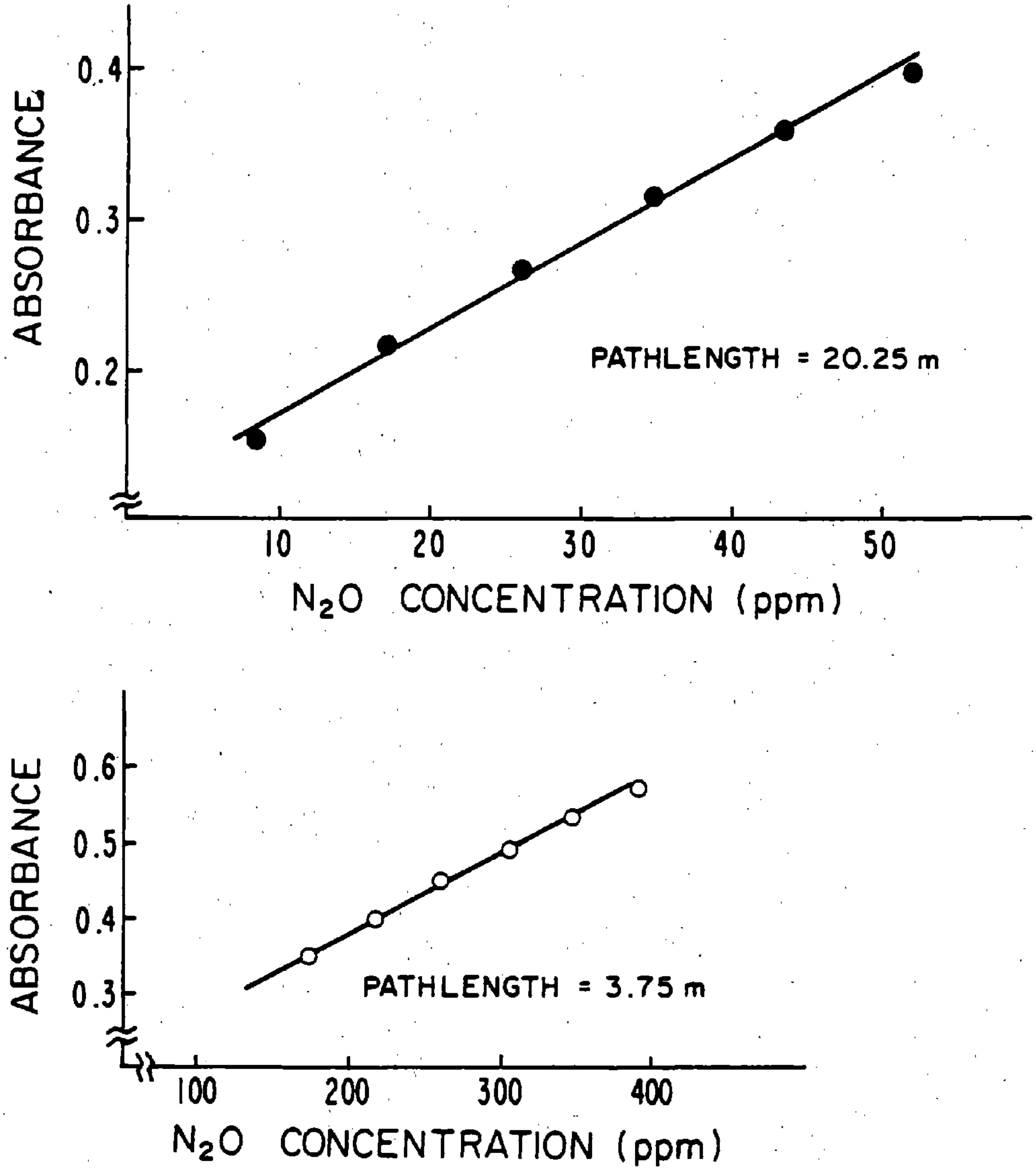
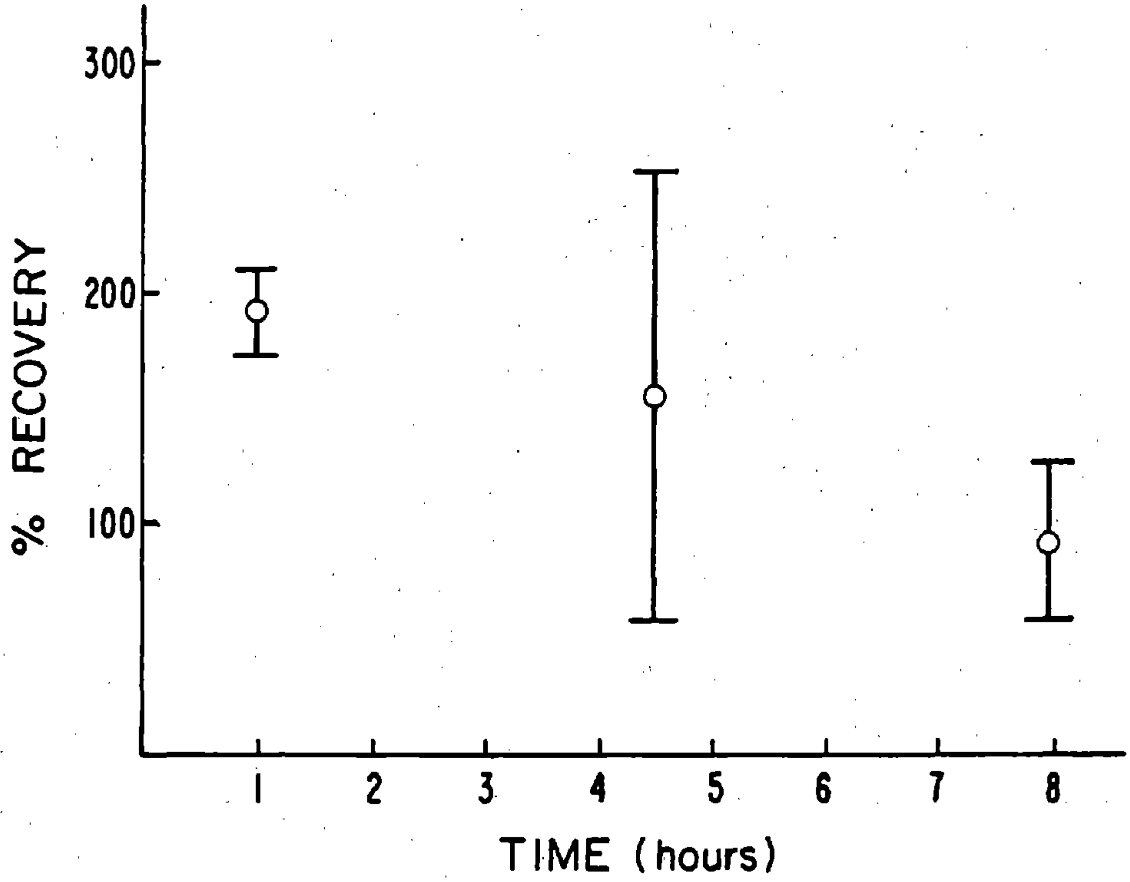
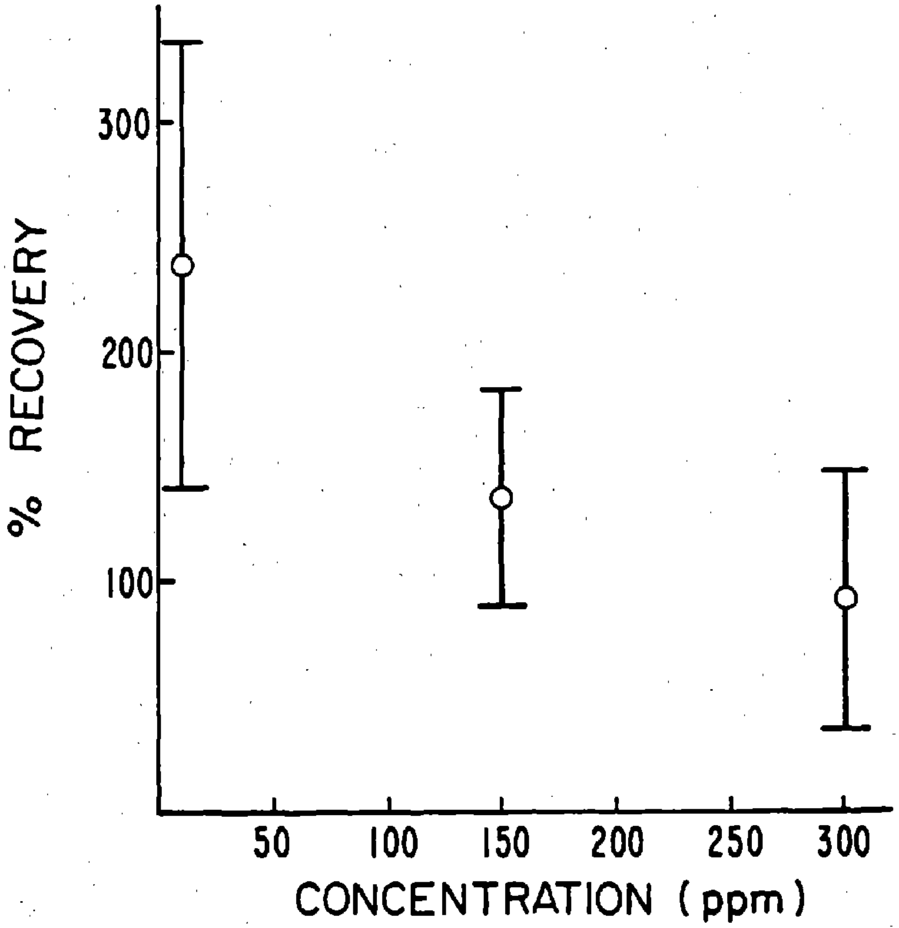

ABSORBANCE
0.4
0.3
0.2
PATHLENGTH = 20.25 m
10
20
30
40
50
$N_2O$ CONCENTRATION (ppm)
ABSORBANCE
0.6
0.5
0.4
0.3
PATHLENGTH = 3.75 m
100
200
300
400
$N_2O$ CONCENTRATION (ppm)

FIGURE 7



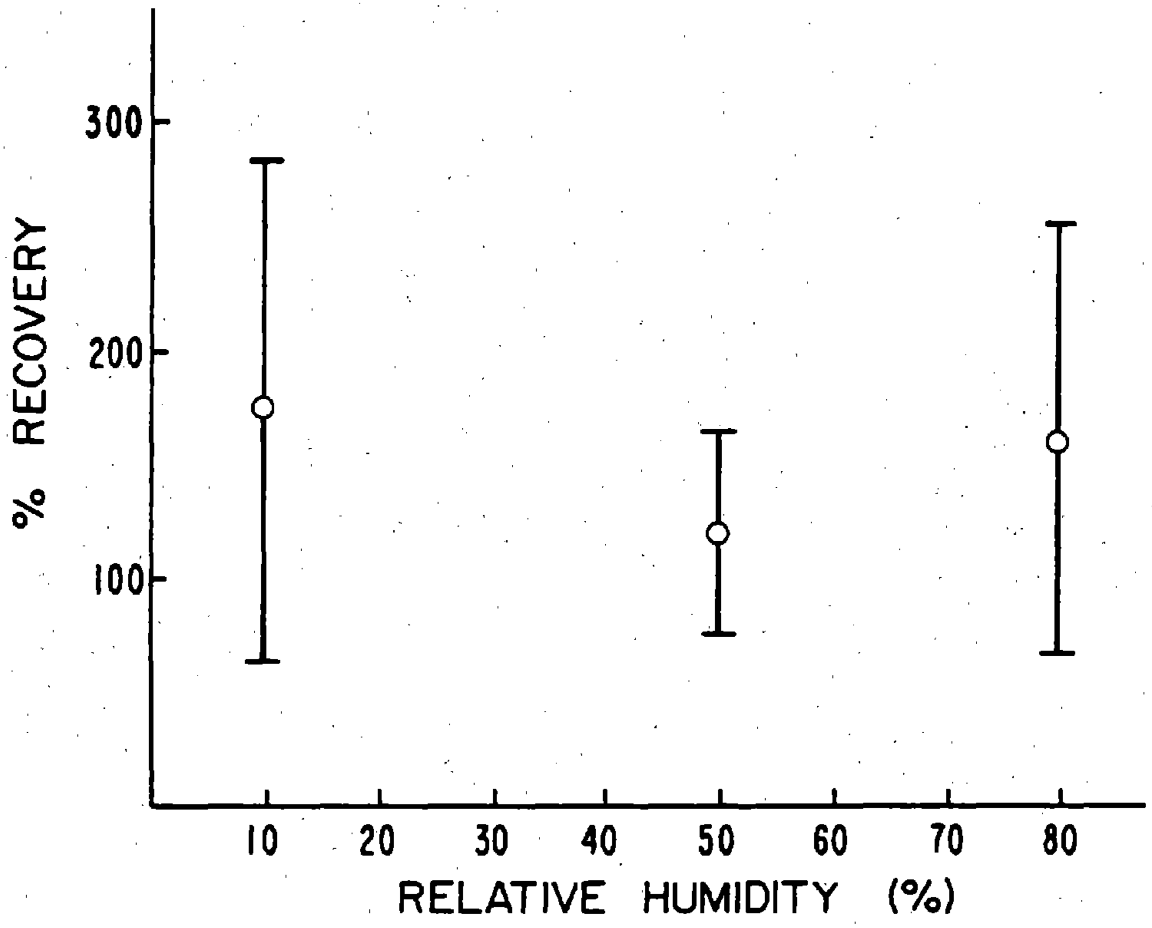
$N_2O$ RECOVERY vs. TIME

FIGURE 8



$N_2O$ RECOVERY vs. CONCENTRATION

FIGURE 9



$N_2O$ RECOVERY vs. RELATIVE HUMIDITY

FIGURE 10

## BOX-BEHNKEN DIAGRAM

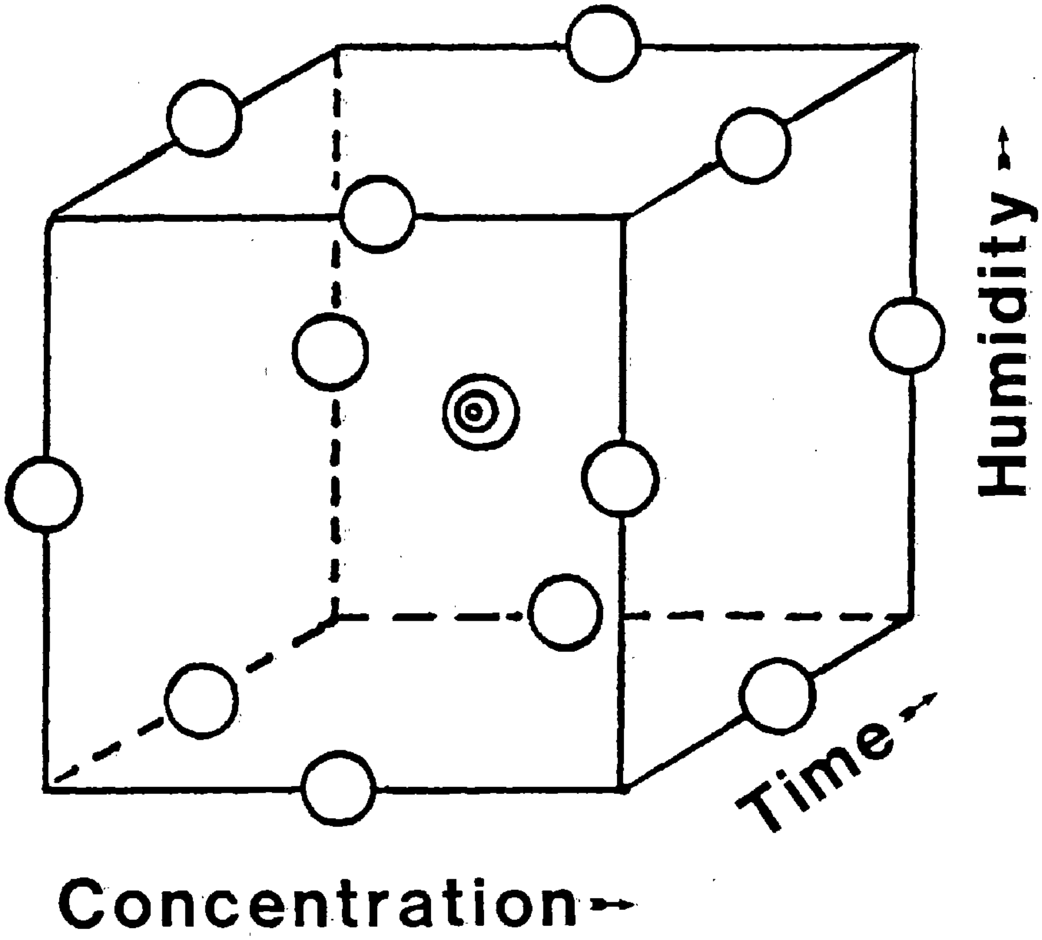
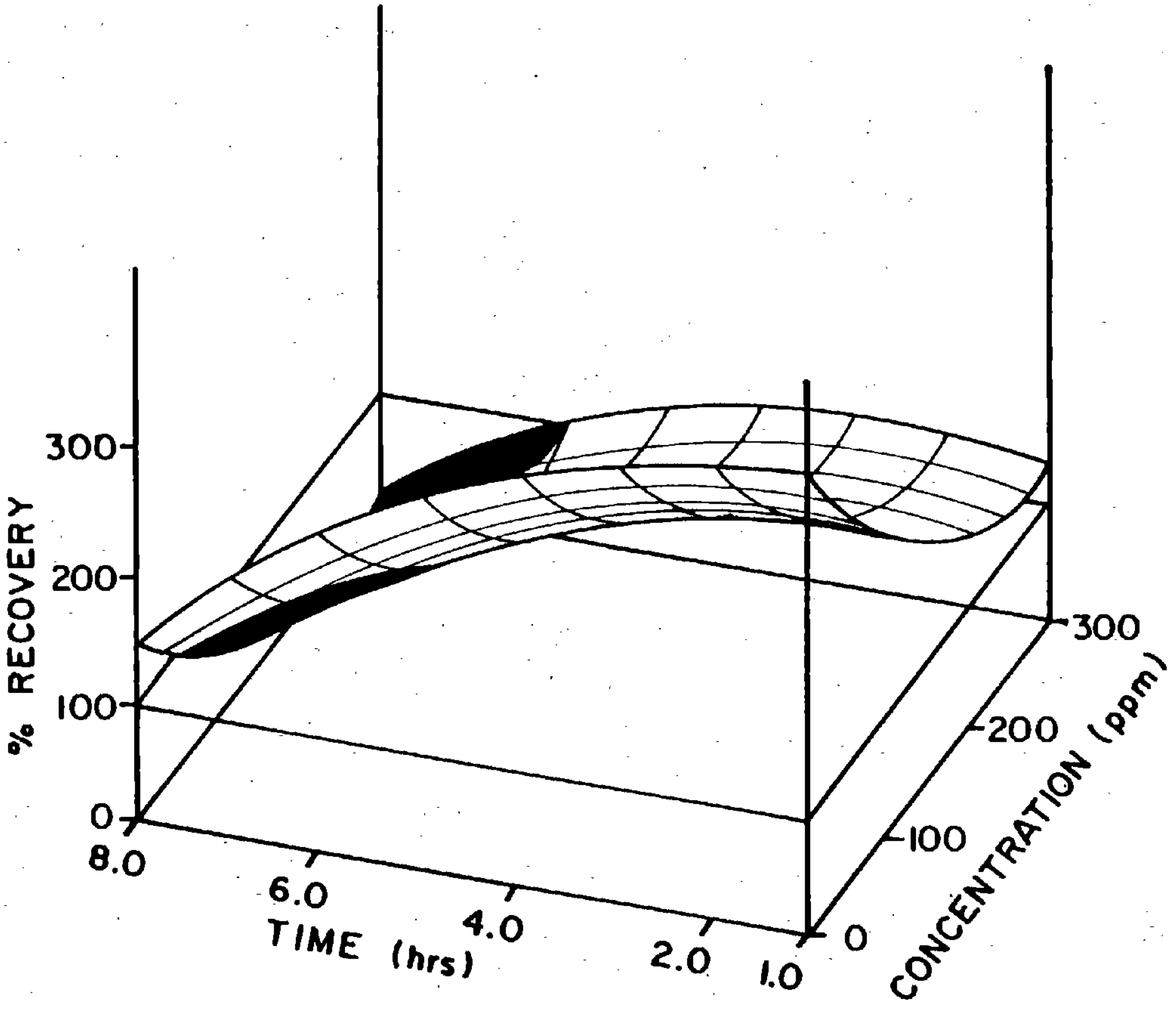
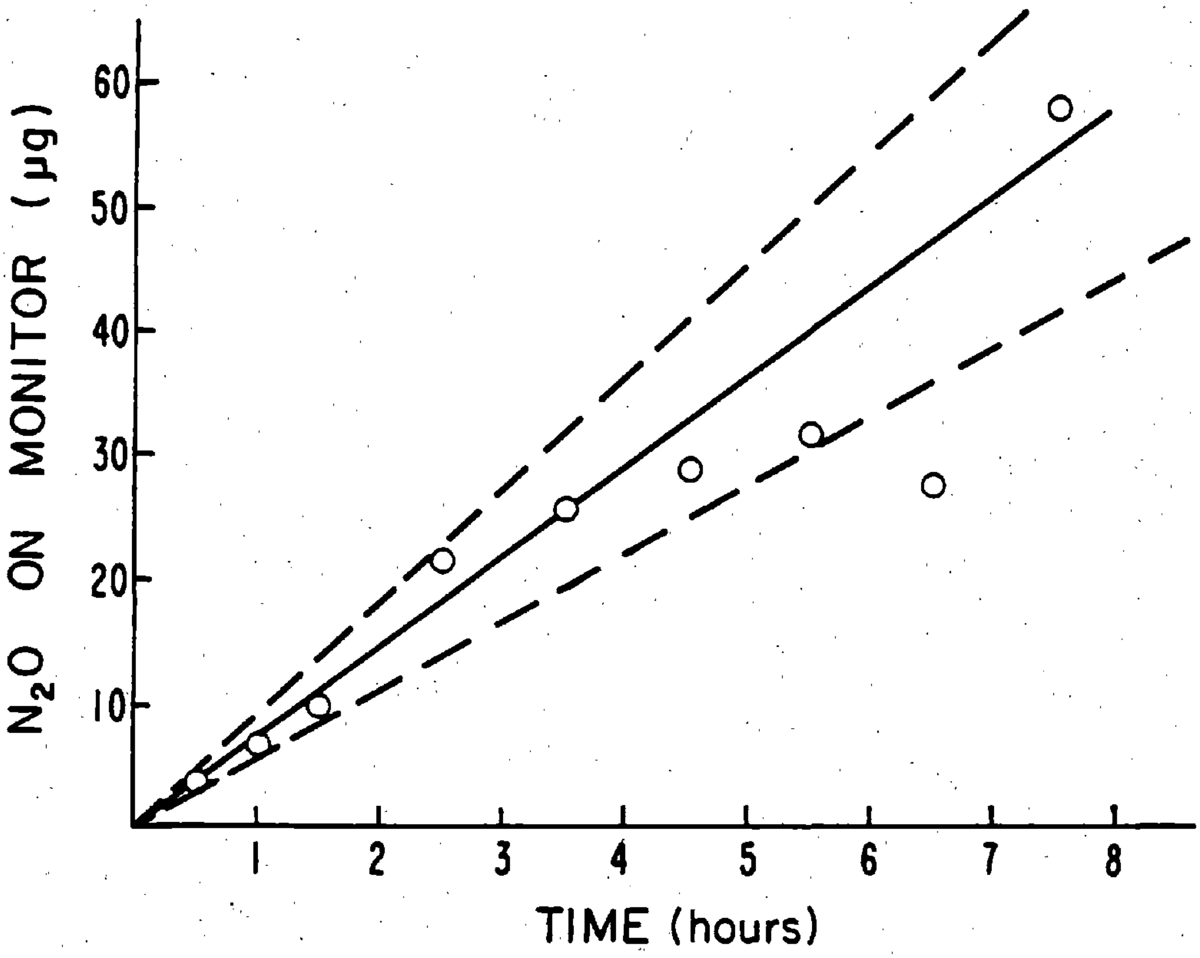


FIGURE 11



MONITOR RESPONSE

FIGURE 12



DOSIMETER UPTAKE

FIGURE 13

## SAMPLING RATE

Calculated from monitors analyzed by NIOSH

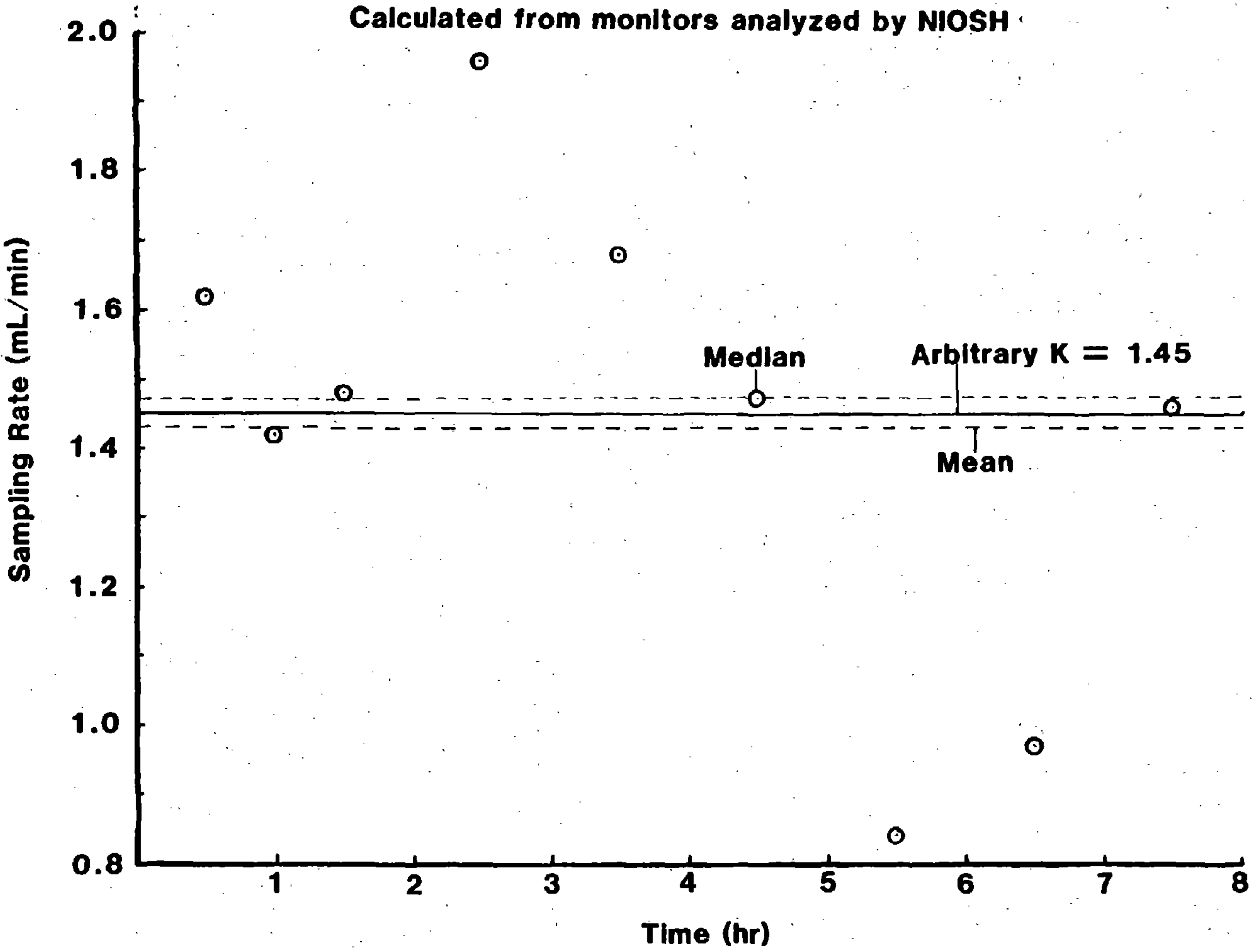
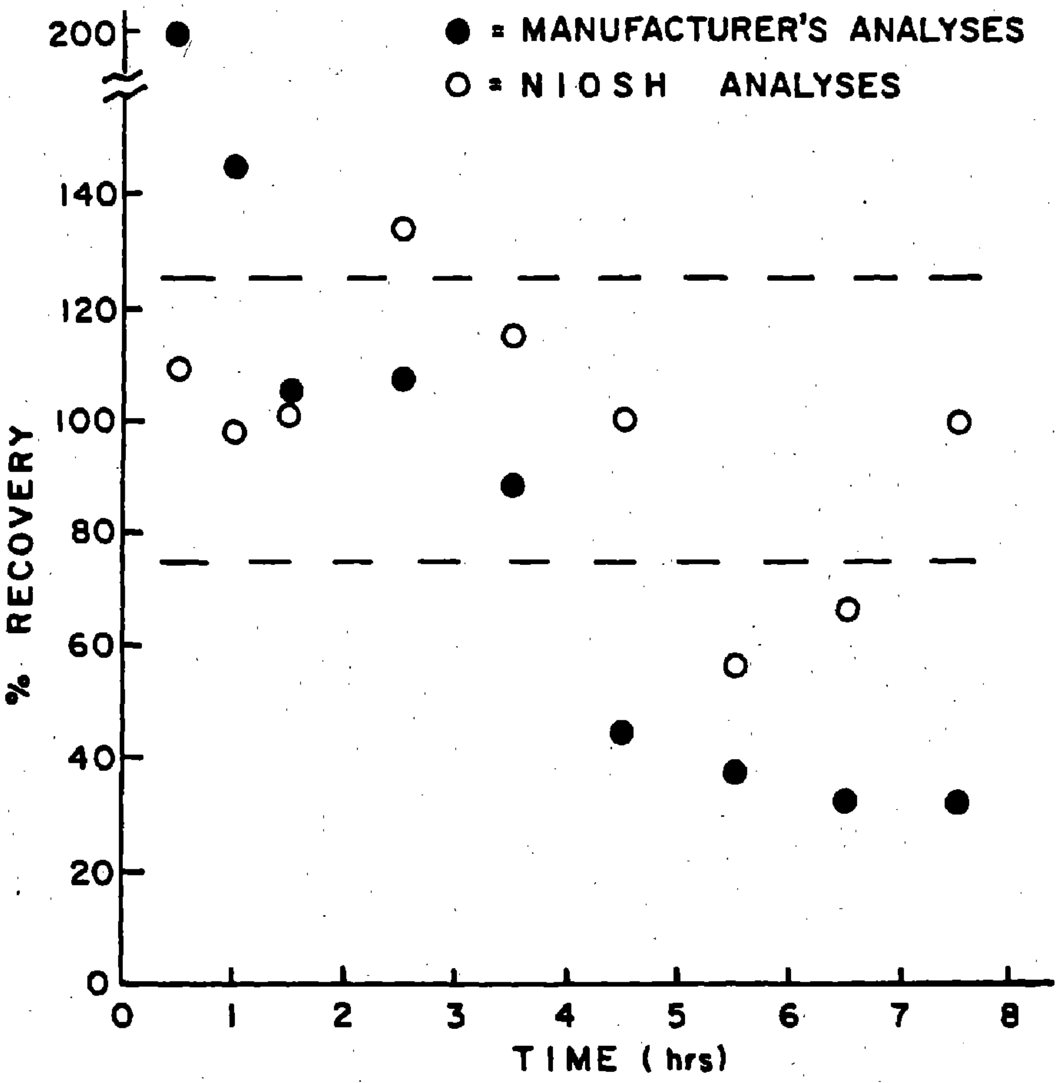


FIGURE 14



RECOVERY FOR VARIOUS EXPOSURE TIMES

FIGURE 15

## HOSPITAL OPERATORY SAMPLES

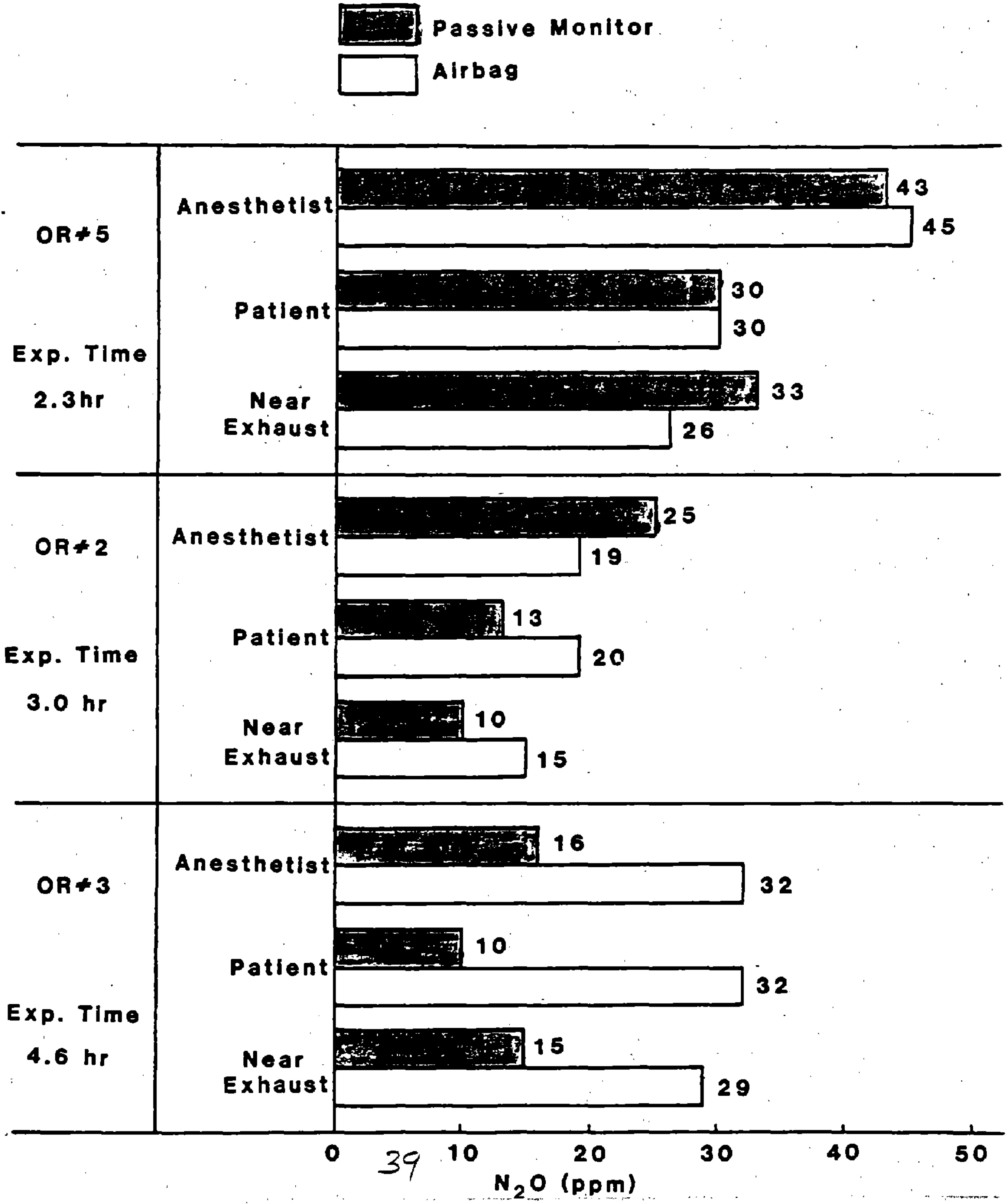


FIGURE 16

DENTAL OFFICE SAMPLES