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A Personal Ammonia Monitor Utilizing Permeation Sampling

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A method has been developed for the determination of the time-weighted-average personal exposure to ammonia. Sample collection was achieved by permeation through a silicone membrane into a boric acid solution. The trapped ammonia was then determined spectrophotometrically with Nessler's reagent or potentiometrically with an ion selective electrode. The device may be used for sampling periods as short as 5 minutes and was not affected by changes in the environmental parameters normally encountered at industrial locations. The detection limit is 0.4 ppm for an 8 hr sampling period and the monitor responds linearly to at least 150 ppm. The Nessler's method may be utilized in industrial environments containing monoethanol amine in conjunction with ammonia with no significant interference. Although some interference was observed from ethylenediamine with the Nessler's technique, little interference was found with the potentiometric determination.

Introduction

The intent of this study was to develop a personal, as well as an area, monitoring system for occupational exposure to ammonia. Although ammonia is not regarded as a problem in ambient air, industrial monitoring of ammonia is of utmost importance due to the effects of chronic exposure at much higher than ambient concentrations. The Threshold Limit Value (TLV) is 25 ppm per 8 hr workday.(1)

Present monitoring of ammonia requires a pump and impinger or bubbler. The method developed here eliminates the need for such bulky equipment by utilizing the permeation sampling approach.(2) Although no consideration is given here for optimal mechanical design, it is seen as a straightforward task to adapt the monitor to a badge configuration that is currently in use.

Permeation occurs in three distinct steps. The gas is dissolved in the membrane material, migrates through the membrane by a permeation process and finally dissolves at the other side of the membrane into an available absorber.(2,3) The ideal absorber is one that completely removes any gas that permeates through the membrane, yet permits release of the sample for final analysis.

Experimental

Preparation and Calibration of Permeation Devices

Permeation tubes which were made and calibrated in this laboratory were used to prepare standard concentrations of ammonia in air. The tubes were made of FEP (tetrafluoroethylene, hexafluoropropylene co-polymer) Teflon® tubes, sealed or stoppered at both ends after being filled with liquefied ammonia.(4,5) A comparison of various techniques for sealing the ends of permeation tubes was conducted. Heat sealed tubes were used for most of this work.(5) The ends of the tubes were heated with a heat gun until the material became transparent, and then collapsed to form the end seals.

The standard air-ammonia mixtures were prepared by passing dry filtered air over the permeation tubes which were maintained at 30.00 ± 0.05 °C. Except for minor changes the equipment was essentially similar to that described by Reiszner.(2) The tubes were calibrated by weight loss.

Humid ammonia air streams were prepared by mixing a humid air stream with the dry standard air-ammonia mixtures in various ratios. The humid air was prepared by passing dry filtered air through two bubblers in series. The first bubbler, containing water, was heated while the second bubbler was maintained at room temperature serving as a condensation trap. Humidity studies were conducted by comparing the "humid" data with the "dry" data, obtained by omitting the water in the bubbler train.(2) The relative humidity was measured with a solid state LiCl probe electrohygrometer, catalogue no. 2200 (Lab Line Instruments, Inc.).

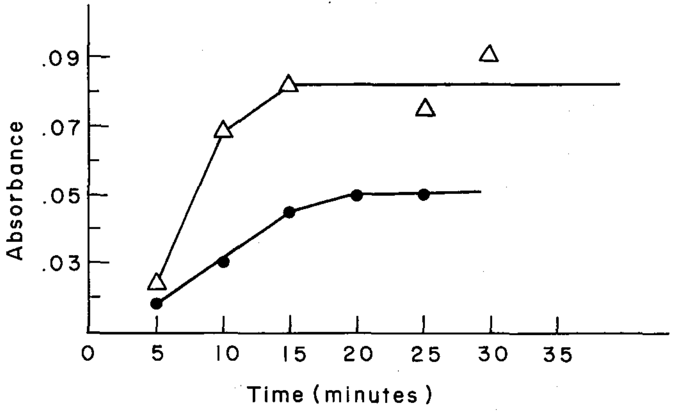

Figure 1 — Lag time response 1 mil GE membrane monitor #1 ●, monitor #2 △. Samples taken at 5 min intervals.

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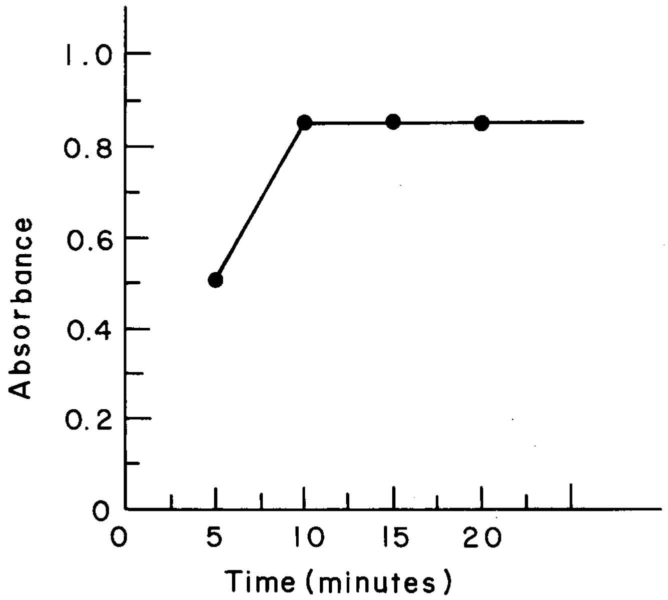

Figure 2 — Lag time response 3 mil sci med. Samples taken at 5 min intervals.

After exposure to a known concentration of ammonia the permeation constant (k) of each device was calculated from the equation,

$$k = \frac{ct}{w}$$

where:

k = permeation constant in ppm-h/μg (typically $\frac{3.3 \text{ ppm-h}}{\mu\text{g-NH}_3}$)
t = exposure time in hours
c = concentration of NH_3 in ppm
w = μg of NH_3 absorbed

The test monitors(2) consisted of a 41 mm OD glass tube sealed at one end with a polymeric membrane and at the other with Saran Wrap. Saran Wrap was chosen instead of a rubber stopper, because erratic data indicated that the stoppers were absorbing ammonia from the airstream or that they contained ammonia naturally and were emitting it sporadically.

The membranes were: (1) single backed (General Electric, Schenectady, N.Y.), (2) a silicone polycarbonate MEM 213 membrane (General Electric), and the vinyl silicone membranes, (3) standard knit fabric supported membrane loops down, (4) standard knit fabric membrane loops up, (5) 5 mil unsupported membrane, (6) 2.7 mil unsupported membrane and (7) a woven fabric 3.5 mil supported membrane, (Sci-Med Life Systems, Minneapolis, Minnesota.).

Reagents

Nessler's Reagent

Nessler's reagent was prepred by dissolving 50 g of HgI_2 and 35 g of KI in a small quantity of NH_3-free water and adding this slowly to a cool solution of 80 g NaOH in 500 mL of NH_3-free water. The solution was then diluted to 1 L and stored in a stoppered brown bottle.

Boric Acid Solution

This solution was prepared by dissolving 3.0 g of boric acid in a small quantity of water and diluting to 500 mL.

Standard Ammonia Solution

A concentration of 1000 ppm NH_3 was prepared by dissolving 0.3141 g of ammonium chloride in water and diluting to 100 mL.

Analytic Procedure

The analytic procedure was identical to that used for the calibration of the permeation monitoring devices. This consisted of adding 10 mL of boric acid to the permeation monitor which was then placed in the exposure chamber for a pre-determined time interval. After exposure, the device was removed from the chamber and allowed to stand for 2-3 minutes to permit the ammonia remaining in the membrane matrix to be absorbed in the boric acid. After transferring the solution to a 25 mL Erlenmeyer flask, 1 mL of Nessler's reagent was added, the mixture was stirred and the absorbance measured at 430 nanometers after five minutes. The concentration was determined from a calibration curve previously prepared from a serial dilution of an ammonium chloride standard solution with the boric acid absorbing solution. The calibration curve was linear up to at least 11 μg/mL in the boric acid absorber with a detection limit of 0.1 μg/mL at the 95% confidence level with a slope of 9.0 absorbance units per μg/mL. Samples that were expected to exceed the upper range of the analytic procedure were diluted with absorber.

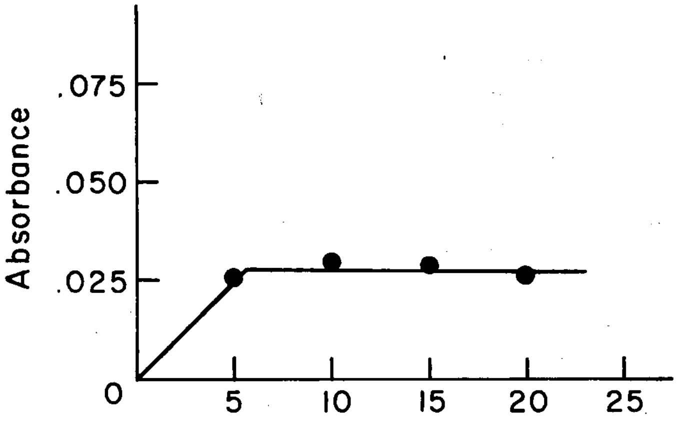

Figure 3 — Lag time compensation.

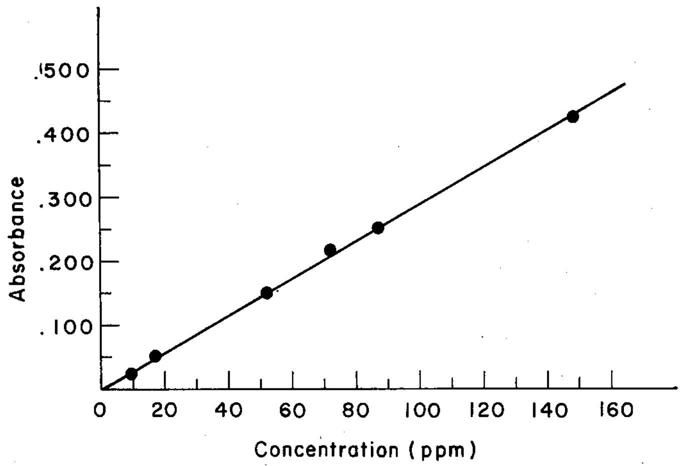

Figure 4 — Effect of varying concentration.

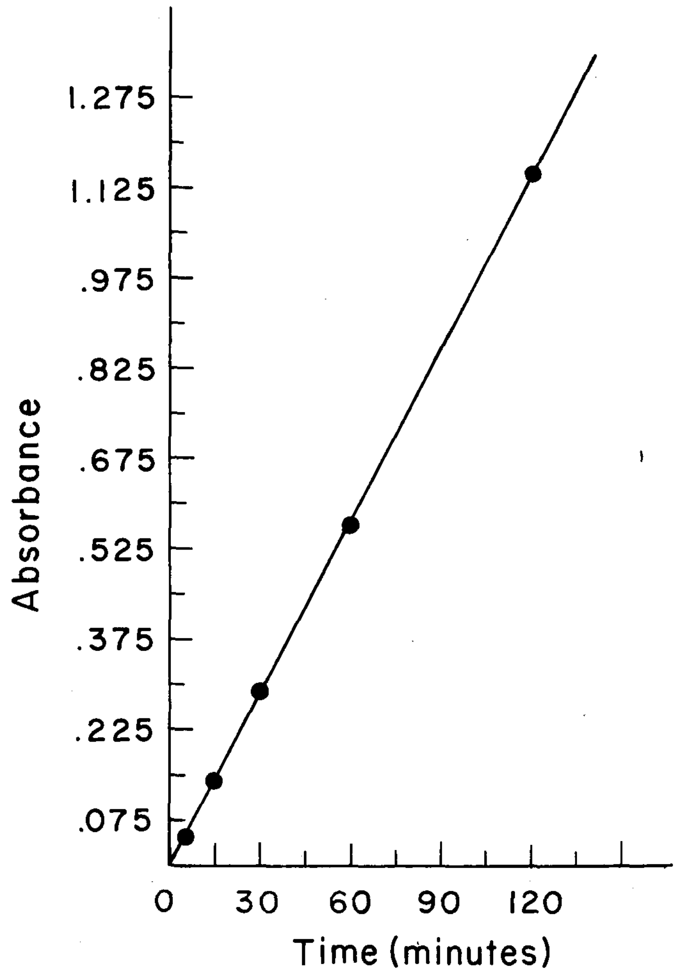

Figure 5 — Effect of varying time at high concentration.

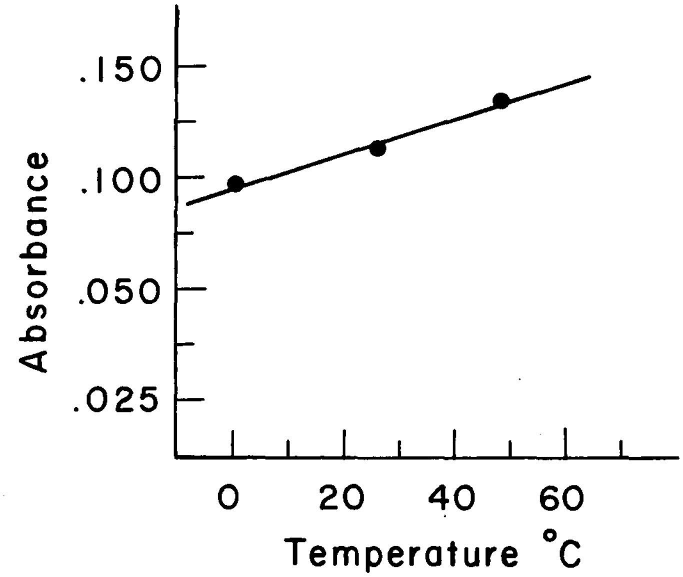

Figure 6 — Effect of temperature on permeation rate.

Alternatively, an Orion ammonia ion selective electrode was placed in the sample solution, and one mL of 10 M NaOH was added to adjust to the proper pH. The millivolt reading was recorded and the sample concentration was determined from a calibration curve prepared with standards containing 1 ppm, 10 ppm and 100 ppm of ammonia in boric acid.

Results and Discussion

An absorber containing a glycerine-water mixture was examined initially in an attempt to lower the freezing point of the absorber. However, the solution reacted with the Nessler's reagent to form an opaque solution making spectrophotometric analysis impossible. In the subsequent search for a useful absorber, dilute hydrochloric, nitric, sulfuric and boric acids and de-ionized water were investigated. The initial comparison was made by connecting two bubblers in series. A standard ammonia airstream was passed through the bubblers containing the particular solution to be investigated after which a 10 mL aliquot was removed from each bubbler and analyzed, and the relative efficiency calculated. The simplifying assumption that no ammonia passed through the second bubbler was made for convenience because only strong absorbers were being sought.

Although most of the absorbers worked well, boric acid was chosen because it displayed high collection efficiency, it was compatible with the test monitors and it would present no hazard to the employee if breakage or spillage occurred. A collection efficiency of 99.5% was found when as much as 50 μg/mL ammonia was absorbed from an airstream containing 23.9 ppm ammonia.

In initial studies a GE 1 mil dimethyl-silicone membrane was utilized. However, its use was discontinued because problems were encountered due to erratic response, a long response time and atypical permeation response. The behavior of this membrane was presumably due to the interaction of ammonia with the polyester backing material rather than to characteristics of the membrane itself (Figure 1). At this point a comparison study was conducted with vinyl silicone membranes and the silicone polycarbonate membrane. The membrane chosen for final study was a 3 mil loops-up knit-backed supported membrane because it was mechanically stronger and different portions of the sample sheet gave similar permeation rates. All materials exhibited significant permeation rates. The lag time due to the thickness of the membrane is shown in Figure 2. A response of 100% of theoretical was obtained for these short exposures when the monitors were allowed to stand for 2-3 minutes after removal from the exposure chamber before transferring the absorbing solution for analysis (Figure 3). This did not eliminate the lag time response, it simply allowed ammonia already in the membrane to pass into the absorbing reagent.

The limit of detection for the monitor was of considerable importance since it was desirable to have a monitor that would function at low concentrations of ammonia as well as high concentrations. The linearity of the monitor was demonstrated by exposing the monitor to concentrations ranging from 10 to 150 ppm for a set time interval (Figure 4). The linearity was further tested by exposing the monitor to 210 ppm for various time intervals (Figure 5). Both of the studies confirmed the expected linear response of the monitor. The detection limit at the 95% confidence level was 0.4 ppm for 8 hr (3.2 ppm-hr) and the precision was better than 5% at

TABLE I
Relative Interference of Monoethanolamine[A]
(Percent)

Ammonia Added	2.5 μg	10 μg	20 μg	50 μg
I. 506 μg Monoethanolamine added				
A. Spectro. Analysis	+8	+5	0	+2
B. Ion Sel. El. Analysis	+8	+13	+5	+9
II. 2024 μg Monoethanolamine added				
A. Spectro. Analysis	+2	+2	+7	+4
B. Ion Sel. El. Analysis	+61	+36	+21	+28

[A]All amounts were in a total sample volume of 11 milliliters.

the 95% confidence level. The monitor should be suitable for area as well as personal monitoring with such a broad linear range.

The next phase was a study of environmental parameters that might adversely affect the performance of the monitor. Particular attention was given to temperature, sunlight and humidity, because large variations in the magnitude of these parameters can occur during normal sampling. The monitor was found to exhibit a slight increase in collection rate as the temperature was increased (Figure 6). The increase of 0.57% per °C increase in temperature can be considered to be essentially negligible for normal sampling requirements. The sample solutions were allowed to come to room temperature before beginning the analyses.

Humidity studies were conducted at 20%, 50%, 70% and 95% relative humidity and compared to 0% relative humidity "dry" exposures (see experimental). The maximum deviation between a "wet" and "dry" run was 4%.

The stability of the absorbed ammonia was determined by exposing a solution of known concentration to various environmental conditions. The solution was exposed to direct sunlight for 13.5 hr over a two-day interval. The absorbance value obtained for a 10 mL aliquot was identical to that of the unexposed solution indicating that no decomposition of the absorbed ammonia occurred with exposure to intense sunlight.

The stability was studied further by placing the solution of known concentration in a 40 °C temperature bath for a 10-day interval. The absorbance value obtained was essentially the same as the value obtained initially. A solution of the same concentration as above was also allowed to stand at room temperature for a 30-day interval. The absorbance of 10 mL aliquots was measured at pre-selected time intervals. The value obtained initially and those obtained during the 30-day interval.

Although there are numerous potential interfering substances, particularly amines that could be studied, the number is so large that it would be impractical to attempt a comprehensive study. Two substances which have been studied in the past are monoethanolamine and ethylenediamine.(6) The TLV is 3 ppm for monoethanolamine and 10 ppm for ethylenediamine.(1) When the monitors were exposed to concentrations several times these levels for the respective interferences alone, they appeared to permeate the membrane. Because quantitative preparation of standard gas mixtures of these two pollutants was difficult, spiked solutions were used assuming the k value of monoethanolamine and ethylenediamine to be approximately the same as that for ammonia. Exposure to monoethanolamine at the maximum of 3 ppm for an 8 hr day would represent an absorption of 0.90 μg and exposure to ethylenediamine at the maximum of 10 ppm for an 8 hr day would correspond to 30.3 μg of material absorbed in solution. The spiked samples used in these studies contained as much as 100 times the amount that would be expected to be absorbed in 8 hr at the maximum allowable concentrations. Therefore, any difficulties with the analysis procedure would be expected to show up under these conditions that grossly exceed the recommended standards.

Solutions containing from 2.5 μg to 50 μg ammonia and either 506 or 2024 μg monoethanolamine or 900 to 3600 μg ethylenediamine per 11 mL were used to determine the relative extent of the interference. As seen in Table I, the average deviation for the colorimetric procedure for monoethanolamine was between 0 and 8% as opposed to between 4-61% deviation in the ion selective electrode method. Therefore, the Nessler's method may be utilized in environments where ammonia and monoethanolamine both exist. Ethylenediamine prohibits the analysis of ammonia solutions colorimetrically due to the formation of a milky solution with Nessler's reagent. The deviations (Table II) were generally small and acceptable for industrial monitoring when the ion selective electrode technique is used.

Conclusions

The ammonia monitor developed here responds linearly and is not affected by environmental factors that are normally encountered at industrial locations. The monitor is relatively free of interference from amines. Environments containing monoethanolamine can be monitored utilizing the Nessler's method as described in this study. Although the Nessler's method cannot be utilized for solutions containing ethylenediamine, these can be measured by ion selective elec-

TABLE II
Relative Interference of Ethylenediamine[A]
with Ion Selective Electrode Technique
(Percent)

Ammonia Added	2.5 μg	10 μg	20 μg	50 μg
900 μg Ethylenediamine added	+59	+2	+18	+4
1800 μg Ethylenediamine added	+80	+25	+16	+5
3600 μg Ethylenediamine added	+127	+28	+23	+17

[A]All amounts were in a total sample volume of 11 milliliters.

trode technique. The monitor operates passively and can be used as a badge-type device which is very light-weight and compact. In addition, the results obtained with it are accurate, reliable and reproducible. It is relatively inexpensive to use for occupational monitoring.

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