V. The less volatile components of both mixtures were found to be trapped with more than twice the efficiencies of the more volatile components. At 225 L/min, collection efficiencies ranged from 41% to 95% for Aroclor 1242 and 37% to 90% for Halowax 1001, averaging 75% (for 15 independent determinations) and 57% (for 8 determinations), respectively.

During the course of these studies, weather conditions varied widely. Sampling was conducted in temperatures ranging from −18 °C to +30 °C and during periods of rain and snow, as well as dry, windy conditions. A survey of the data collected shows no measurable effect of weather on sampling efficiency.

CONCLUSIONS

It is apparent from these studies that while polyether-type polyurethane foam is an efficient high-volume air sampling medium for low levels of chlorinated pesticides and polychlorinated biphenyls of low volatility, it is inadequate or only marginally adequate for 24-h sampling of the more volatile members of these families. The greater polarities of organophosphate pesticides assist in their collection, so that acceptable trapping efficiencies (75%) are feasible for many of these compounds despite their higher vapor pressures. The use of tandem traps does not always improve trapping efficiency, despite logical expectations. This latter finding points out the potential fallacy in using "break-through" data (penetration to a secondary trap) for estimation of sampling efficiencies.

In this case, as for all environmental monitoring, the difficulties inherent in the use of nonspecific GC detectors (such as the ECD) to identify and quantify organic compounds are obvious. A considerable advantage in using the high volume sampler for ambient air monitoring, however, is derived from the fact that sufficient quantities of compounds may be collected to permit unambiguous GC/MS confirmation of results for a single sample.

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Stable Free Radical Reagent and Solid Phase Suitable for a Nitric Oxide Dosimeter

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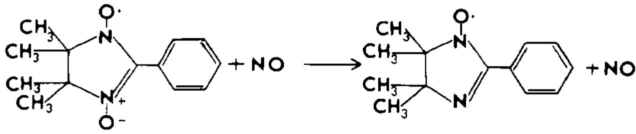
A new reagent combined with a solid phase support has been developed as a system for a nitric oxide dosimeter. The free radical reagent, 2-phenyl-4,4,5,5-tetramethylimidazoline 3-oxide 1-oxyl is applied in chloroform solution to silica gel plates. Reaction with nitric oxide produces a second stable radical which may be quantified by ESR. Plates were exposed to 0.05–1.00 ppm nitric oxide in nitrogen for 1 h inside a 1000-L non-rigid chamber. Commonly occurring ambient gases showed no serious interferences. Sufficient sensitivity remains to allow the incorporation of a membrane for the purpose of buffering mass transfer effects due to wind velocity.

In the early 1950's, it was demonstrated that oxides of nitrogen together with hydrocarbons were the prime ingredients for photochemical smog formation (*1*, *2*). This knowledge focused attention on nitric oxide and nitrogen dioxide. In 1954 Saltzman published a wet chemical technique for the colorimetric determination of nitrogen dioxide (*3*) and later the reagent was modified for recording air analyzers (*4*). The method was extended to the determination of nitric oxide by the use of permanganate as oxidant (*5*). Recently, chemiluminescence methods for the two oxides have been widely adopted.

In our studies we had need of an analytical system which would allow simultaneous measurement of time weighted concentrations of ambient nitric oxide at several locations. We were also mindful of the interest in occupational health and dosimeters and thus directed our efforts toward a system which might serve as a dosimeter. Solid phase systems are obviously attractive for small collectors or monitors. During the progress of this work we became aware of the activated charcoal collector for vinyl chloride described by West (*6*) and the general dosimeter design described by Tompkins and Goldsmith (*7*) in which the reaction/collector phase was not disclosed. A membrane and air gap, respectively, are used in the above methods to buffer mass transfer effects produced by air flow over the sampler.

Reagent. An analytical system, which employs reaction rather than collection on a solid phase, obviously requires a sensitive reagent. We considered organic stable free radicals as possible reagents. Electron spin resonance (ESR) instruments are capable of detecting concentrations as low as 10^{-9} M with respect to paramagnetic species in solvents with low dielectric loss, and therefore free radicals offer a high sensitivity. A method for the determination of morphine in biological fluids using free radicals is already available (*8*). It makes use of the rapid equilibrium between morphine and a radical labeled morphine molecule bound to its antibody.

The first nitronyl nitroxide radical structure **1**, was isolated in 1967 (*9*) and others, in which the phenyl group was replaced by other functional groups, were prepared later (*10*). Nitronyl nitroxides react with nitric oxide (*11*) to yield imino nitroxides (Equation 1).



(1)

[1] [2]

This reaction proceeds with a color change but the extinction coefficients for the visible absorptions of the nitronyl and imino nitroxides are low. In the specific case shown in Equation 1, the color change is from blue to yellow-brown. The fate of the nitrogen dioxide is not known, although silica gel which is used as the reagent support is known to adsorb it quite strongly.

Compound 1 was chosen as the reagent because it is one of the most stable nitronyl nitroxides. In the reaction shown, the radical π system reacts and the organic product is another radical. However, there is no reason why a spin labeled reagent should not react at a position remote from the radical site to yield a new spin labeled product. The electron spin resonance (ESR) spectrum of compound 1 consists of a five-line pattern with first derivative peak height ratios of 1:2:3:2:1, and compound 2 has a seven-line pattern with corresponding ratios of 1:1:2:1:2:1:1 as shown in Figure 1. Calibration curves for solutions of reagent and product in *p*-dioxane were obtained, the height of the largest first derivative peak being measured in each spectrum. The calibration curves were linear in the concentration range of interest, i.e., 0–10^{-5} M. The measurement of the first derivative peak height is justified when peak widths and shapes are unaffected by concentration. The system described here incorporates a separation of reagent and product, and the ESR splitting patterns allow both identification of the product and verification that complete separation has been achieved. The reagent, **1**, may be synthesized (*10*) and a modified procedure for its production from 2,3-bis(hydroxylamino)-2,3-dimethylbutane sulfate (commercially available from Eastman Kodak), is given at the end of the Experimental section.

Solid Phase Support. Silica gel on a flexible polyester backing was chosen as the solid support. This was in the form of Eastman Kodak 6061 silica gel plates containing a polyvinyl alcohol binder. (Eastman Kodak has now changed the binder on the 6061 silica gel plates to polyacrylic acid. This results in a very small, but detectable, increase in plate response, and is presumably caused by a slight increase in reagent spot size.) The silica gel thickness is quoted by the manufacturer as 100 μm and electron micrographs of the plates revealed irregular particles with no dimension greater than 20 μm. Most particles were considerably smaller than this. The surface loading of the silica gel on the plates was 0.036 g cm^{-2}. The internal surface area of silica gel is known to be approximately 800 m^2g^{-1} and this facilitates the interaction of the reagent and the nitric oxide within the pores. The silica gel also allows the separation of the reagent and the product by thin-layer chromatography.

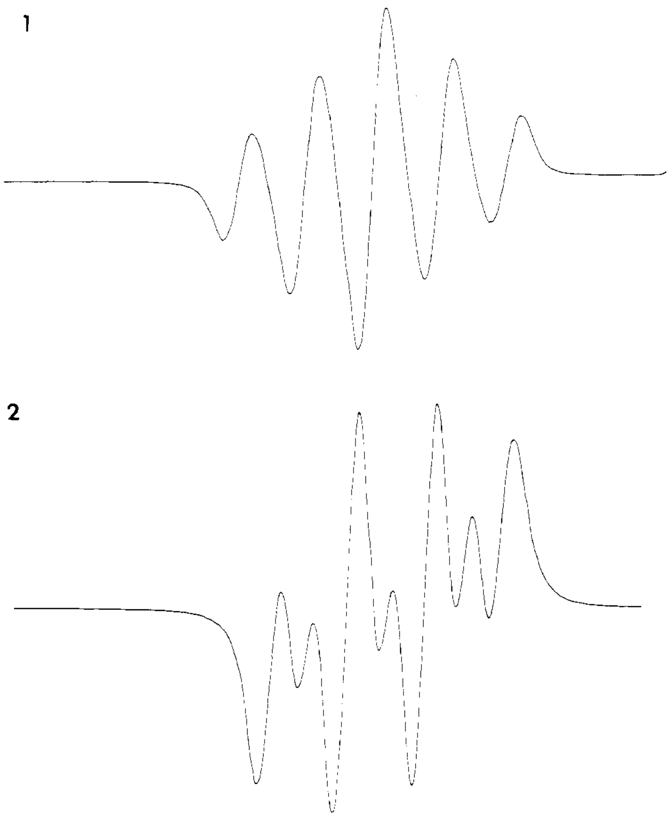


Figure 1. ESR spectra of nitronyl nitroxide **1**, upper spectrum, and imino nitroxide **2**, lower spectrum

EXPERIMENTAL

Silica gel plates, 8 cm × 2 cm were cut from the 20 cm × 20 cm commercially available sheets (Eastman Kodak 6061). At 1 cm from the end of each plate and equidistant from each edge, 10 μL of a chloroform solution of compound 1 (6.28×10^{-2} M) was spotted. The spot was applied by holding the micropipet (10 μL, Clay-Adams) vertically, touching the lower end on the silica gel and allowing the solution to drain and spread with concomitant evaporation of solvent. The spots so produced were approximately 0.9 cm in diameter. The plates were then exposed for 1 h to nitric oxide (0.05–1.00 ppm) in nitrogen. The gas mixtures were contained in a flexible walled chamber which was approximately a cube with one meter sides. This chamber which had glass end plates and 0.0005-in. polyester film walls has been used successfully for the study of photochemical smog forming reactions (*12*). The plates, suspended on fine threads were introduced into the chamber through a zip lock seal. The determinations of nitric oxide and nitrogen dioxide in the chamber were made during the first and last 20 min of the exposure period. The gas sample was passed successively through two Saltzman fritted bubblers, a permanganate impinger, a Saltzman bubbler, a permanganate impinger, and a Saltzman bubbler. The gas flow rate was 0.34 L/min. Fifteen minutes were allowed for full color development of the azo dye and then the absorbance of each Saltzman reagent solution was measured at 550 nm using a Unicam SP1700 spectrophotometer.

Criticisms concerning the modified Saltzman method for the determination of nitric oxide have been reported (*13*). Conversion

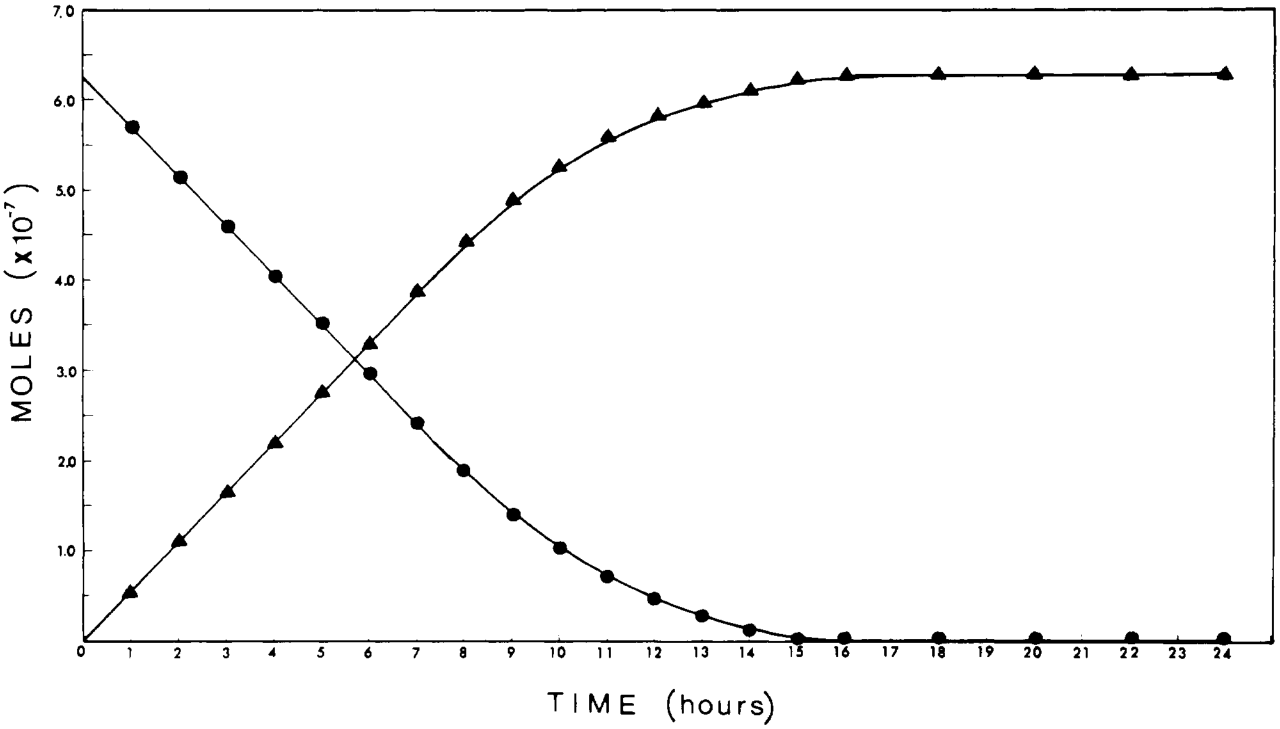


Figure 2. Time study on the nitronyl nitroxide (decreasing with time) and the imino nitroxide (increasing with time) at 0.66 ppm nitric oxide

efficiencies of nitric oxide to nitrogen dioxide by the acidic permanganate have been reported as low as 70%. We therefore checked our system against a ThermoElectron chemiluminescence instrument (model 12A) provided by the Canadian Gas Research Institute. The instrument was calibrated with Airco nitric oxide and also crosschecked against a second instrument from the Air Resources Branch (Ontario Ministry of the Environment). The modified Saltzman method for the determination of nitric oxide gave excellent results in the range 0.05–1.80 ppm under the sampling conditions stated.

After 1 h, or longer for certain experiments, the plates were removed from the chamber. Exposed and unexposed plates could be refrigerated in 0.004-in. thick polyethylene bags inside a brown envelope for at least two-week periods without any chemical changes occurring. Prior to ESR measurements, the plates were developed with an eluting mixture consisting of equal volumes of diethyl ether, *n*-pentane, and carbon tetrachloride. The silica gel containing the product radical **2** was scraped from the plate into small glass 4-mL vials. If the product radical could not be seen, then a sufficient area of silica gel was removed to ensure that all the radical was transferred. In the relevant experiments, the silica gel containing the reagent radical was scraped into a separate vial.

Several solvents were evaluated for their extraction efficiencies for the reagent and the product from silica gel. The effect of solvent on the ESR signal intensity was also studied and the results are shown in Table I. *p*-Dioxane was chosen as the extraction solvent and 1.00 mL of this extracted 100% and 96% of the product and reagent, respectively, from spots produced by 10 μL of 6.28×10^{-2} M solutions of each. The silica gel showed excellent settling properties in *p*-dioxane, thus eliminating a separation step. One disadvantage of *p*-dioxane is its tendency to accumulate peroxides on prolonged standing, and we have some evidence that this may lead to a reversion of product to reagent. The dioxane should therefore be distilled from sodium wire and preferentially stored over the latter. We have not encountered similar problems with the diethyl ether used for plate elution but, if necessary, peroxide problems may be again overcome by the use of sodium.

Samples in 3-mm i.d. quartz tubes were run on a Varian E4 instrument, at a radiation frequency of 9.076 GH_z and a 3225-G magnetic field. The same tube or matched tubes should be used. It is recommended that the tubes be placed in the cavity in the same orientation each time. It is also recommended that a suitable ESR standard be used to check the instrument response on a daily basis. For example, a *p*-dioxane solution of the iminonitroxide sealed under nitrogen in an ESR tube is satisfactory for this purpose.

Table I. ESR Peak Heights for 1.08×10^{-3} M Solutions of Compound 1 in Various Solvents. Receiver Gain = 5

Solvent	Peak height, cm
Methylene chloride	14.8
Carbon tetrachloride	21.0
Chloroform	7.3
Methanol	1.2
p-Dioxane	40.0
Cyclohexane	14.1
Benzene	17.1
Water	0.0

2-Phenyl-4,4,5,5-tetramethylimidazoline 3-oxide 1-oxyl. To a solution of 1.2 g (0.005 mol) of 2,3-bis(hydroxylamino)-2,3-dimethylbutane sulfate in 20 mL of water was added anhydrous sodium carbonate, 0.5 g (0.005 mol) followed by benzaldehyde, 0.5 mL. The resulting slurry was stirred for 24 h in a stoppered flask and then filtered. The precipitate, 1,3-dihydroxyl-2-phenyl-4,4,5,5-tetramethylimidazoline was washed with a small amount of 1% sodium metabisulfite (to remove benzaldehyde) followed by water and then dried. The precipitate was then suspended in water, 50 mL, and ether, 75 mL, was added. A solution of sodium periodate (1.5 molar ratio to the adduct, MW 236) in 10 mL of water was gradually added with continuous stirring. Stirring was continued for 1 h. The ether layer was separated, dried over calcium chloride, and rotary evaporated to approximately 10 mL. This solution was chromatographed on 200 g of silica gel (mesh size 100–200) using ether as eluent. The ether containing the product was dried (anhydrous sodium sulfate), filtered, and rotary evaporated to yield 60% product mp 84–88 °C.

RESULTS AND DISCUSSION

Figure 2 shows the molar balance for the reagent and product radicals studied over a 24-h period at a nitric oxide concentration of 0.66 ppm. The results suggest that no side reactions are occurring, and indicate that with the reagent surface loading, produced by the spotting procedure, close to

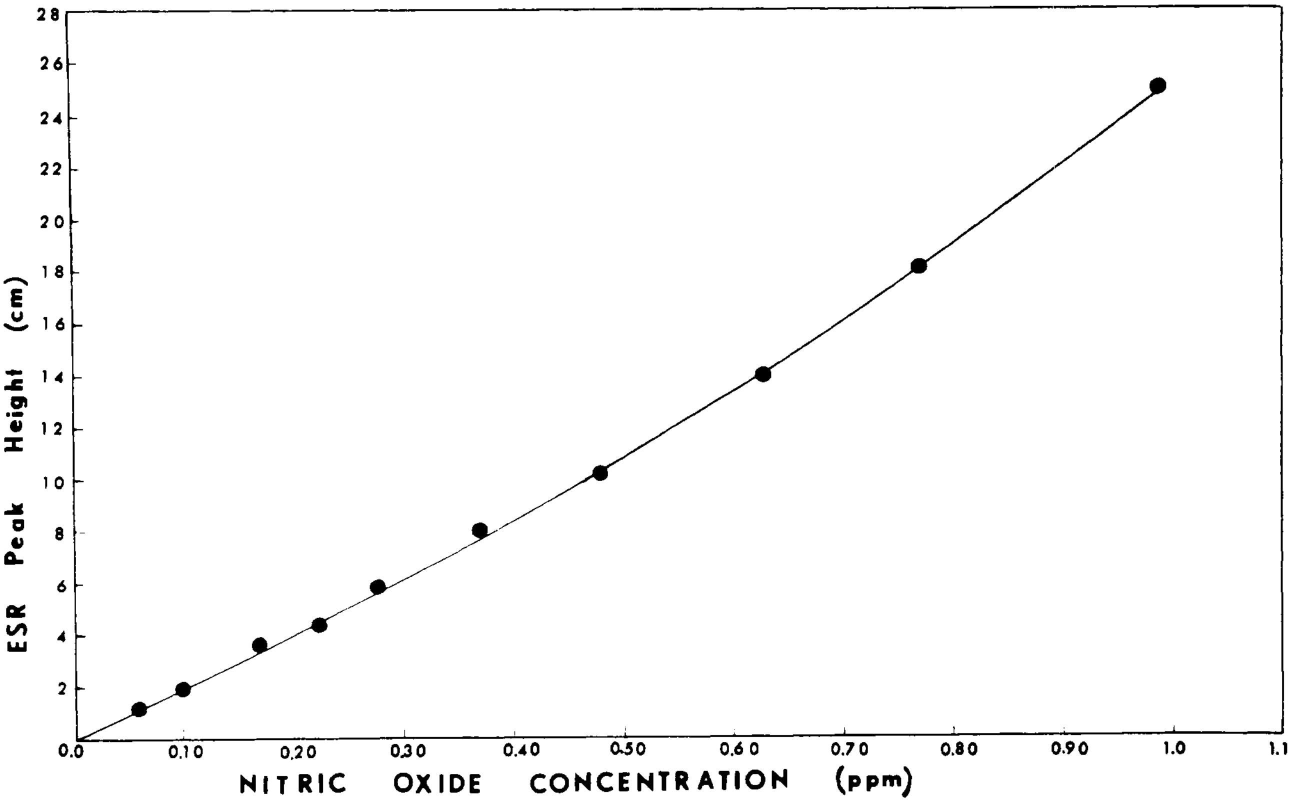


Figure 3. Plate response per hour vs. nitric oxide concentration. ESR receiver gain = 63

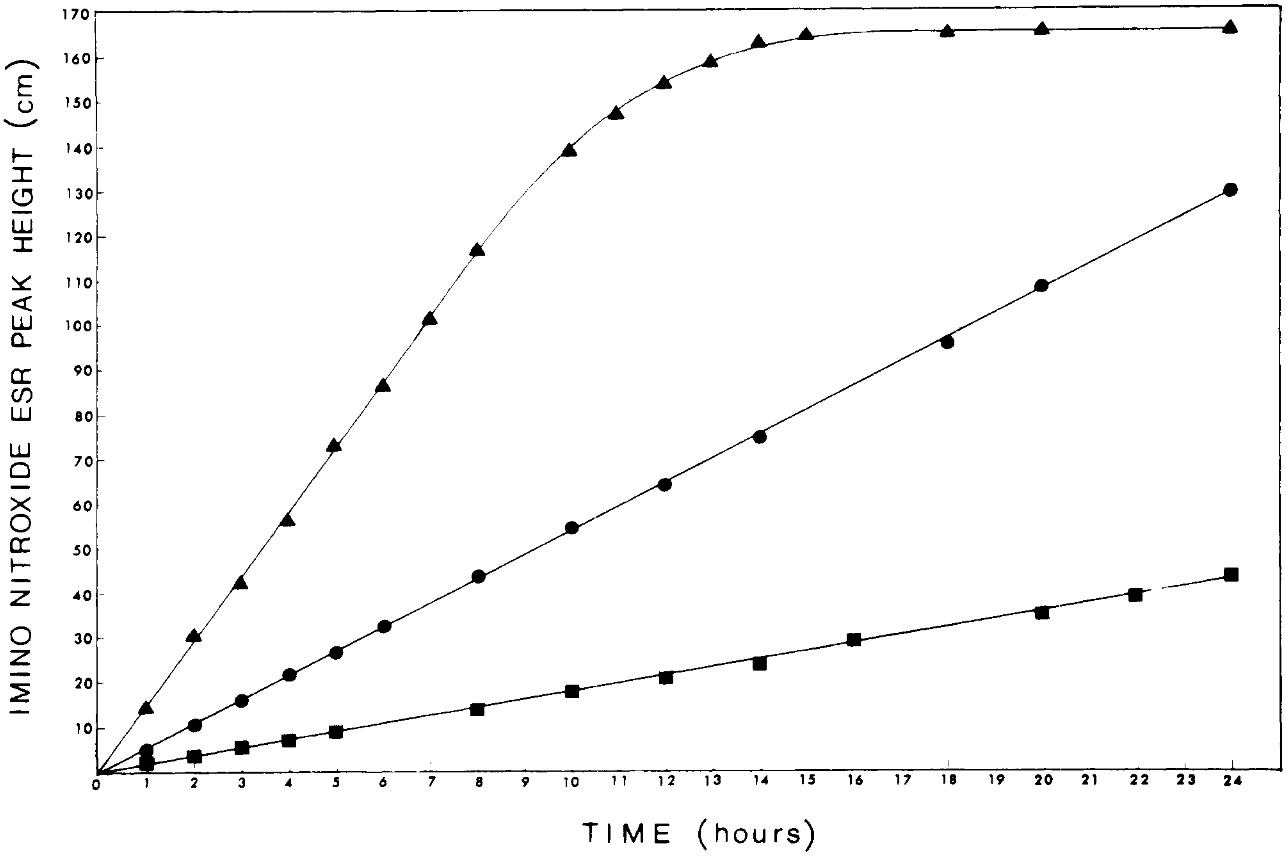


Figure 4. Twenty-four hour time study at three nitric oxide concentrations: Upper curve, 0.66 ppm; middle curve, 0.28 ppm; lower curve, 0.10 ppm. ESR receiver gain = 63

80% of the reagent may be converted before a change in plate response per unit-time is observed. The two curves follow first-order kinetics from the 9-h point onwards when the chemical reaction becomes rate controlling. It thus appears that all the reagent on the silica gel is equally accessible to the nitric oxide and emphasizes the extremely porous structure of silica gel. An increase in reagent surface loading is limited by the length of plate available for chromatographic separation of reagent and product.

Figure 3 shows the plate response per hour vs. nitric oxide concentration. Each point is the average of three plate readings and standard deviations ranged from 0.18 cm at the lowest concentration to 0.45 cm at the highest concentration. A ten-plate standard deviation at 0.14 ppm NO was 0.17 cm. The graph is essentially linear between 0.05 and 0.5 ppm but exhibits a positive deviation from linearity above this range. The system therefore does not conform to simple boundary layer diffusion. However, when the plate is incorporated into a device where virtually all the diffusional resistance is in a membrane, then the plate response per hour should increase linearly with nitric oxide concentration. Sufficient sensitivity remains in the method such that a membrane may be incorporated for the measurement of typical concentrations of ambient nitric oxide.

Figure 4 shows a 24-h study for three different nitric oxide concentrations. The plate response per hour is constant for each of the two lower concentrations (0.10 and 0.28 ppm) throughout the 24-h period, whereas at the higher concentration (0.66 ppm), the plate response per hour decreases after the first 8 h. The slopes of the linear portions of all three graphs are those predicted from the calibration curve, Figure 3.

Interference Studies. Nitrogen dioxide did not react with the reagent or product radicals in the range 0.01–5.0 ppm. Sulfur dioxide did not interfere below 4.0 ppm. There was evidence that above 4.0 ppm SO_2 some deoxygenation of the reagent occurred, but the response in this concentration region was considerably below that for nitric oxide. Ozone below 1.0 ppm did not interfere. Above 1.0 ppm some unidentified brown product was produced and this did not elute with solvent. Hydrogen sulfide in a concentration range of 0–10 ppm did not interfere. Plates which were exposed to 0.48 ppm nitric oxide for 1 h at relative humidities ranging from 0–100% gave the same response. Strong light may cause photochemical deoxygenation of the reagent but this will not be a problem when a membrane is incorporated.

Temperature Studies. Simple boundary layer theory predicts that the number of moles of nitric oxide diffusing to the plate per unit time and per unit area of plate should be proportional to the square root of the absolute temperature. Plates were exposed to an atmosphere of 0.40 ppm nitric oxide in nitrogen contained in 200–300 L polyester bags. Cold rooms were used to attain the various temperatures between +23 and −23 °C. It was found that plate response appeared to vary linearly over this range, the response at −23 °C being 10.5% lower than that at +23 °C. The small change in plate response with temperature again indicates the lack of chemical control under the experimental conditions.

Present Studies. Work is continuing on mass transfer effects due to wind velocity and also on the incorporation of a suitable membrane to complete the device. These studies which are near a successful conclusion will be published shortly.

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Determination of 2,4- and 2,6-Diaminotoluene in Flexible Urethane Foams

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A fluorimetric method has been developed for the measurement of the diaminotoluenes (TDA) in flexible polyurethane foams. The precision of the method at the 20 ppm level is ±30%. TDA can be detected in foams at 1 ppm concentration. A large part of the scatter appears to be due to nonuniform distribution of TDA in foams. Using this method, we have found 2–400 ppm of TDA in 11 foams from various sources. There was 2,4-TDA in all samples, but 2,6-TDA appeared only in the conventional "hydrophobic" foams. The method consists of extraction with methanol, separation of the amines by thin-layer chromatography, and fluorimetric assay with the Fluram reagent.

Polyurethane foams derived from the toluene diisocyanates (TDIs) would be expected to contain small amounts of the corresponding diamines (TDAs). To our knowledge, no measurement of the diamines has been reported, because of their extremely low concentration.

We have developed a method which can detect as little as one part per million (ppm) of 2,4- or 2,6-TDA in flexible foams. Using this procedure, we have found 2–400 ppm of TDA in 11 commercial flexible polyurethane products. This is of interest because 2,4-TDA is included in the NIOSH list of potential carcinogens (*1*) and has been the subject of a number of toxicological studies (*2–11*). Also, the amine content of polyurethane foams is a factor in color stability, humid aging resistance, and other physical properties.

Our interest in amine analysis stemmed from measurements of aging resistance. Polyurethane foams are often used in warm, humid environments where loss of properties through hydrolysis is of concern. For this reason, some foam products have "autoclave stability" specifications such as the well-