

COLORIMETRIC REAGENTS FOR NITROGEN DIOXIDE

by

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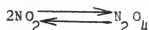
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Chapter I
INTRODUCTION

Nitrogen dioxide, NO_2 , is a reddish-brown gas having a boiling point of 21.15°C . The commercial brown liquid under pressure which is known as "dinitrogen tetroxide" is actually an equilibrium mixture of NO_2 and N_2O_4 :



where N_2O_4 dominates at low temperatures or high pressures and NO_2 is favored at low pressures or higher temperatures.

Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) are an important class of air pollutants which play a role in photochemical smog production. Most of the NO_x emitted by internal combustion engines (their chief source) is NO which is subsequently oxidized to NO_2 by atmospheric oxygen. Nitrogen dioxide affects smog chemistry by influencing the production of hydroxyl (OH) radicals and ozone and by reacting with organic radicals to form peroxyacetyl nitrate (PAN), which is a strong eye irritant[1]. Nitrogen dioxide can also be oxidized to nitric acid, a component of acid rain[2].

Nitrogen dioxide can be perceived by smell in concentrations as low as 0.1 ppm. However, it is possible to become accustomed to its odor; the odor threshold may become

as high as 25 ppm by slowly increasing the NO_2 concentration. In terms of harm to the human body, at 13 ppm NO_2 starts to irritate the respiratory mucous membrane and at 100 to 150 ppm after 30-50 minutes may cause death from edema of the larynx[3]. The allowable exposure of nitrogen dioxide for an eight-hour day is 5 ppm[4].

The most commonly used method for NO_x determination is the chemiluminescent method based on the gas phase reaction of NO and ozone[5]. This method is specific for NO and is used to measure NO_2 by catalytically reducing it to NO prior to reaction with ozone. However, other species, such as PAN or nitric acid may also be reduced to NO and therefore interfere with NO_2 measurement.

Recently, another chemiluminescent method based on the reaction of NO_2 with luminol was reported, but it was also subject to PAN interference[6]. Other spectroscopic methods for ambient NO_2 monitoring include: photoacoustic spectroscopy[7], long path differential optical absorption spectroscopy[8], and Fourier Transform infrared spectroscopy[9] using tunable dye lasers.

The classical method for NO_2 determination is the Griess-Saltzman[10] method based on the absorption of NO_2 into a sulfanilic acid solution. This product is then coupled with an azo dye forming reagent and measured colorimetrically at 540 nm. This was a modification of the Griess method[11], to which a number of modifications have been devel-

oped by Warrington[12], Illosvay[13], Weston[14], and others. The Griess-Saltzman procedure has been modified by Jacobs[15], who used an aqueous NaOH solution to trap nitrogen dioxide, and Levaggi[16], who used triethanolamine as the trapping reagent.

Instrumental and classical ("wet") methods both suffer from a lack of portability. The classical methods referred to are complicated and time consuming, considering all the reagent solutions and standards which must be prepared. The instrumental methods mentioned can be quite expensive. Therefore, the goal of this research is to develop a simple, portable, and inexpensive method for ambient NO₂ measurement. One means of achieving this is to develop a solid phase analytical reagent which can be applied to filter paper, detecting NO₂ by a color change. This laboratory[17] has succeeded in the synthesis of N-(4-aminophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine, but this solid reagent is not stable in storage.

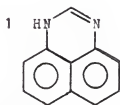
Primary, secondary, and tertiary 1-naphthylamines are known to react with nitrous acid, HONO, to form diazonium salts, N-nitrosamines, and p-nitroso compounds, often with a color change. The reaction of nitrogen dioxide with water vapor[18] to form nitrous acid and nitric acid



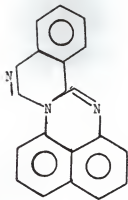
may explain the mechanism of nitrosation of these amino compounds in a gas-solid reaction. Yet primary, and frequently, secondary naphthylamines are subject to air oxidation which results in darkening. Lower molecular weight naphthylamines such as 1-amino-, 2-amino-, and 1-(N-methylamino)-naphthalene are unsafe to use because they are not only volatile but are also suspected to be highly carcinogenic [19].

In this study, the author avoided the volatility problem by preparing reagents which are derivatives of the cyclic amine perimidine: (Numbers show substituent positions).

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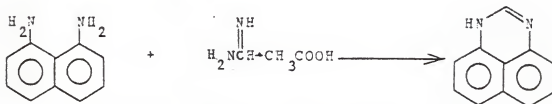
Compounds prepared included 1-methyl-, 2-methyl-, 2-phenyl-, 1-acetyl, 1-acetyl-2-methyl-, and 1-methyl-2-dimethylamino-perimidine. The author also attempted the synthesis of (1,3)-benzodiazino-(3,4)-perimidine:



Chapter II

SYNTHESES

2.1 PREPARATION OF PERIMIDINE

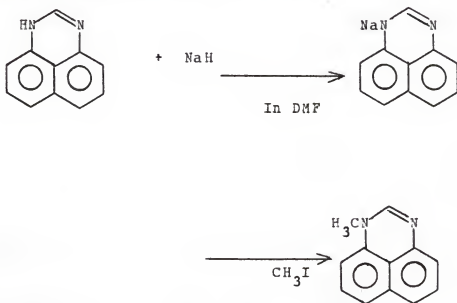


The starting material common to the synthesis of perimidine and perimidine derivatives, 1,8-diaminonaphthalene, is available commercially as a purplish-black solid in technical grade. When purified, this compound forms white crystals which darken in a matter of hours upon exposure to air. For this reason, it is of no value to attempt to obtain higher commercial grades. 1,8-diaminonaphthalene is purified by recrystallization from 1:1 water/ethanol. Usually an additional recrystallization is necessary. Further decolorization, if necessary, may be accomplished by heating an ethanolic solution of the diamine with a small amount of activated charcoal and filtering. The white crystals obtained should be used immediately.

Brown[20] suggests refluxing the diamine in ethanol with formamide acetate, but gives no details. The author prepared perimidine by weighing out 15.8 g (0.100 mole) of

the purified 1,3-diaminonaphthalene, dissolving it in 400 ml of ethanol in a 1000 ml round-bottomed flask, and adding 12.0 g (0.115 mole) of formamidine acetate. A reflux condenser is attached to the round-bottomed flask and the mixture is refluxed for at least 4 hours. The reaction should be carried out in a fume hood, since ammonia gas is evolved. Any formamidine acetate which is undissolved prior to refluxing will dissolve upon heating. Perimidine is obtained by crystallization as light yellow needles.

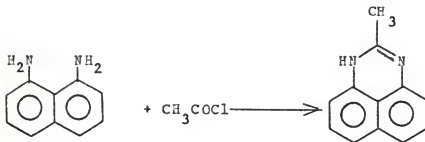
2.2 PREPARATION OF 1-METHYL PERIMIDINE



One prepares 1-methyl perimidine by first dissolving 1.68 g (0.01 mole) of perimidine in 200 ml of dimethyl formamide (DMF) which has been distilled over calcium hydride in thoroughly dry glassware at 1 torr pressure. This solu-

tion is then placed in a glove bag containing a dry nitrogen atmosphere. One then weighs out 0.48 g of sodium hydride, NaH, available commercially as a 50% dispersion in oil, and washes it inside the glove bag with ether that has been dried first with drierite and then with a few pieces of sodium metal. The NaH is added to the DMF solution, followed by 1.42 g of methyl iodide. Even when a stoichiometric amount of methyl iodide is used, a small amount of a highly water-soluble red substance is formed, possibly a quaternary salt. The DMF solvent is removed by distillation at 50-60°C and 1 torr pressure. A Soxhlet extraction is performed on the solid residue using ether as a solvent. The by-products, sodium iodide and the quaternary salt, are insoluble in ether and are not extracted. The product, 1-methyl perimidine, is obtained by evaporation of the ether. It is yellow and very similar in appearance to perimidine. Figures 1 and 2 show, by the mass spectra of perimidine and 1-methyl perimidine, that methylation took place.

2.3 PREPARATION OF 2-METHYL-PERIMIDINE



Donaldson[21] suggests the use of acyl chlorides to prepare general 2-substituted perimidines, but gives no details. One prepares 2-methyl-perimidine by dissolving 2.0 g of 1,8- diaminonaphthalene in 200 ml of pyridine (purification of the diamine is not necessary). The solution is chilled in an ice bath while 1 ml of acetyl chloride is added very carefully dropwise. The yellow precipitate which is formed is collected by suction filtration and washed with cold 1:1 EtOH/water. The precipitate is dissolved in about 50 ml of boiling water. Crystallization occurs as the solution is allowed to cool for several hours. As an aside, the author attempted the synthesis of this compound in a manner analogous to the preparation of perimidine, that is, by substituting acetamide acetate for formamide acetate and refluxing in ethanol with 1,8-diaminonaphthalene, but the desired reaction did not take place. Attempts to add an acetyl group, and later a methyl group, to the 1-position were unsuccessful. Figure 3, the mass spectrum, confirms the molecular weight.

2.4 PREPARATION OF 2-PHENYL-PERIMIDINE

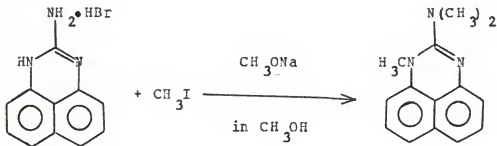
2-phenyl-perimidine is prepared by dissolving 2.0 g of 1,8- diaminonaphthalene in 200 ml of pyridine, adding 1.5 ml of benzoyl chloride and refluxing for one hour. The precipitated 2-phenyl-perimidine is collected by suction filtration and washed with ethanol. This rust-colored compound is

virtually insoluble in all organic solvents and water. Its mass spectrum is shown in Figure 4.

2.5 PREPARATION OF 1-ACETYL-PERIMIDINE

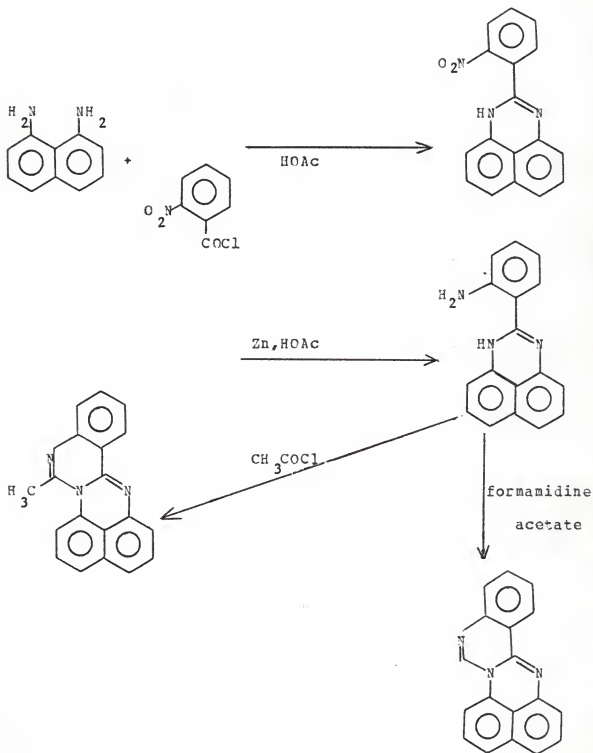
Approximately 1 g. of perimidine is suspended in 50 ml of water. To this is added 2 ml of acetic anhydride. The mixture is allowed to stand for 15 minutes. The perimidine goes into solution and the 1-acetyl derivative slowly precipitates out. The precipitate is collected by suction filtration while washing several times with water.

2.6 PREPARATION OF 1-METHYL-2-DIMETHYLAMINO-PERIMIDINE



One dissolves 0.2 g. of 2-aminoperimidine hydrobromide and 0.5 ml of methyl iodide in 100 ml of methanol containing 0.5 g. sodium methylate. The reaction is allowed to stand several hours. Precipitated 1-methyl-2-dimethylamino perimidine is removed by filtration. The author evaporated the methanol from the filtrate and found all the remaining solids to be highly water soluble.

2.7 ATTEMPTED SYNTHESIS OF
(1,3)-BENZODIAZINO-(3,4)-PERIMIDINE



The preparation of the first and second intermediates, 2-(o-nitrophenyl)- and 2-(o-aminophenyl)-perimidine, is described by Sachs and Steiner[22]. To synthesize 2-(o-nitrophenyl)-perimidine, one dissolves purified 1,8-diaminonaphthalene in glacial acetic acid and adds 2-nitrobenzoyl chloride. The reaction is allowed to continue for one hour. The bright red precipitate is collected by suction filtration and redissolved in 50% acetic acid. One then adds granulated zinc, attaches a reflux condenser to the flask and refluxes for one hour. The mixture is allowed to cool to room temperature and is filtered to remove all solid residue. Next, hydrogen sulfide gas is bubbled into the solution for one hour and the zinc sulfide precipitate is removed by suction filtration. The amine is precipitated by adding cold dilute ammonium hydroxide dropwise to the solution. The light yellow precipitate of 2-(o-aminophenyl)-perimidine is then collected by suction filtration.

An attempt to close a ring between the amino group on the phenyl group and the secondary amino group--by refluxing with formamidine acetate in ethanol in a manner analogous to the ring closure of 1,8-diaminonaphthalene to form perimidine-- failed. Even after 24 hours, the reaction vessel contained only the starting materials.

A similar attempt at ring closure by adding acetyl chloride to a solution of the amine in pyridine produced a

yellow precipitate which spontaneously exploded. The author made a second attempt to close this ring with acetyl chloride, but after the precipitate again exploded, the syntheses of (1,3)-benzodiazino- (3,4)-perimidine and its methyl derivative were abandoned.

Figure 1: Mass Spectrum of Perimidine

MASS SPECTRUM
07-23-94 11:45:00 + 0101
SMFLEU1

DATE ACQUIRED 11
CALIBRATION 41

FILE NAME 11
405-484

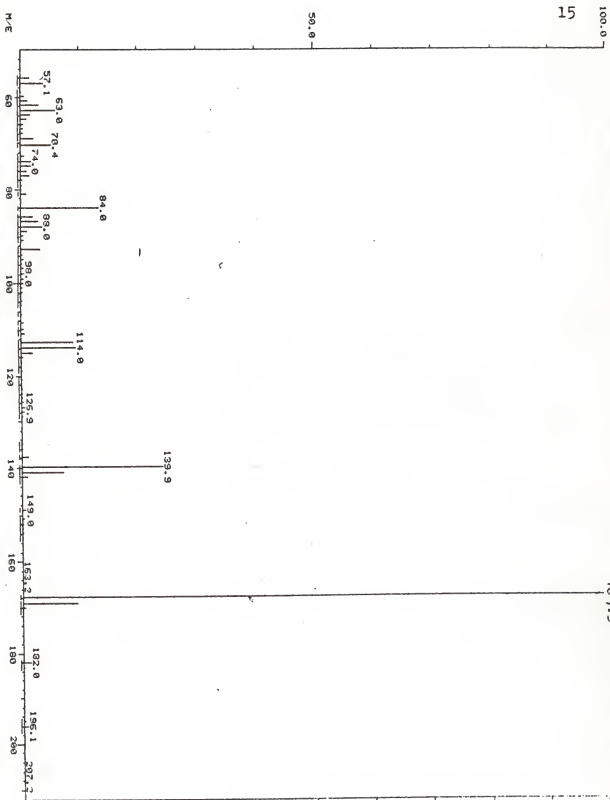


Figure 2: Mass Spectrum of 1-Methyl-Perimidine

MASS SPECTRUM
04/26/84 14149100 + 0101
SAMPLE1

DATA: E043662 #1
CALL: CM0310 #1

BASE M/E: 193
R1C1 21535.

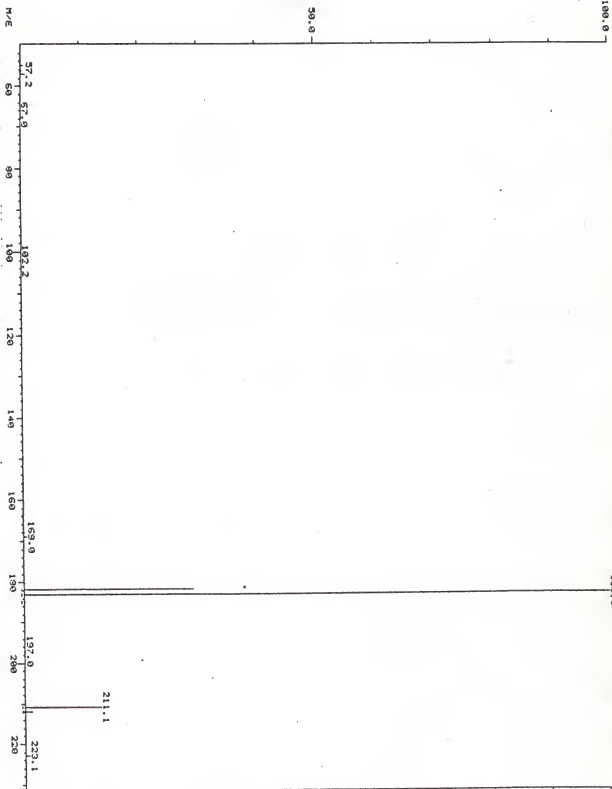


Figure 3: Mass Spectrum of 2-Methyl-Perimidine

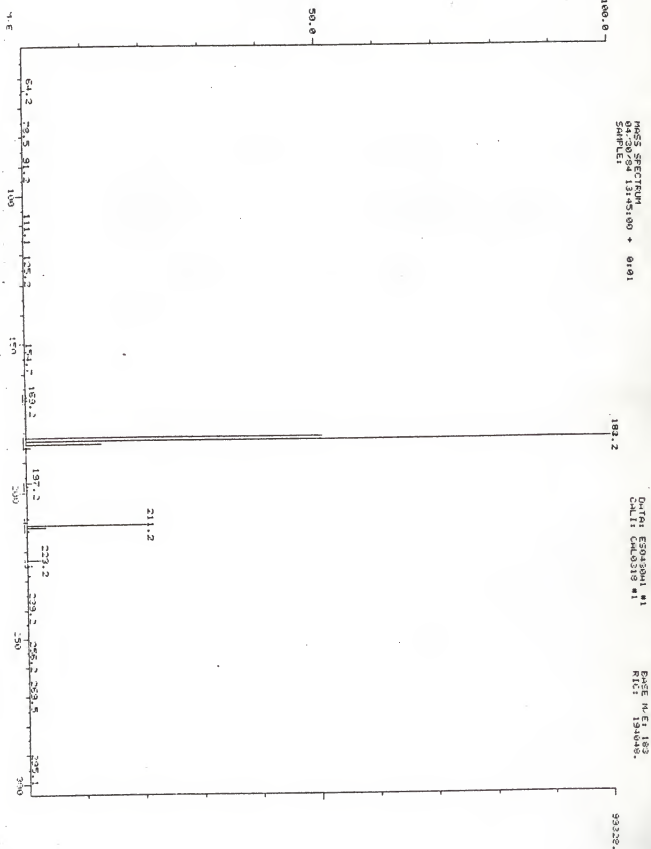
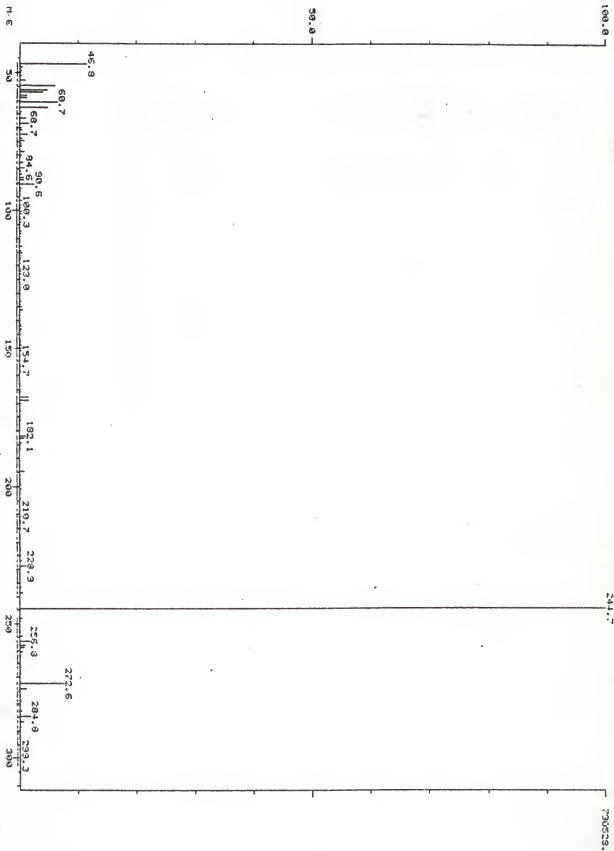


Figure 4: Mass Spectrum of 2-Phenyl-Perimidine

MASS SPECTRUM
 REF# 14109100 + 0102
 SAMPLE 1

DATA: E10715A #1
 CALL: CAL0509 #1

BASE M/E: 245
 RIC: 159330.



Chapter III

DETERMINATION OF NITROGEN DIOXIDE

3.1 REAGENTS AND EQUIPMENT

Test Paper: No. 2 filter paper, 4.25 cm diameter, obtained from Whatman Ltd.

Teflon Tubing, 1/4" O.D., 1/16" and 1/32" thickness

Nitrogen Dioxide: commercial grade, obtained from Union Carbide Corporation

Thermostatic Bath Circulator and Controller: obtained from E. H. Sargent and Co., Chicago, Ill.

Gas Flowmeter: Gilmont Instruments, Inc., Great Neck, N.Y.

Spectrophotometer: double-beam Perkin-Elmer Coleman Model 124 with reflectance attachment.

Aquarium Pumps: Penn Plax II-440-X Twins.

3.2 QUALITATIVE TESTING

The reagents whose preparation is described in the previous chapter were, except for 2-phenyl-perimidine, each dissolved in a solvent. Three pieces of filter paper were wetted in each solution and air dried. 2-phenyl-perimidine was used in solid form (not supported on filter paper). Two papers from each solution, one dry and one moistened with

water, were exposed to NO_2 from a cylinder in a fume hood. Results are summarized in the table below:

RESPONSE OF PERIMIDINE DERIVATIVES TO NO_2

Substituents	Solvent	Color		
		Before	After Wet	Dry
None	EtOH	pale yellow	red	orange
1-Methyl	EtOH	pale yellow	red	orange
2-Methyl	hot water	pale yellow	red	orange
1-Methyl-2-Dimethylamino	DMF	green	greenish-brown	greenish-brown
2-Phenyl	None	brown	brown	brown
1-Acetyl	DMF	pale yellow	red	

On the basis of this test, 2-phenyl-perimidine and 1-methyl-2-dimethylamino-perimidine were eliminated from further consideration as analytical reagents for nitrogen dioxide because visual detection of color changes was difficult. The parent compound, perimidine, was eliminated because of its gradual darkening over a period of a few hours when exposed to air. Although it showed a good response to NO_2 , 1-acetyl-perimidine was also eliminated because it was considerably less sensitive than the remaining two compounds. During quantitative testing, 2-methyl-perimidine was shown to be unsatisfactory.

3.3 PREPARATION OF TEST PAPERS FOR QUANTITATIVE TESTING

At first, test papers were prepared by immersing 18 pieces of Whatman No. 2 filter paper at a time in a 0.1 M solution of the reagent for 15 minutes. Ethanol was the solvent for 1-methyl-perimidine and hot water was the solvent for 2-methyl-perimidine. Both solvent tanks were kept covered to minimize evaporation. The filter papers were then air dried.

Later, it was discovered that the reagent was more sensitive if a deliquescent compound was also applied to the filter paper. Calcium chloride was dissolved in water and mixed with the two reagent solutions. The filter papers were soaked as before, but were dried overnight in an oven at 90°C and cooled in a desiccator until ready for use.

3.4 PREPARATION OF KNOWN LOW CONCENTRATIONS OF NO₂

Known concentrations of gas can be prepared in a variety of ways using either static or dynamic methods. The principal disadvantage of static methods is that adsorption of the gas on the container walls occurs. With dynamic methods, concentrations of test gas from 50% down to part-per-billion ranges can be easily controlled and altered. Adsorption on container walls is negligible because an equilibrium is established after a short time.

A diagram of the gas dilution system used is shown in Figure 5. The apparatus was constructed from Pyrex glass,

Teflon joints, Tygon tubing, and copper tubing. Two aquarium pumps supplied the air flow. Permeation tubes were used to generate NO_2 . To prepare a permeation tube, one selects a Teflon tube, one-fourth inch O.D., 5-7 cm. long, and immerses it in liquid nitrogen. The tube is then filled from a nitrogen dioxide cylinder and NO_2 is trapped. Both ends of the tube are sealed using glass rods whose ends have been enlarged by melting. One should wait a day or two after filling to begin calibration. Permeation tubes are calibrated gravimetrically by collecting weight data over a period of time and determining the rate of weight loss. The rate of weight loss equals the permeation rate of nitrogen dioxide. (See Figure 6)

Because permeation rates are sensitive to temperature, the system was immersed in a constant temperature water bath at 25°C . The nitrogen dioxide concentration was determined by the rate of air flow and may be calculated according to the following expression:

$$C = \frac{(22,400) \times (T/273 \text{ K}) \times (760\text{mm}/P) \times dp/dt}{dG/dt \times M}$$

T: Temperature of the system (298°K)

P: Pressure of the system (735 mm Hg)

dp/dt : Permeation rate (g/min)

dG/dt : Flow rate of the diluent gas (ml/min)

M: Molecular weight of nitrogen dioxide (46.0 g)

The air entering the permeation chamber containing the permeation tube (Figure 7) is dried by molecular sieves and drierite because moisture adsorbed on the permeation tube changes the rate of permeation and can cause blistering and thereby shorten the life of the tube. It was discovered that moisture is essential for the reaction of NO_2 with 1-methyl- and 2-methyl-perimidines. Therefore, a second stream of air was saturated with moisture by passing it through a water bubbler. The flow rates of both streams were adjusted to equal each other within the precision of the flowmeter. The two streams entered different branches of a glass "Y" connection and mixed before entering the exposure chamber to yield air of approximately 50% humidity. The exposure chamber (Figure 8) was fashioned from a 60 mm I.D. low-form cap-style weighing bottle which was inverted and had inlet and outlet ports glassblown onto it.

Figure 9 shows a system for testing the effect of humidity on the reaction. Six air streams were mixed before entering the exposure chamber. These air streams were adjusted to equal each other within the precision of the flowmeter. The air stream passing through the permeation chamber was always kept dry. The other five streams were also passed through drying tubes to yield 0% relative humidity. The relative humidity was increased in a stepwise manner by successively replacing each drying tube with a water bubbler. Relative humidity can then be calculated from the expression:

$$RH = \frac{\text{No. of moisture saturated air streams} \times 100\%}{\text{Total No. of air streams}}$$

3.5 QUANTITATIVE TESTING OF REAGENT RESPONSE TO NO₂

Quantitative testing of the 1-methyl- and 2-methyl-perimidines began by introducing air dried filter papers containing the reagent, one at a time, into the exposure chamber of the system shown in Figure 5. The exposed papers were compared with unexposed reagent papers both visually and spectrophotometrically at 460 nm--using a double-beam UV-VIS instrument modified by replacing standard cuvette holder with a reflectance attachment. This attachment deflects the incident light upwards onto the surface of the sample, while a second mirror returns the reflected light to the original path and into a slit to the photomultiplier tube. The loss of reflected radiation relative to a reference (reagent paper unexposed to NO₂) is read as absorbance in the usual manner and given the name "reflected absorbance."

The concentration of nitrogen dioxide was kept constant at 6.79 ppm and the relative humidity was maintained at 50%. For both reagents, the filter paper changed from nearly colorless to red within one minute. As exposure time was increased, the red color became more intense (Figure 11). After about one hour of exposure, however, a second reaction began to occur: the filter paper turned from red to

yellow. (See Figure 12). There was a decrease in reflected absorbance at 460 nm for the paper exposed for one hour compared to those exposed for shorter times. As exposure time increased beyond 1 hour, the yellow color became more intense and yielded higher reflected absorbance values at 460 nm. Readings were not very reproducible from day to day. Those filter papers having both red and yellow coloring showed the greatest variation in readings. The color stability of the red and yellow 1-methyl-perimidine- NO_2 complexes was very good, but the color of the 2-methyl-perimidine papers which had been exposed to NO_2 faded after a few hours.

After it was observed that moist reagent papers turned red in the presence of NO_2 , the author decided to also apply a deliquescent compound (CaCl_2) to the papers. This deliquescent compound ruined the 2-methyl-perimidine, but produced no ill effects on the 1-methyl-derivative.

1-Methyl-perimidine papers were tested at constant NO_2 concentration and relative humidity, but exposure times were varied. Figure 13 shows a nearly linear relationship between exposure time and reflected absorbance from approximately 30 minutes to 3 hours. Next, exposure time was held constant at 45 minutes, and the relative humidity was maintained at 50%, but NO_2 concentration was varied (Figure 14). Again, there is a nearly linear relationship when concentration is plotted against reflected absorbance. The curve be-

gins to level off at the right side of the graph, possibly because a) the starting reagent is being depleted, b) the penetration of nitrogen dioxide into the reagent paper has reached its limit, or c) the penetration of the light source of the spectrophotometer into the reagent paper has reached its limit. Finally, Figure 15 shows that, as the relative humidity increases for a given exposure time and NO_2 concentration, the reflected absorbance increases nearly linearly. In all three of these experiments, no yellow color was observed; Even at high concentrations of nitrogen dioxide, the papers remained red. The addition of calcium chloride approximately doubled the linear range of reflected absorbance values.

3.6 STRUCTURE ELUCIDATION OF REAGENT- NO_2 COMPLEXES

The author suspended a small amount of 2-methyl-perimidine in about 25 ml of dimethyl sulfoxide (DMSO). Nitrogen dioxide was bubbled into the solution for about five minutes. The bright red product went into solution as soon as it was formed. Feigl[23] reports a highly specific simple chemical test for N-nitrosamines using hydrogen azide, HN_3 . Hydrogen azide, formed by dissolving sodium azide in cold concentrated hydrochloric acid, denitrosates N-nitrosamines, emitting nitrogen and nitrous oxide gases. Such a denitrosation occurred when HN_3 was added to the DMSO solution. Not only was the gas evolution observed,

but the red solution returned to a yellow suspension. Feigl also reports a test that is specific for p-nitro- aromatic amines. A small amount of the solid analyte is mixed with a small amount of diphenylamine in a casserole and heated until the diphenylamine melts. The formation of a deep blue color indicates a positive test. Some of the red solution described earlier was evaporated to dryness and tested. A deep blue color was observed.

An ethanolic solution of 1-methyl-perimidine-NO₂ complex showed no response to hydrogen azide. Feigl's test for a p-nitro- aromatic amine was positive. Using another of Feigl's tests, this time for a p-nitroso- aromatic amine, phenol and sulfuric acid were mixed with the solid analyte to produce a blue color, indicating that the test was positive.

Figure 5: Permeation Gas Dilution System for Nitrogen Dioxide

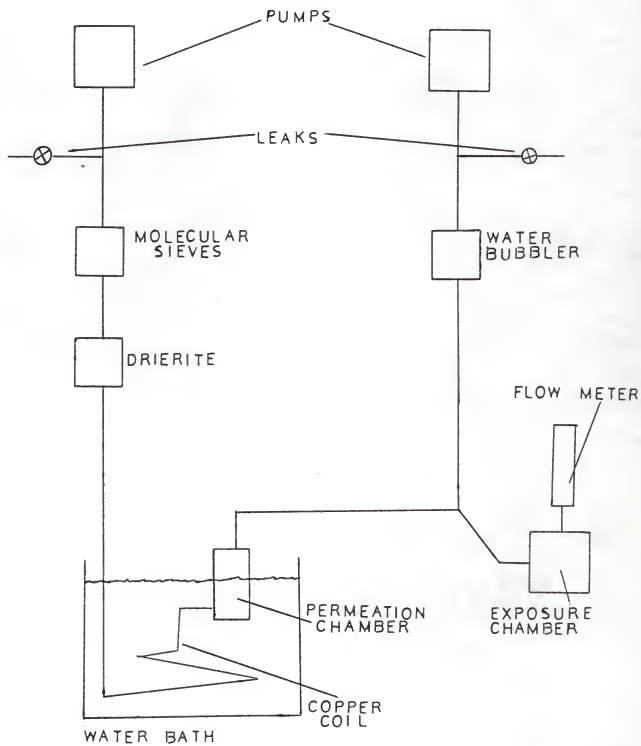


Figure 6: Calibration of the Permeation Tube

Permeation Rate = 476.0 ng/min

Correlation Coefficient = -0.9966.

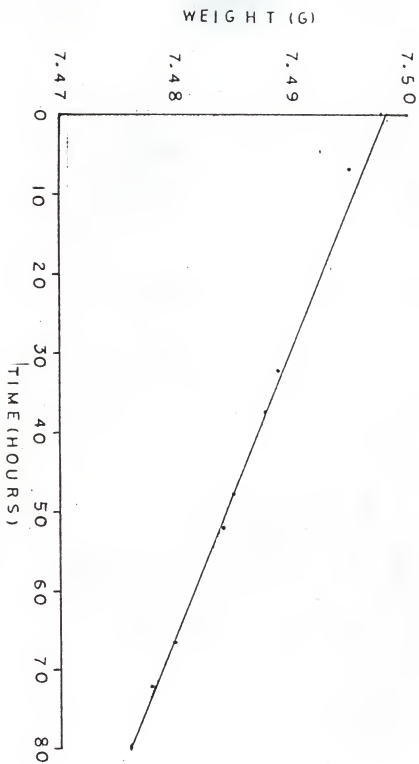


Figure 7: Variable Humidity Gas Dilution System

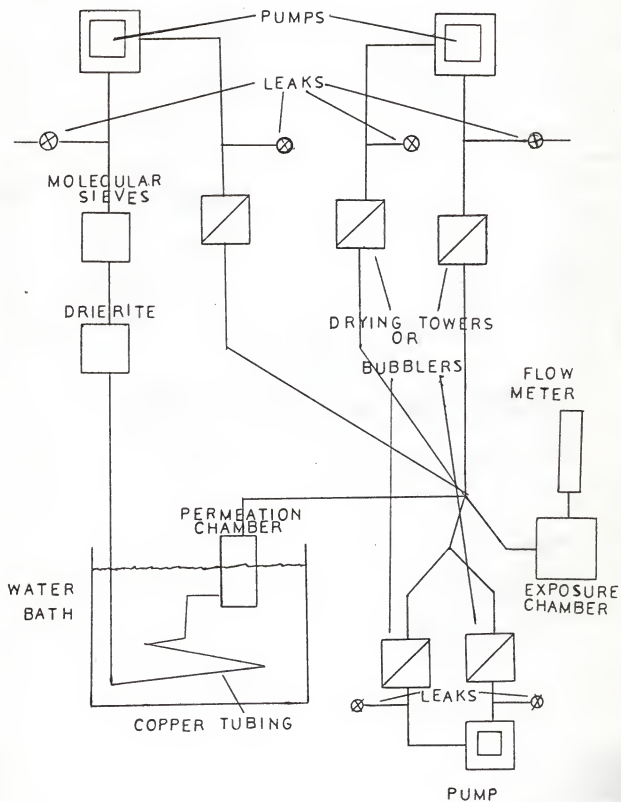


Figure 8: Permeation Chamber Containing Permeation Tube

Figure 9: Exposure Chamber

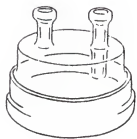
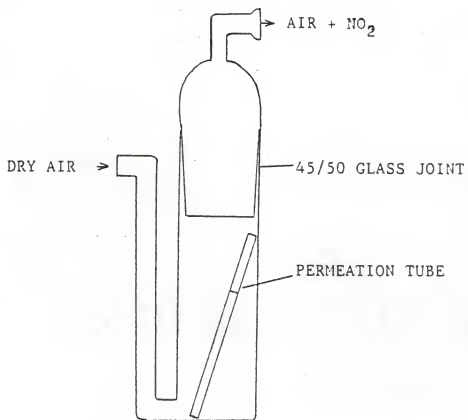


Figure 10: Reagent Blank Spectrum of 1-Methyl-Perimidine

Reference: Whatman No. 2 Filter Paper with No Reagent Applied

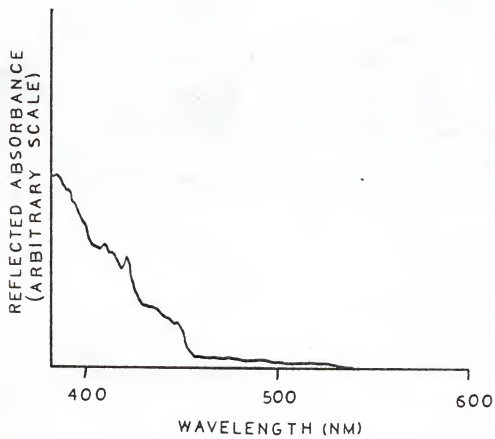


Figure 11: Spectra of 1-Methyl-Perimidine Reagent Papers

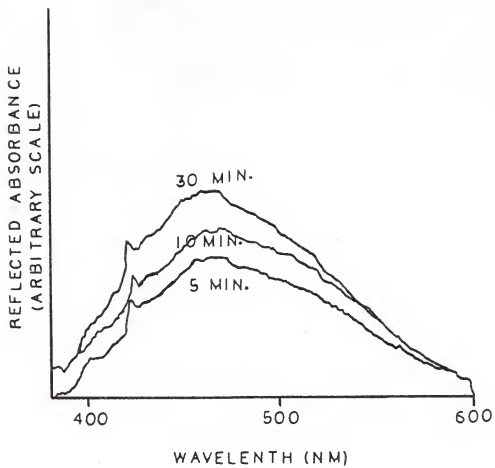


Figure 12: Spectra of 1-Methyl-Perimidine Reagent Papers

Note that as the exposure time is increased from 30 minutes to 3 hours: 1) the wavelength maximum shifts to a shorter wavelength, and 2) the intensity decreases.

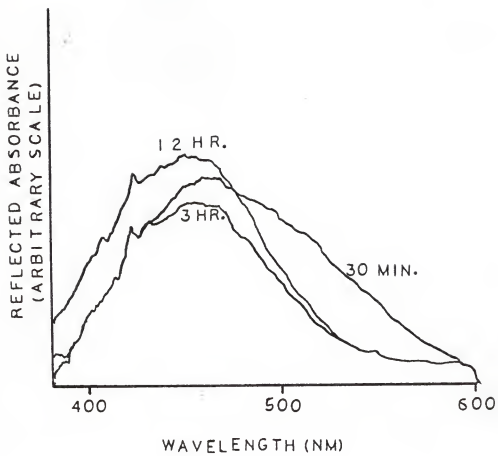


Figure 13: Reflected Absorbance vs. Time

Relative Humidity = 50%

NO₂ Concentration = 0.423 ppm

Range of Individual Measurements for Three Trials I

Standard Deviation ○

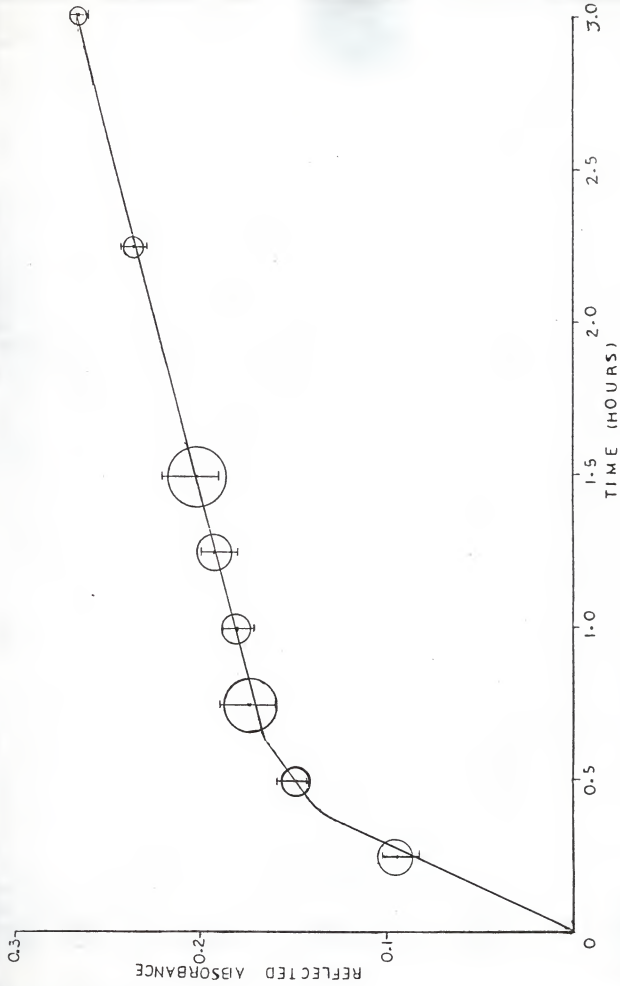


Figure 14: Reflected Absorbance vs. NO_2 Concentration

Relative Humidity = 50%

Exposure Time = 45 Minutes

Range of Individual Measurements for Three Trials I

Standard Deviation ○

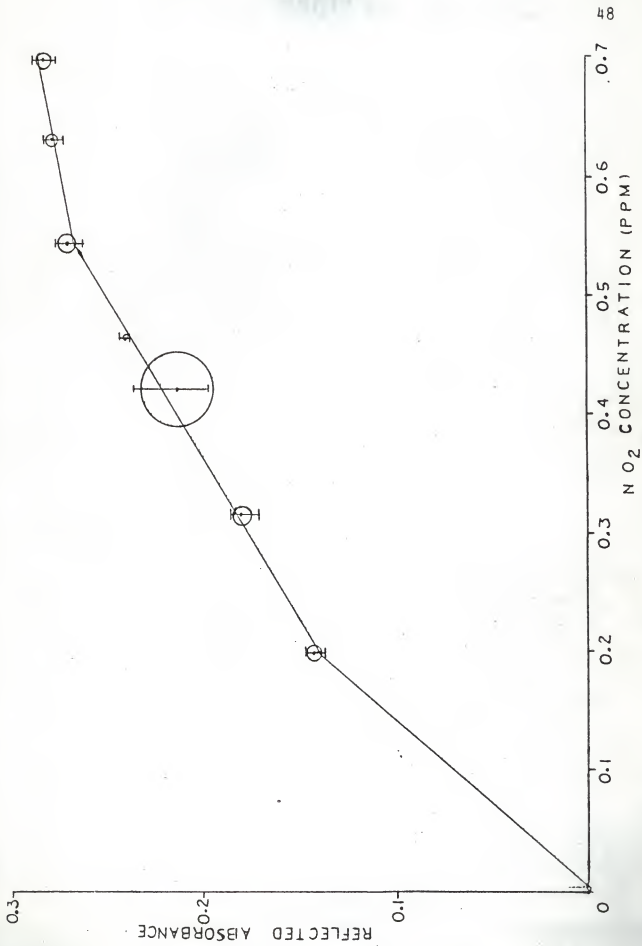


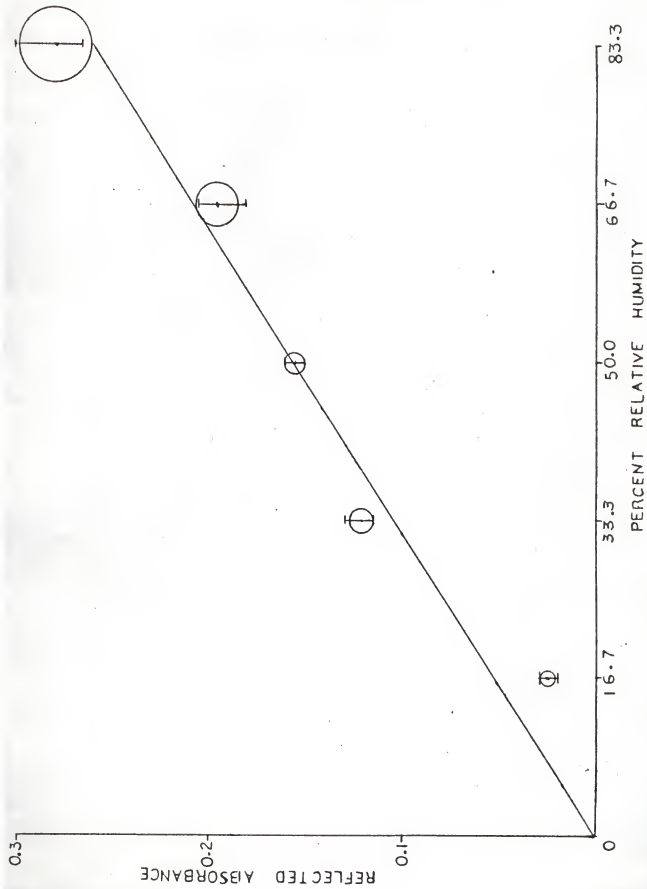
Figure 15: Reflected Absorbance vs. Relative Humidity

Exposure Time = 45 Minutes

NO₂ Concentration = 0.315 ppm

Range of Individual Measurements for Three Trials I

Standard Deviation ○



Chapter IV

CONCLUSION

Of all the reagents prepared and tested, only one, 1-methyl-perimidine, proved to be satisfactory as an analytical reagent for nitrogen dioxide because of its stability and sensitivity. It is capable of detecting fairly low levels of that atmospheric pollutant, as one can see from Figure 14. The quantities of NO_2 measured, from approximately 0.2 to 0.7 ppm, for a 45 minute exposure, are well below the allowable limit of 5 ppm. For this compound to be a truly quantitative reagent, however, a support material of constant or controllable moisture content must be found, because of the sensitivity of its reaction with NO_2 to changes in relative humidity. Nevertheless, 1-methyl-perimidine reagent papers are useful for qualitative testing (similar to litmus or Uristix papers) in that, while they may not yield values as precise as those from instrumental methods, they can very quickly tell even scientifically unskilled personnel whether ambient nitrogen dioxide levels in the air are cause for concern.

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VITA

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COLORIMETRIC REAGENTS FOR NITROGEN DIOXIDE

by

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AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

This research investigated the use of several derivatives of perimidine as solid colorimetric reagents for detection of nitrogen dioxide. The preparations of perimidine and its 1-methyl-, 2-methyl-, 2-phenyl-, 1-acetyl-, and 1-methyl-2-dimethylamino- derivatives are described. Attempts to synthesize (1,3)-benzodiazino-(3,4)- perimidine failed.

Each reagent was then qualitatively tested for response to nitrogen dioxide, which eliminated all but perimidine and its 1-methyl and 2-methyl derivatives from further consideration. Perimidine, however, proved to be subject to air oxidation.

The 1-methyl- and 2-methyl- perimidines were applied to filter paper and tested quantitatively using known concentrations of nitrogen dioxide. The 2-methyl-perimidine-nitrogen dioxide complex, however, lacked color stability. The amount of humidity was found to have a profound effect upon the reagents' response. Reagent sensitivity for 1-methyl-perimidine was increased by applying the deliquescent compound calcium chloride to the reagent paper. This compound, however, destroyed 2-methyl-perimidine. Finally, structure elucidation of the products is described.