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A NEW UNIMOLECULAR REAGENT FOR NITROGEN DIOXIDE ANALYSIS

by

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Manhattan, Kansas

1981

Approved by:

Jack L. Lambert

Major Professor

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Chapter I

INTRODUCTION

Industrial poisoning from the oxygen compounds of nitrogen is a hazard in many industries. They may be found in the atmospheres of chemical plants manufacturing nitric acid and may occur in the welding, metal cleaning and nitration purposes industries. Nitrogen dioxide is the most toxic of the various oxides of nitrogen.

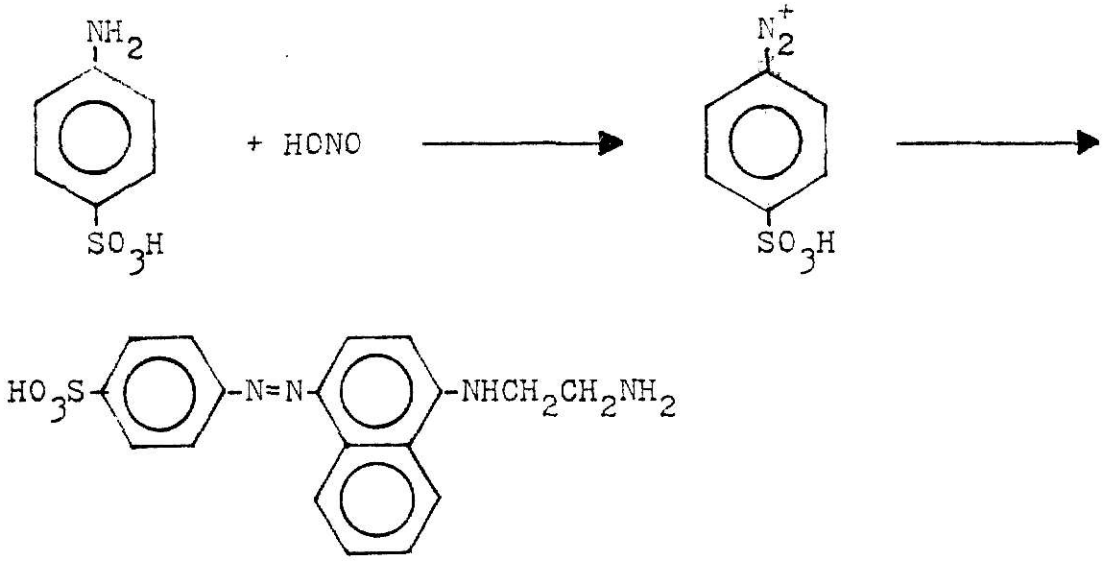
The fumes of nitrogen dioxide are extremely dangerous because of their insidious character. The bad feature of this type of poisoning is that little warning is given to the workers for the nitrogen dioxides fail to set up defensive respiratory reflexes. A concentration of 20 - 25 ppm could irritate the eye, while 150 ppm may bring about strong local irritations, especially in the respiratory organs (1). The generally allowable concentration of daily eight-hours exposures is 5 parts of nitrogen dioxides per million parts of air (2).

Many methods have been developed for the detection of nitrogen dioxide. An early method, although tedious, involves the conversion of nitrogen dioxide to nitrite and the nitration of phenoldisulfonic acid (3, 4). Another approach to this trace analysis is the Griess method (5), which utilizes the nitrite formed from nitrogen dioxide to diazotize sulfanilic acid which in turn couples with 1-naphthylamine to form an azo dye. Many variations of this method have been developed by changing the

coupling reagent or the acid in the solvent. Instrumental methods have also been developed, such as gas chromatography (6), ultraviolet photometry (7), and chemiluminescence (8). Instrumental methods are important but usually expensive in terms of initial cost and maintenance. They also suffer from lack of portability. In many instances, chemical methods of analysis are capable of greater sensitivity in comparison to instrumental methods, and the cost is usually much less.

The most widely used test for the determination of nitrogen dioxide involves the method of Saltzman (9). In this method a reagent mixture of sulfanilic acid, N-(1-naphthyl)-ethylenediamine dihydrochloride and acetic acid is used. Nitrogen dioxide reacts with water to produce nitrous acid, which is the reactive species in a diazotization reaction, only one half of the nitrogen dioxide produces nitrous acid. A further diazotization reaction then takes place, with sulfanic acid, which can couple with N-(1-naphthyl)-ethylene diamine to form red-violet colored azo dyes. After 15 minutes the color is completely developed and the absorbance is measured at 550 nm. This color is then compared with colors produced by adding known amounts of standard sodium nitrite to the absorbing solution and developing the color as described. The reaction is believed to occur according to scheme below:

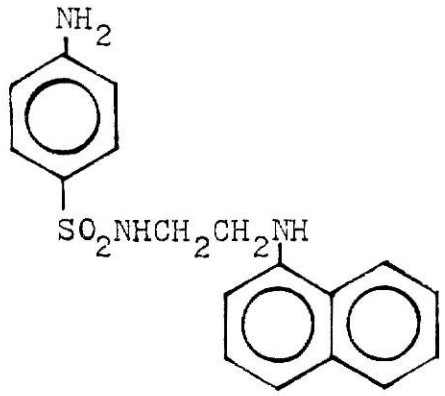
$$2\ NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$



There are several disadvantages for this method. 1. Delicate equipment such as a spectrophotometer, a fritted-glass bubbler, and an aspirator are required. 2. The determination takes a long time and the job is tedious. 3. It is a "wet analysis", so it can not be portable and independent of laboratory services. It is thus very important to develop a convenient and reliable method for a nitrogen dioxide assay. Workers in this laboratory are interested in developing solid state reagents for environmental pollutants (20).

The thesis of this study is that the introduction of both the diazotizing agent and the coupling agent into a single molecule would improve the method by reducing the reaction time and simplifying the analysis. Because procedures for the colorimetric determination of nitrite basically follow the same pattern (10), initial studies were undertaken to determine the nitrite ion in water. Then a solid reagent was developed for determining the nitrogen dioxide concentration in the atmosphere. The proposed

reagent is N-(4-aminophenylsulfonyl)-N'-(1-naphthyl)-ethylene-diamine.



Chapter II

EXPERIMENTAL

This chapter will describe the preparation of the new reagent. The starting materials for both parts of the reagent, acetanilide and N-(1-naphthyl)-ethylenediamine dihydrochloride, were obtained from the Fisher Scientific Company and RSA Corporation, respectively.

This was a three-step synthesis. The first step was the chlorosulfonation of acetanilide. The second step was the combination of the chloride of the 4-acetamidophenylsulfonyl chloride with the amine of N-(1-naphthyl)-ethylenediamine and the last step was the hydrolysis of N-(4-acetamidophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine. The synthetic scheme is shown in Figure 1.

Once the compound was synthesized, it then was studied to determine if it could be used to detect or analytically determine ion and nitrogen dioxide in the concentration range encountered in the atmosphere.

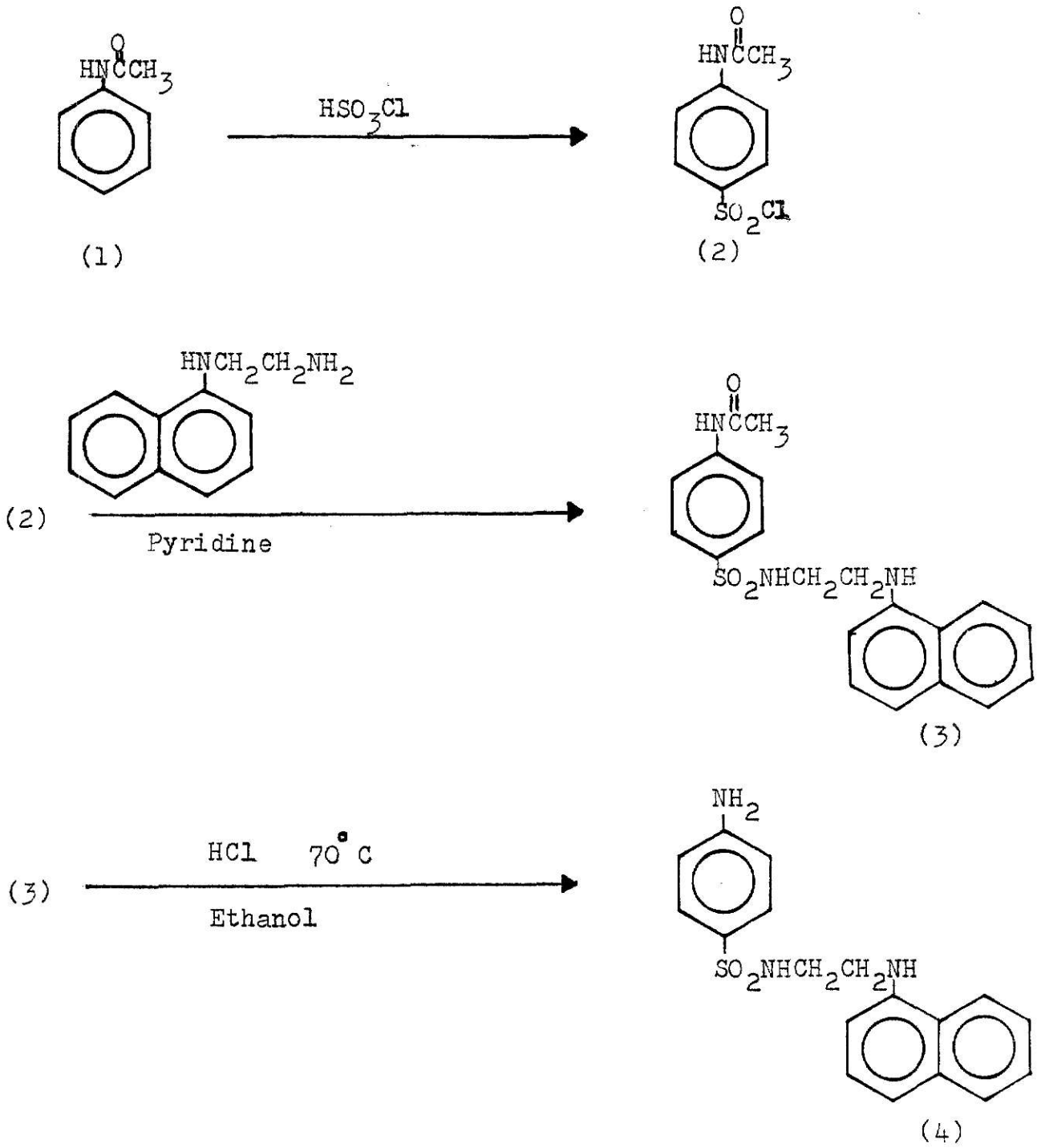

HNCCH3
O
HSO3Cl
SO2Cl
(1)
(2)
HNCH2CH2NH2
(2)
Pyridine
SO2NHCH2CH2NH
(3)
(3)
HCl 70° C
Ethanol
NH2
SO2NHCH2CH2NH
(4)

Figure 1.

Part I

Synthesis of N-(4-aminophenylsulfonyl)-N′-(1-naphthyl)-ethylenediamine

Preparation of p-acetaminobenzenesulfonyl chloride (11)

Chlorosulfonic acid 290 g. (165 c.c., 2.49 moles) was placed in a 500 cc. flask and cooled to below 5°C in an ice bath. Acetanilide 67.5 g. (0.5 mole) was slowly added to the chlorosulfonic acid and the temperature was maintained at approximately 15°C. This reaction should be done in a hood due to the release of large volumes of hydrogen chloride. The mixture was then heated to 60°C for 3 hours to complete the reaction. The syrupy liquid was poured, with stirring, into 1 kilogram of ice water. The white precipitate was then collected by suction filtration. The yield of crude material was 91.1 g. (78%), recrystallized from benzene, m.p. 147°, lit. m.p. 149°; IR (KBr pellet) (Figure 12) 1700 cm^{-1}(C=O), 3300 cm^{-1}(NH); NMR (d_6-DMSO) (Figure 7) 2.21 (s, $-CH_3$, 3H), 7.30-8.03 (m, aromatic, 4H), 8.30 (s, -NH, H).

Preparation of N-(4-acetamidophenylsulfonyl)-N′-(1-naphthyl)-ethylenediamine

To a solution of 18 g. (0.0695 mole) of N-1-naphthyl ethylene diamine dihydrochloride in water, sodium hydroxide (40%) was added until the solution was basic. The oily drops which collected over the water were extracted with three 30 ml portions

of ether. The ether extracts were combined and dried over anhydrous sodium sulfate. After evaporation of the ether, the sticky N-(1-naphthyl)-ethylenediamine was dissolved in 125 ml pyridine. 16.4 g. (0.07 Mole) of p-acetaminobenzene sulfonyl chloride was added gradually, with stirring, at such a rate that the temperature did not exceed 55°C.

The reaction product was then separated by distillation under reduced pressure. The tarry product was obtained by pouring the dark solution into ice water. Crude N-(4-acetamidophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine was formed as a brown solid after several hours. The product was then collected and crystallized from ethanol, yield, 16.1 g. (45%) of purified product. m.p. 171°C. IR(KBr pellet) (Figure 13) 1700 cm^{-1}(NH); NMR (d_6-DMSO) (Figure 8) 2.2 (s, $-CH_3$, 3H), 3.1-3.5 (m, $-CH_2CH_2$, 4H), 5.9 (s, -NH, H), 6.4 (d, -NH, H), 7.2-8.1 (m, aromatic, 11H), 10.1 (s, -NH, H): C-13 NMR (d_6DMSO) (Figure 10) 24.2 ($-CH_3$), 41.2, 43.0 ($-CH_2CH_2$), 102.9, 115.9, 118.8, 121.3, 123.0, 124.0, 125.6, 126.7, 127.7, 128.0, 134.0, 134.2, 142.9, 143.4 (14 aromatic C's), 169.0 (-NHC=O).

Hydrolysis of N-(4-acetamidophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine

N-(4-acetamidophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine, 4.1 g. (0.011 mole), was added to a solution containing 30 ml ethanol and 10 ml concentrated hydrochloric acid, and refluxed for two hours. The reaction mixture was then poured into 30 ml

of ice water and neuturalized with 40% sodium hydroxide solution. The precipitate was filtered and recrystallized from a mixture of tetrahydrofuran and ethanol (1:1). White crystals were obtained; the yield was 3.3 g. (90%). m.p. 180°C; IR (KBr pellet) (Figure 14) 3320, 3420 cm^{-1}(NH_2); NMR (d_6-DMSO) (Figure 9), 3.05-3.5 (m, $-CH_2CH_2$, 4H), 5.7-5.9 (m, -NH, 3H), 6.4 (d, -NH, 1HO, 7.1-8.1 (m, aromatic, 11H); C-13 NMR (d_6-DMSO) (Figure 11) & 41.2, 43.0 ($-CH_2CH_2$), 102.9, 112.9, 115.9, 121.3, 123.0, 124.1, 125.6, 125.7, 126.8, 128.0, 128.6, 134.1, 143.5, 152.6 (14 aromatic C's).

Part II

Nitrite ion determination

Reagent and equipment

Chemicals used were reagent grade or the purest grade available. Deionized water was used for preparing all reagent solutions and for making dilutions. The apparatus used to measure the absorption spectra and data was a Coleman 124 spectrophotometer.

Preparation of the colorimetric reagent

Into a 100 ml volumetric flask, 1 gram of the reagent, N-(4-aminophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine, was placed with 10 ml of concentrated hydrochloric acid, then diluted to the mark. The solution was stored in a refrigerator where it was stable for over six months.

Standard nitrite solutions

These solutions were used to determine if the reagent would work and at what concentration ranges. A stock solution, 250 ppm as nitrite nitrogen, was prepared by dissolving 1.232 grams of sodium nitrite in deionized water and diluting to 1 liter, with 1 ml chloroform as a preservative.

Procedure

To a 50 ml volumetric flask, 20 ml of standard nitrite solution, 1 ml of reagent, and 1 ml of concentrated hydrochloric

acid were added. The solution was diluted to the calibration mark with deionized water and mixed thoroughly. A portion of the solution was then transferred to a 1-cm cuvette. A wavelength of 522 nm was employed in all the following measurements. The absorbance curve is shown in Figure 2. A suitable series of visual color standards were prepared by adding the following volumes of standard nitrite solution with 1 ml of reagent and diluting to 50 ml with 1 ml of concentrated hydrochloric acid: 0, 1, 5, 10, 15, 20, 25, and 30 ml corresponding, respectively, to 0, 0.02, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 ppm nitrite nitrogen. After thorough mixing and 15 minutes color development time, the absorbance was measured. The calibration curve of absorbance versus ppm nitrogen is shown in Figure 3.

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Figure 2. Absorbance curve for the reagent, N-(4-amino-phenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine, in 3.34×10^{-5} M nitrite ion solution.

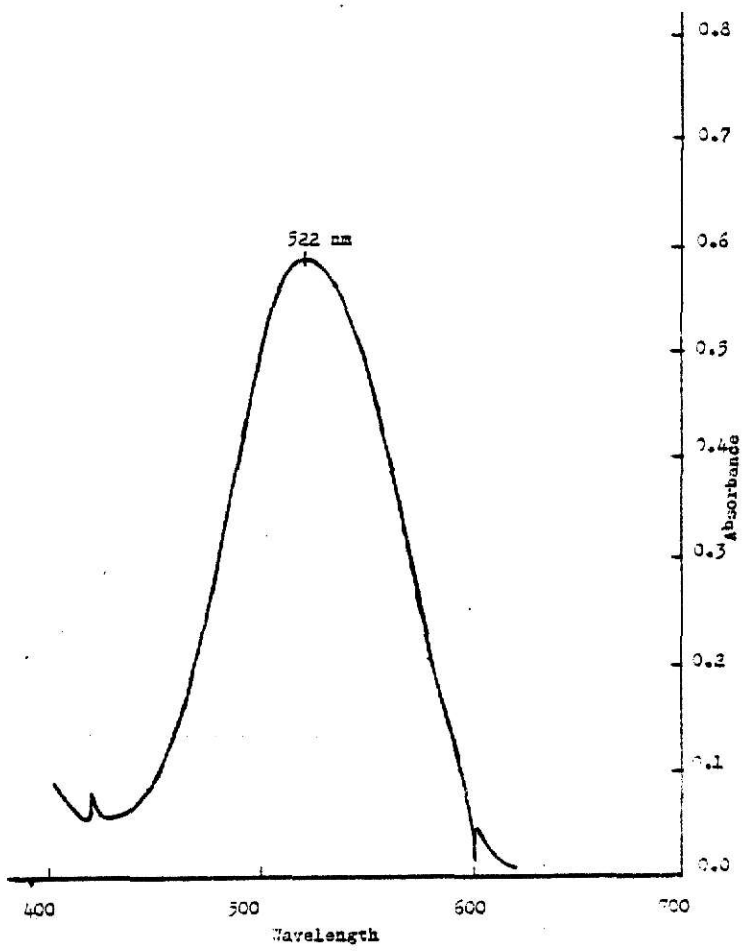

522 nm
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Absorbance
400
500
600
700
Wavelength

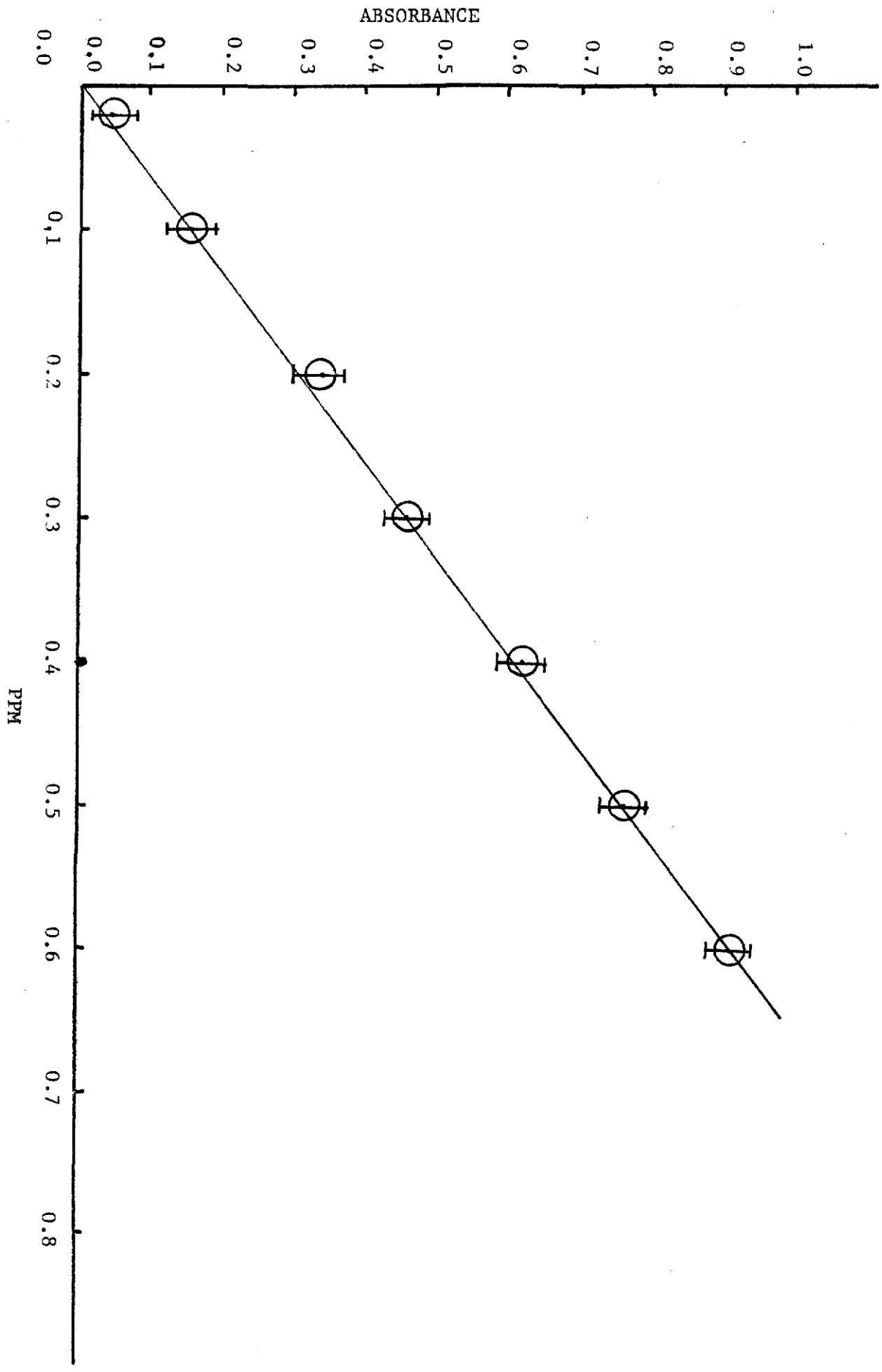
Figure 3. Calibration curve for nitrite N.

(0 - 0.7 ppm)

. Average

I Range

○ Average deviation


ABSORBANCE
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
PPM
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

Part III

Nitrogen dioxide determination

The usefulness of this reagent would be principally for nitrogen dioxide determination. This part of the experiment deals with the development and testing of solid-phase reagents that will determine nitrogen dioxide concentration.

Reagents and equipment

Test paper: Glass microfiber filters, 4.25 cm (diameter), grade GF/C, obtained from Whatman Ltd..

Permeation tube: Teflon 0.3 cm inside diameter, 0.17 cm wall thickness.

Nitrogen dioxide: Commercial grade, obtained from Union Carbide Corporation.

Infusion/withdrawal syringe pump: Model 901, obtained from Harvard Apparatus Co. Inc., Millis, Mass..

Thermostatic bath circulator and controller: Obtained from E. H. Sargent & Co. Chicago, Ill..

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

Preparation of the test paper

A sample of 1.5 ml glycerol was added to 5 ml of reagent solution and mixed well. The solution should preferably be prepared each time a batch of papers is made. A package of 20 pieces of glass filter paper was immersed into the solution for 20 minutes.

The papers were dried in vacuum oven for 6 hours at 56°C. These filter papers were stored in wide-necked glass bottles in the refrigerator.

Preparation of low concentration nitrogen dioxide

Known concentrations of gases may be prepared in a variety of ways (13, 14, 15). Both static and dynamic methods have been used. Static methods have very serious limitations at low concentrations, especially for strong oxidizing gases such as nitrogen dioxide and ozone. The principal disadvantage of a static system is adsorption of the active gas on the container walls. Dynamic methods have many advantages over static methods and are especially useful in producing reactive gas mixtures. The concentration of test gases from 50% down to the part-per-billion range can be controlled and altered easily with conveniently compact equipment. Wall adsorption usually becomes negligible since an equilibrium is established after operating for a sufficiently long time period.

Two flow dilution methods of nitrogen dioxide introduction were used in this experiment.

A. Motor-driven injection method: A diagram of the dilution system used is shown in Figure 4.. A motor-driven syringe filled with pure nitrogen dioxide gas from a tank was used to inject the nitrogen dioxide into the air stream flow at a constant rate. The air was throughly mixed in a mixing chamber, then passed through the sample holder. The concentration of

nitrogen dioxide was regulated by the rate of the motor-driven syringe and adjusting the flow of air. The flows were accurately measured by a gas flowmeter.

B. Permeation method: A diagram of the dilution system used is shown in Figure 5. The entire apparatus was constructed from Pyrex glass with Teflon joints. A 7 cm Teflon tube was selected and then immersed in liquid nitrogen. Nitrogen dioxide gas was condensed and sealed in the permeation tube by using beads as seals. It is desirable to wait several days after filling before calibration. The primary calibration of the tube consisted of collecting weight data (losses) over a period of days, weeks or months. Weight losses were converted to permeation rates, expressed as μg/minute.

The nitrogen dioxide permeation rate of this permeation tube is 3.2 μg/minute. Since the permeation rate is very sensitive to temperature, the whole system was maintained in a constant temperature bath. The constant temperature of this system was 24°C. The nitrogen dioxide dilution was determined by the air flow rate. The standard nitrogen dioxide concentration can be calculated from the expression:

$$C = \frac{(22.4 \times 10^6) \times (T/273^\circ K) \times (760mm/P) \times Pm\_R}{Gs\_R \times MW} \quad (A)$$

T: Temperature of the system (297°K).

P: Pressure of the system (735 mm Hg).

Pm_R: Permeation rate (3.2 μg/minute).

Gs_R: Flow rate of the diluent gas (L/min) (See figure 6).

MW: Molecular weight of the permeating material (46.0 g/mole).

The motor-driven syringe used in method A does not have the advantage of continuous operation, although under proper conditions filling may not be necessary more often than every several hours. Metering of nitrogen dioxide from the syringe containing the pure gas was troublesome due to the fact that the gas is very close to its liquefaction point (21.3°C at 1 atm pressure). The permeation method offers several advantages over method A, such as its simple operation, its accuracy and its high precision. Therefore, method A was used during most of this experiment.

Procedure

The air pump was turned on and the air flow rate was adjusted by means of the gas flowmeter. The system was flushed for five minutes before use. The nitrogen dioxide concentration related to the flow rate as shown in equation A. A piece of the impregnated glass filter paper was placed in the sample holder, and the apparatus connected to the test atmosphere. The mixture of nitrogen dioxide and air was passed through the sample holder for five minutes. The test paper was removed from the sample holder and compared to the purple color developed with standards prepared by other situations.

Figure 4. A Motor-driven Injection Nitrogen Dioxide Gas Dilution System.

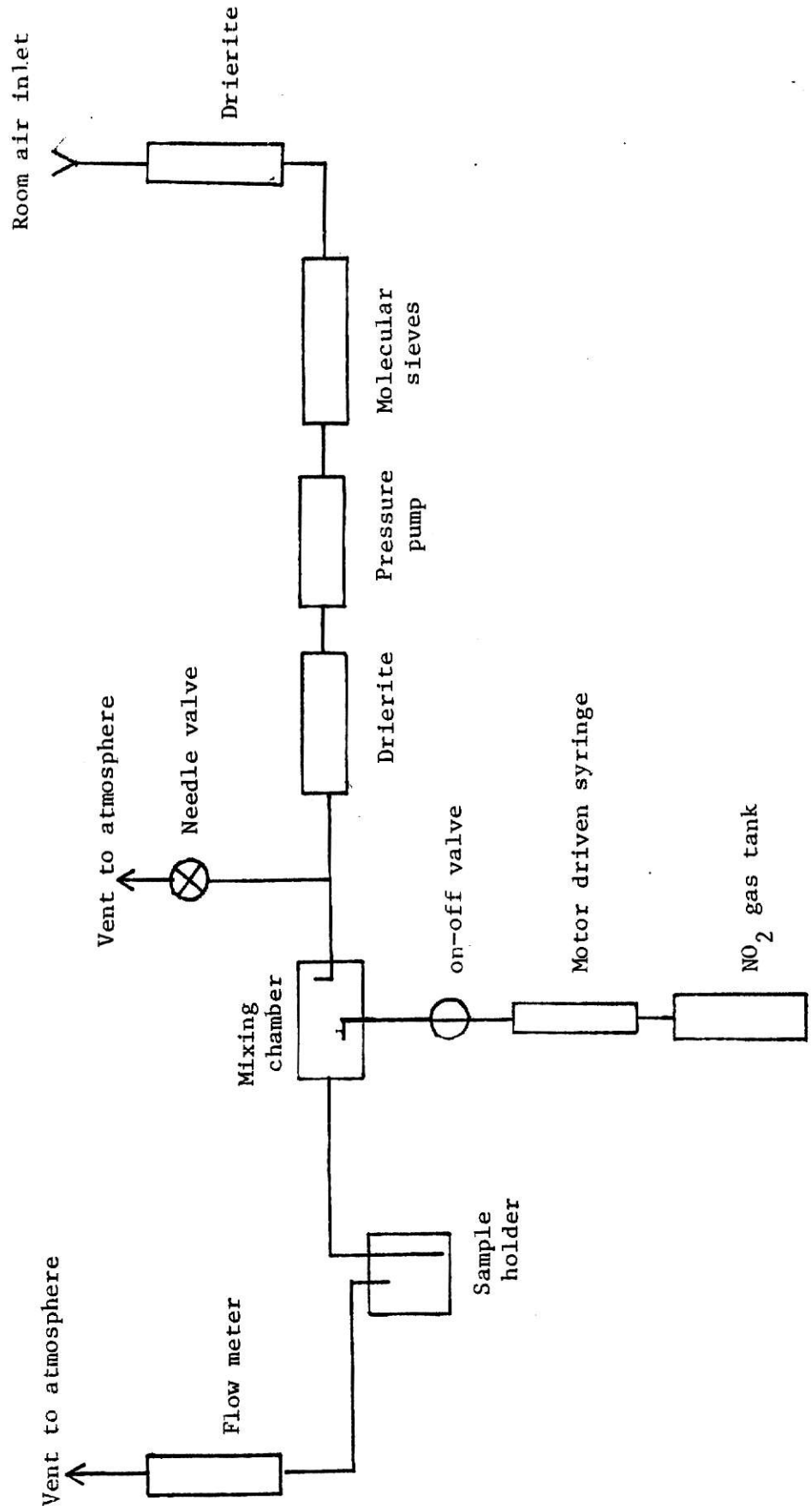

Room air inlet
Drierite
Molecular sieves
Pressure pump
Drierite
Vent to atmosphere
Needle valve
on-off valve
Motor driven syringe
NO_2 gas tank
Mixing chamber
Sample holder
Flow meter
Vent to atmosphere

Figure 5. A Permeation Nitrogen Dioxide Gas Dilution System.

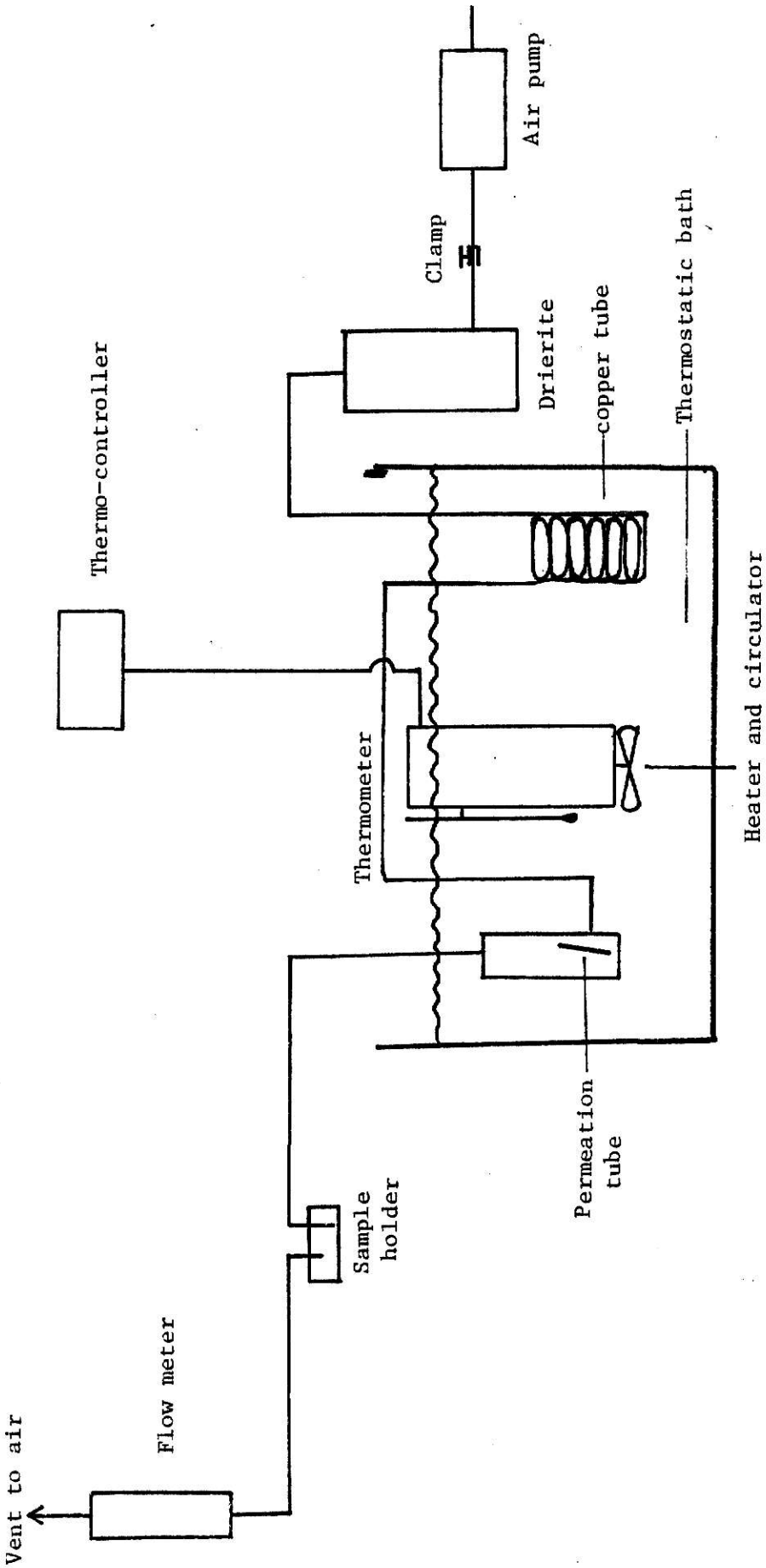
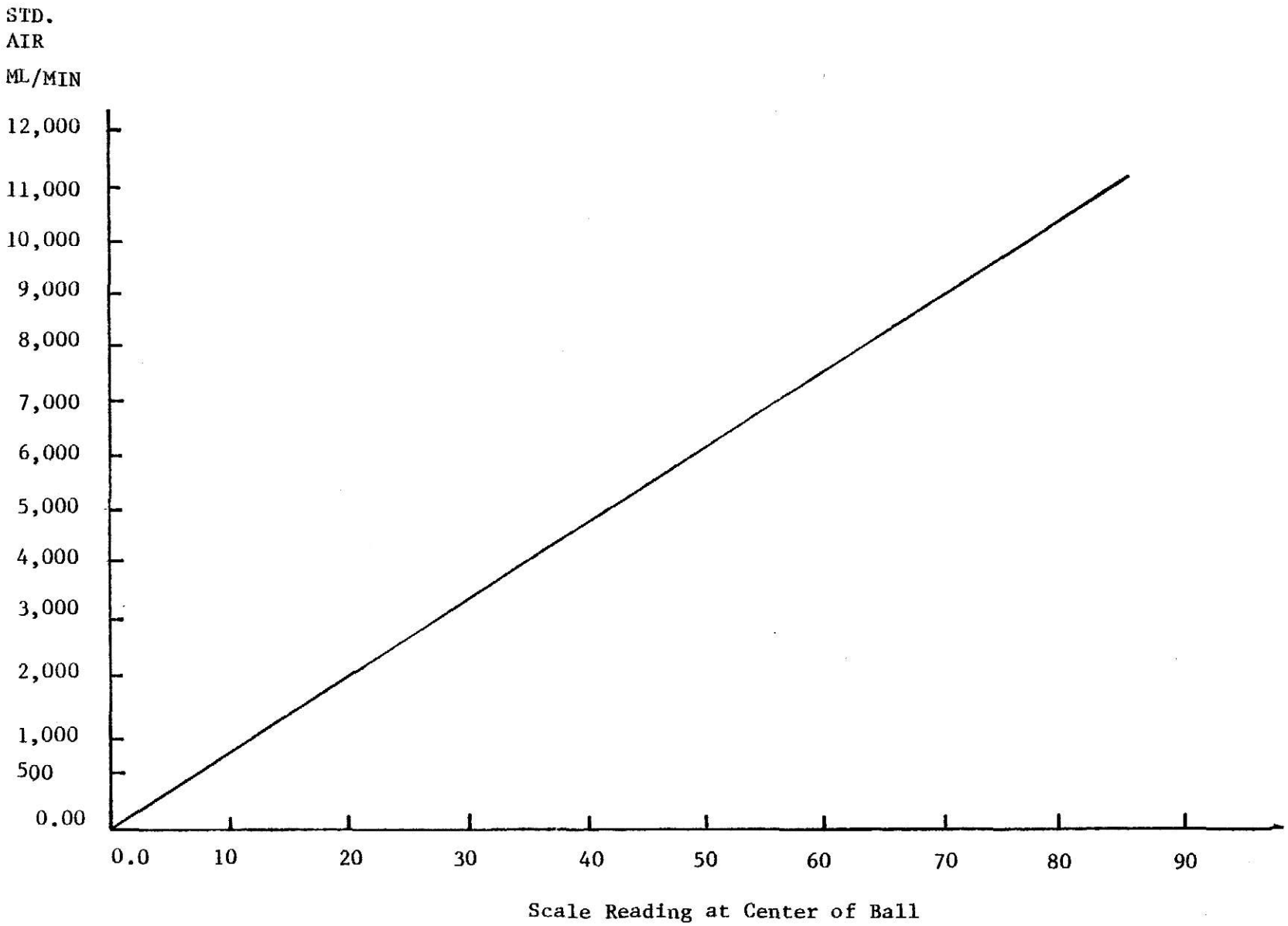

Air pump
Clamp
Drierite
copper tube
Thermostatic bath
Thermo-controller
Heater and circulator
Thermometer
Permeation tube
Sample holder
Flow meter
Vent to air

Figure 6. Calibration Chart of Flowmeter.


STD.
AIR
ML/MIN
12,000
11,000
10,000
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
500
0.00
0.0
10
20
30
40
50
60
70
80
90
Scale Reading at Center of Ball

Chapter III

RESULTS AND DISCUSSION

The successful synthetic route used for making the new reagent, N-(4-aminophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine, could be modified for the design of other new reagents or types of chromophores for nitrite and nitrogen dioxide determination. The major weakness in the synthetic route was the second step that gave low yields and a product that was not easily isolable.

The determination of nitrite in a variety of matrices is very important in air pollution control. Numerous analytical methods have been developed for the determination of nitrite (16, 17). The most widely used methods are spectrophotometric ones. The method in which sulfanilamide is diazotized by nitrite and coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to produce a highly colored azo compound has for many years been the main colorimetric method for nitrite determination. The advantages of this method include its rapid color development, the color stability, high sensitivity, and simplicity (18). In the nitrite determination using our new reagent the time required for full development of color was less than 15 minutes and the intensity of color remained constant for over 3 hours. These values agree well with the values found in the literature (19).

The reagent is fairly stable in the solid state and in solution. Figure 3 shows a plot of absorbance versus standard nitrite concentrations. It clearly shows a good linear relation-

ship in the range of 0.02 to 0.6 ppm of nitrite nitrogen ion. This level of sensitivity is quite acceptable for the analytical determination of nitrites.

In reviewing the literature, little information was found concerning gas solid reactions of nitrogen dioxide. Most studies of the reactions of nitrogen dioxide with organic compounds have been concerned with solution systems. This research deals with a solid state reagent and uses a test-paper method which is a common method for solid reagent analysis. Test-papers play an important role in this kind of analysis. Various types of filter papers were studied in this research. The author found that Whatman glass filter paper (grade GF/C) was the best of the other filter papers tested. However, a problem arises in that the impregnated test-papers can not be stored over three weeks at room temperature. The impregnated test-papers turn dark gray and lose their sensitivity. This gradual deterioration may be due to temperature instability, hydrolysis or traces of oxidants absorbed on the test paper which react with the reagent. Storing the test-papers in a refrigerator at low temperature appreciably increases its storage life. A comparsion of this reagent with its separated fragments (N-(1-naphthyl) ethylenediamine dihydrochloride & sulfanilic acid) was made. The results show that the color development of the new reagent is faster than the color development of the separated reagents, and the color intensity of the new reagent is much stronger than the intensity obtained of the separated reagents with similar concentrations of nitrogen dioxide. These

results can be explained by the close proximity of the reactive components, where phase separation cannot occur as is possible with the separated components. Humidity is an important factor in the results of this experiment. Glycerol is a well known humectant and was incorporated in the test-paper design. It may, however, contribute to the instability of the reagent on storage. The addition of gercerol considerably increased the sensitivity. Other kinds of humectants such as stannic chloride, sodium bisulfate, and ammonium bisulfate were also tried, but the results were poor.

This investigation shows the advantages of gas solid analysis, such as

(a) It has high sensitivity - the detection limit of this reagent for nitrogen dioxide was approximately 0.4 ppm. This level is far below the general standard 5 ppm required.

(b) It has good speed - usually, the reaction time is less than 5 minutes which is shorter than the usual time of a nitrogen dioxide assay.

(c) It has simplicity - only one unimolecular reagent was used in the analysis. Sophisticated instruments were not needed.

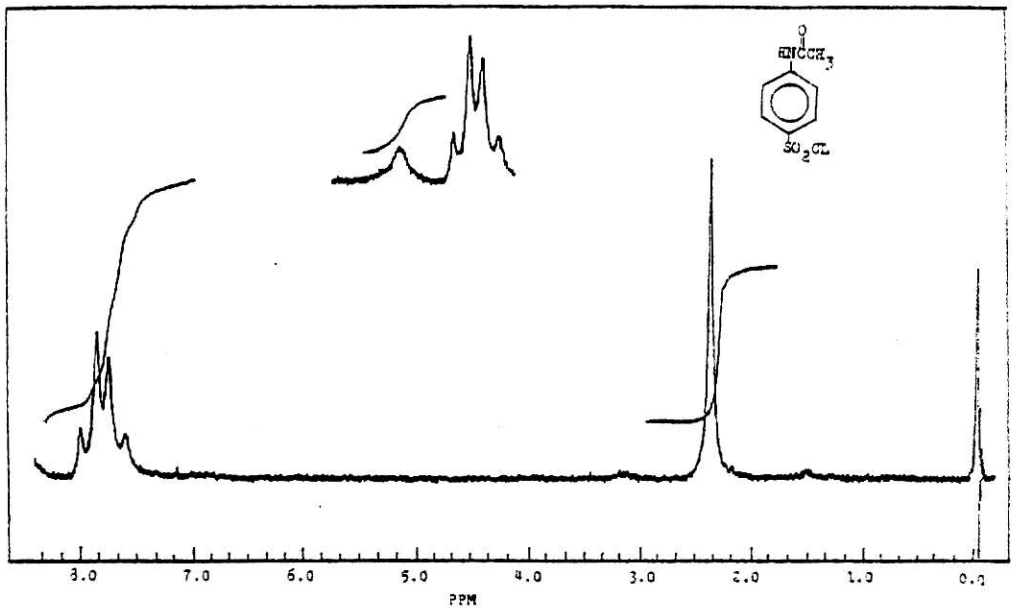
Although test-paper methods often lack accuracy, they have the important advantage of being easy to operate even by scientifically unskilled personnel. Such methods are therefore frequently prefer for use in factory conditions, especially when a rapid determination of the concentration of a toxic constituent

of the atmosphere is required.

Further studies of this new reagent should be undertaken to increase its storage life on test-papers at room temperature, learn how other interferences effect the results, and quantitatively determine nitrogen dioxide by this reagent in its solid state. As the short storage life (at room temperature) may be due to hydrolysis, or solvolysis by glycerol, a linkage different from the sulfamino should be explored. Use of a quaternary ammonium group attached to the naphthylamino moiety would avoid the possibility of hydrolysis, contribute to color stability of the reacted reagent, and serve the same electron-withdrawing capability as the sulfamino group. In addition, a set of permanent color-comparison standards must be developed for quantitative comparison.

Figure 7. NMR spectrum of p-acetaminobenzenesulfonyl chloride. (d_6-DMSO-internal TMS)

Figure 8. NMR spectrum of N-(4-acetamidophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine.
(d_6-DMSO-internal TMS)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7.0
6.0
5.0
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3.0
2.0
1.0
0.0
PPM

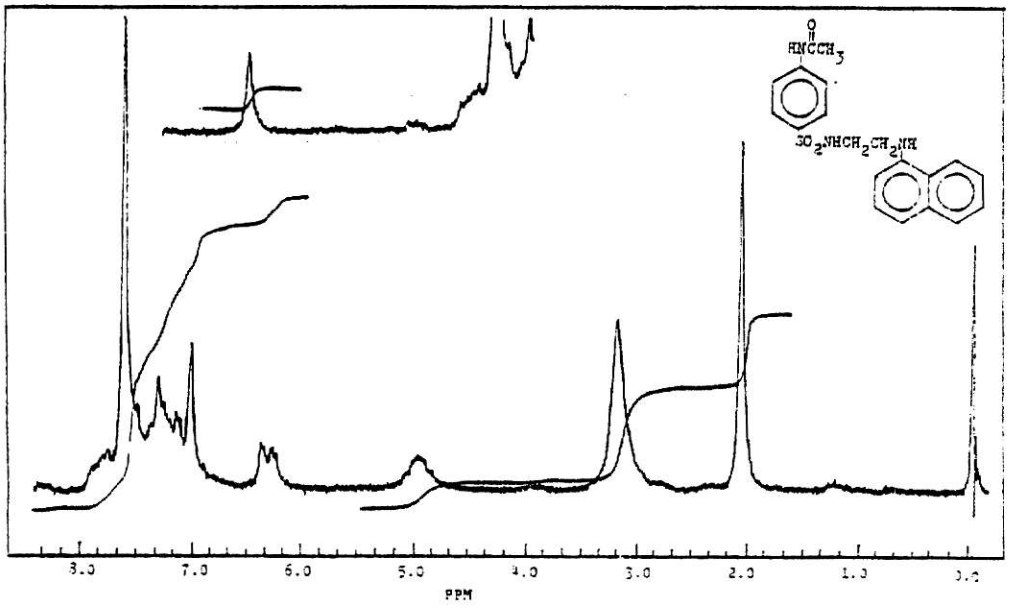

HNCCH3
SO2NHCH2CH2NH
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

Figure 9. NMR spectrum of N-(4-aminophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine.
(d_6-DMSO-internal TMS)

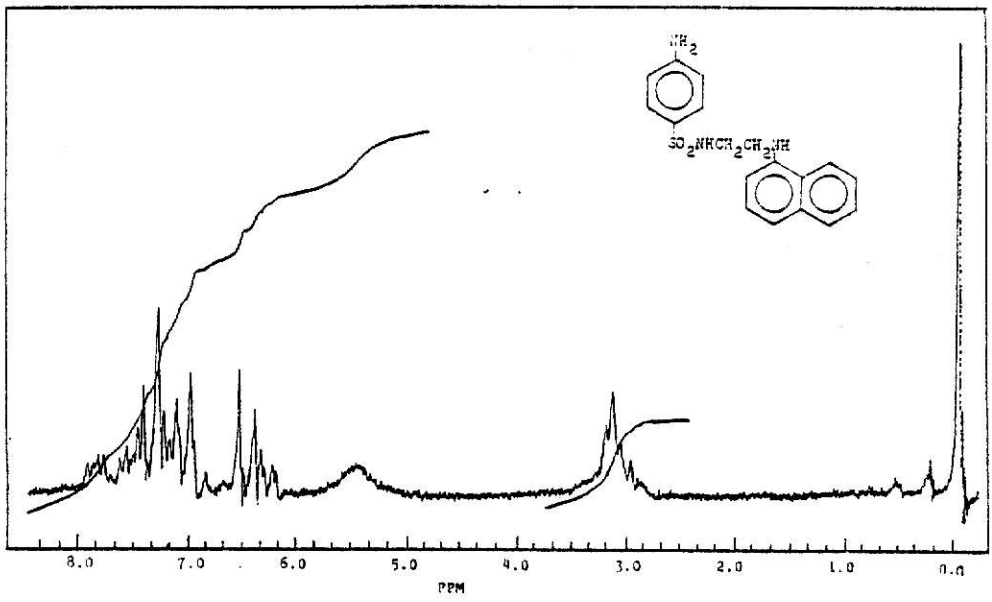
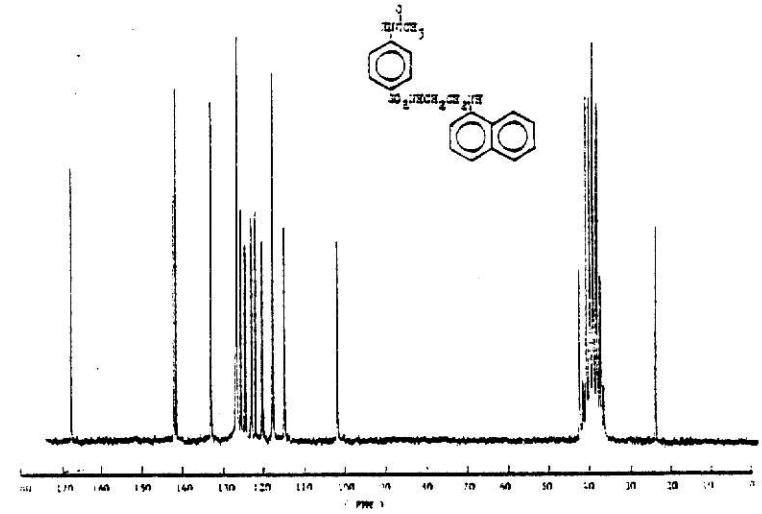

NH2
SO2NHCH2CH2NH
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

Figure 10. C-13 NMR spectrum of N-(4-acetamidophenylsulfonyl)-N′-(1-naphthyl)-ethylenediamine.
(Solvent : d_6-DMSO)

Figure 11. C-13 NMR spectrum of N-(4-aminophenylsulfonyl)-N′-(1-naphthyl)-ethylenediamine.
(Solvent : d_6-DMSO)



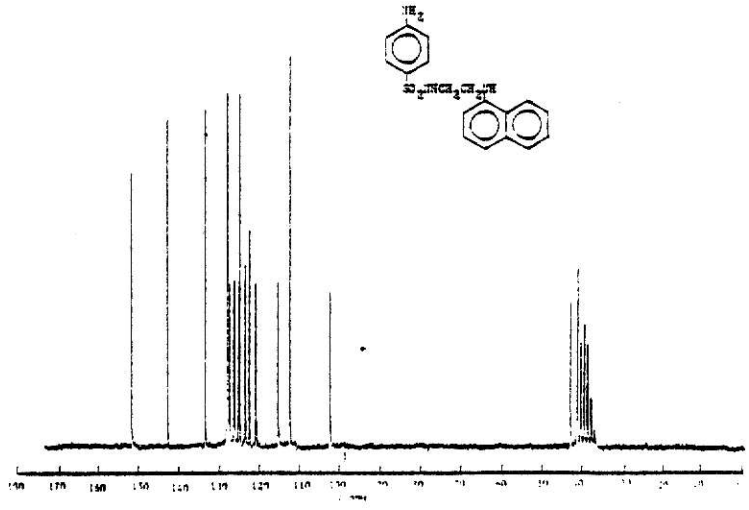
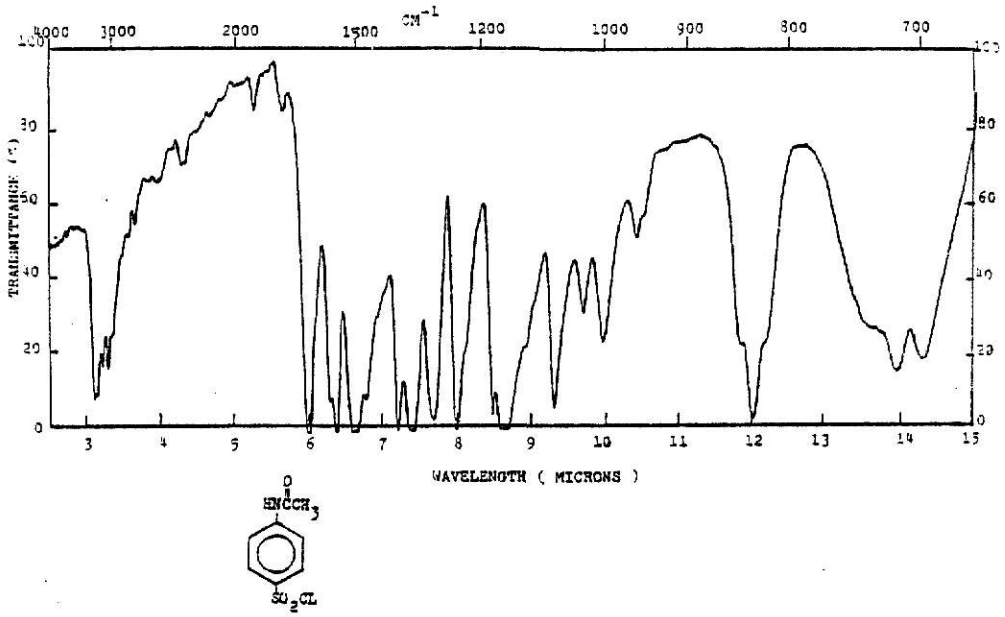


Figure 12. IR spectrum of p-acetaminobenzenesulfonyl chloride. (KBr pellet)

Figure 13. IR spectrum of N-(4-acetamidophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine. (KBr pellet)


4000
3000
2000
1500
CM-1
1200
1000
900
800
700
TRANSMITTANCE (%)
WAVELENGTH (MICRONS)
HNCCH3
SO2CL

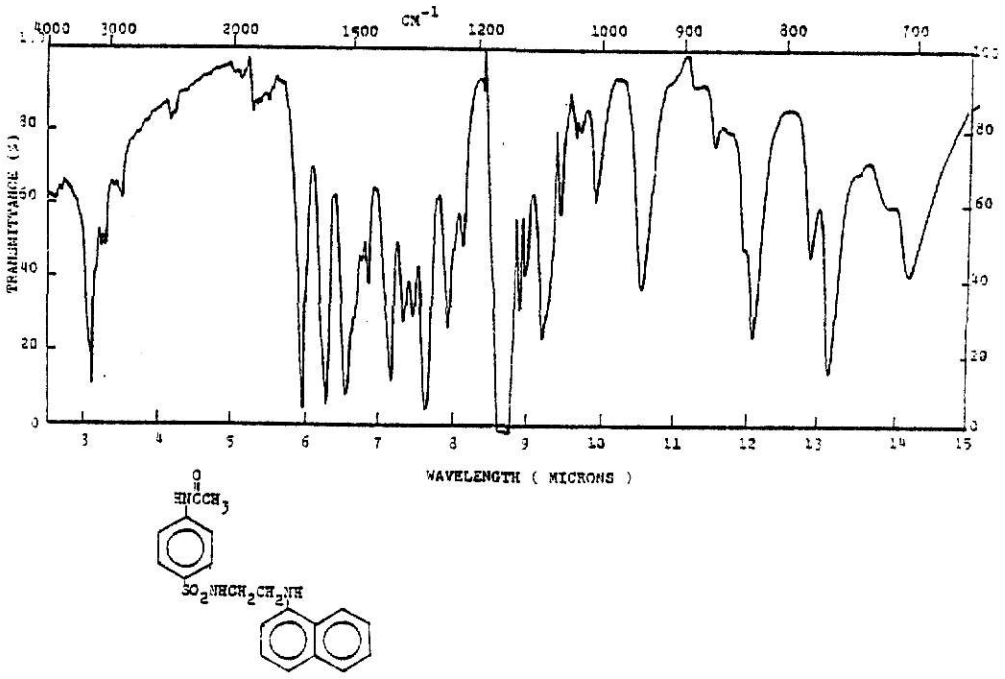
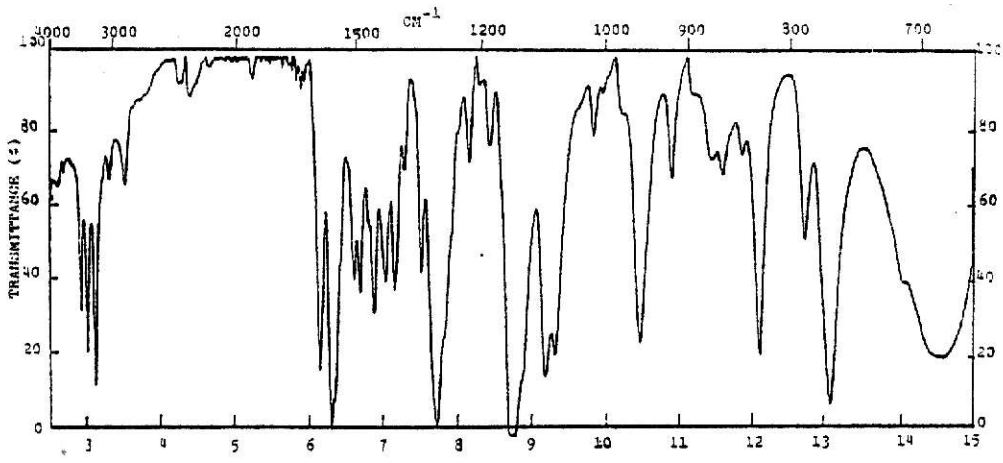
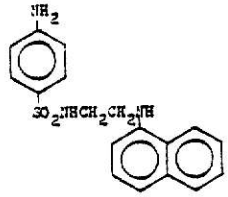

4000
3000
2000
1500
CM-1
1200
1000
900
800
700
TRANSMITTANCE (%)
WAVELENGTH (MICRONS)
HNCCH3
SO2NHCH2CH2NH

Figure 14. IR spectrum of N-(4-aminophenylsulfonyl)-N´-(1-naphthyl)-ethylenediamine. (KBr pellet)


cm-1
4000
3000
2000
1500
1200
1000
900
800
700
TRANSMITTANCE (%)
100
80
60
40
20
0
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)


NH2
SO2NHCH2CH2NH

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A NEW UNIMOLECULAR REAGENT FOR NITROGEN DIOXIDE ANALYSIS

by

TIEN-YOU CHENG

B.S., Tung Hai University, 1974

M.S., Tsing Hua University, 1976

AN ABSTRACT OF A MASTER'S THESIS

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requirements for the degree

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Manhattan, Kansas

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ABSTRACT

In the course of this research, a new solid reagent, N-(4-aminophenylsulfonyl)-N'-(1-naphthyl)-ethylenediamine, was developed for the analysis of nitrogen dioxide. Three steps were required for this synthesis which started with acetanilide an and N-(1-naphthyl)-ethylenediamine dihydrochloride. Once the compound was synthesized, it was used in the analysis of nitrite ion and nitrogen dioxide. In the nitrite determination, the results showed than such a reagent could be used for the detection of nitrite in solution in the range of 0.02 to 0.6 ppm. This is acceptable for the analytical determination of nitrites.

The solid state analysis system was developed for nitrogen dioxide determination using the same reagent. The permeation tube method served as an acceptable technique for preparing standard low nitrogen dioxide concentrations. The reagent was impregnated on the test-paper which was later used to determine the nitrogen dioxide concentration. The reagent's detection limit for nitrogen dioxide was approximately 0.4 ppm. This investigation showed the advantages of gas solid analysis such as high sensitivity, short analysis time and simple procedure. A problem which occurred when working with this reagent was its instability when stored at room temperature. Further research should be done in order to prolong its storage life, and to develop a set of permanent color comparison standards for quantitative comparisons.