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Determination of aromatic amines by diazonium salt

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ABSTRACT

Title of Thesis: Determination of Aromatic Amines by Diazonium Salt

Hong-hue Hsu, Master of Engineering Science, 1988

Thesis directed by: Dr. Barbara Kebbekus
Professor of Chemistry
Assoc. Chair, Department of Chem. Eng., Chem., and Eng. Science.

There are many analytical methods used in the identification of aniline by the production of various colors upon treatment with certain reagents. In this work a new inexpensive, easy and sensitive methods to quantitate aniline is developed. The change of absorbance is large enough to measure with a difference of only 1 ppm in the aniline concentration.

In this method, the reagent (2,4-dinitrodiazonium sulphate) which reacts with aniline produces a yellow color. Formation of this color (which absorbs at 486 nm) indicates the presence of aniline. The amount of aniline can be determined by measuring the absorbance at 486 nm.

When this was applied to a simulated air sample, the results show a linear relation between the concentration of aniline and the absorbance. It indicates that this method can be used in analysis of air samples for aniline.

DETERMINATION OF AROMATIC AMINES BY DIAZONIUM SALT

by

Hong-hue Hsu

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of
Master of Engineering Science

September 1, 1988

APPROVAL SHEET

Title of Thesis: Determination of Aromatic Amine by Diazonium Salt

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Signatures of Other Members of The Thesis Committee.

9/8/88
9/9/88

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I. INTRODUCTION:

Aniline is the oldest of the commercial synthetic organic chemicals. It was initially produced in quantity by Sir William Henry Perkin about 1858 as an intermediate in the manufacture of the world's first synthetic dye, mauve. The early commercial success of dye manufacture rapidly led to many other industries based on the use of synthetic organic chemicals. Three of these, the pharmaceutical, rubber processing, and photographic industries, in addition to the dye industry, consume very large quantities of aniline today. In 1962, more than 137,000,000 pounds of aniline were produced in the United States for domestic use alone(1).

Aniline is a highly toxic chemical; it is readily absorbed through the skin in dangerous amounts and may be fatal if its vapors are inhaled. Therefore good ventilation is highly important. There should be substantial air flow away from all working areas. In a laboratory, aniline should be stored and used only in a hood. It should be handled with proper precautions and any careless operation should be prohibited(2).

There are several analytical methods for the determination of aniline(3). Preliminary examination may be done by visual inspection or by a more exact comparison using APHA cobalt-platinum color standards, as outlined in ASTM D 1209-62. Most of the identification methods are accomplished by the production of various colors upon treatment with certain reagents(4-17). Some other analytical methods include direct analysis by Ultraviolet (UV) Spectroscopy(18-23), Infrared Spectroscopy, or Gas Chromatography.

In this research, we develop a new colorimetric method to quantitate aniline. This method is inexpensive, simple and very sensitive when the amount of aniline is more than four ppm in solution.

The chemistry of this analytical method comes from dyestuffs chemistry. Aniline shows a very sensitive reaction with diazonium salts and a characteristic color appears immediately when these reagent are mixed together. Formation of the color (usually yellow but dependent on the specific diazonium salt) indicates the presence of aniline. The amount of aniline can also be determined via UV spectrometry by measuring the absorbance difference even at very low concentration.

In order for this method to work, it is necessary to form a stable diazonium salt. Diazotisation of 2,4-Dinitroaniline produces a diazonium salt (2,4-Dinitrodiazonium sulphate) which is stable in concentrated sulfuric acid(24). Its reaction with aniline produces a yellow color, which absorbs at 486 nm. This diazonium salt is not stable when isolated from solution, but it is very stable in concentrated sulphuric acid solution. A number of experiments can be done with this diazonium salt solution without isolation(25-28).

When this analytical method is applied to a simulated air sample, the result shows a linear relation between the concentration of aniline and absorbance. It indicates that this method can be used in analysis of air samples for aniline.

II. THEORY:

Aniline is an aromatic primary amine. Hence, its reactions may involve either its amine group or one or more of its aromatic carbons. In a number of cases, such as cyclic condensations, both types of reactive points of its structure may be involved(26).

Diazonium salts are oxidising agents; they are electrophilic reagents which may replace a hydrogen atom attached to carbon when that atom is activated by an activating group. A covalent N-C link is formed and the diazo-compound is said to have coupled:

$$ArN_2X + HR \dashrightarrow ArN_2R + HX$$

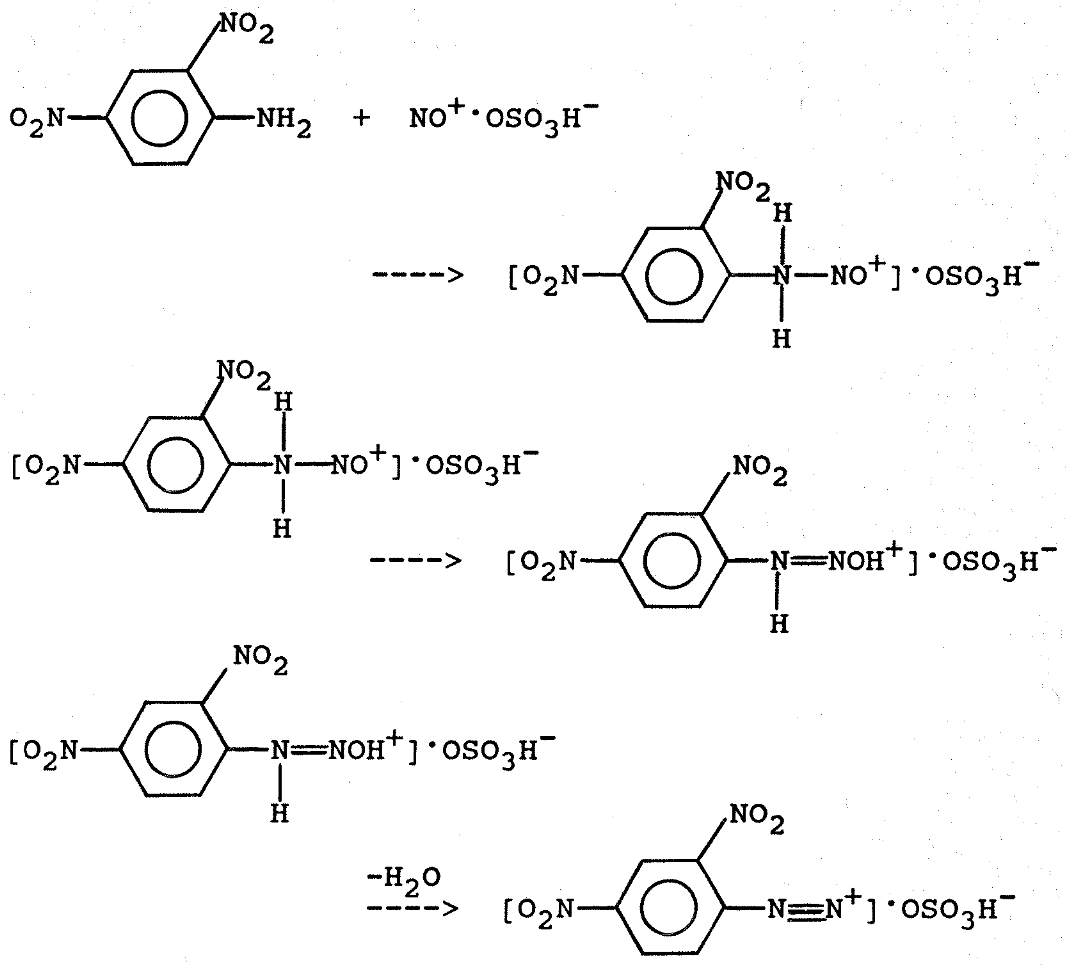
HX may be a molecule of either acid or water. If the coupled compound contains more than one hydrogen atom of suffient reactivity, then coupling may take place twice or more(26).

The reaction of aniline with 2,4-Dinitrodiazonium sulfate is one kind of coupling reaction. Both of the reagents are almost colorless and lack any absorption at 486 nm. After the coupling reaction, a strongly colored azo-compound is formed which can be detected at very low concentration.

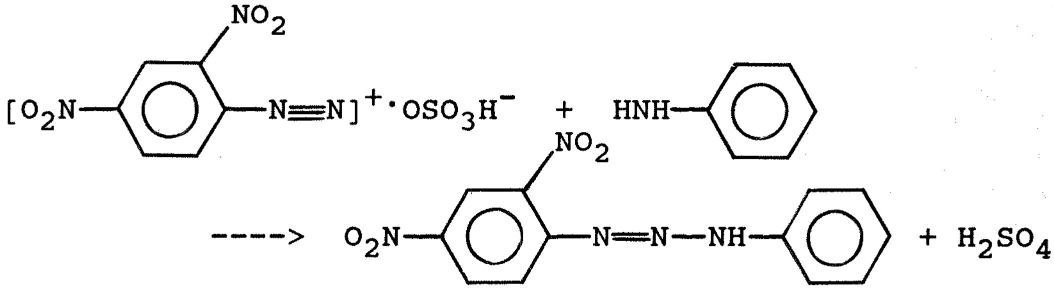
A possible mechanism of this reaction is summarized as follows(27-31):

(1) Formation of diazonium salt by diazotisation of 2,4-Dinitroaniline.

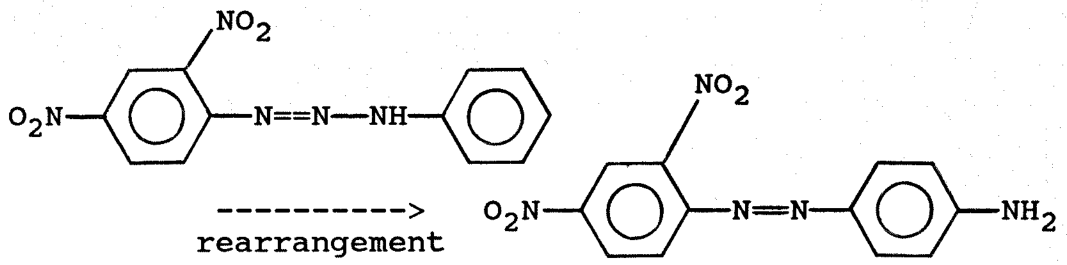
$$NaNO_2 + H_2SO_4 \dashrightarrow NO^+ \cdot OSO_3H^-$$



(2) Formation of Azo-compound from coupling reaction.



2,4-Dinitrodiazoaminobenzene
(Yellow)



2,4-Dinitroazoaminobenzene
(yellow)

The coupling reaction is spectacular because of the rapid formation of brightly colored products from colorless components. The products have a specific absorption at 486 nm. From the absorbance, and according to Beer’s law, the amount of aniline can be determined spectrophotometrically by the intensity of the yellow color at 486 nm.

III. EXPERIMENTAL:

A. Preparation of 2,4-Dinitrodiazonium sulfate.

Dry sodium nitrite (ACS grade; by J.T. Baker) (3.5 g) is slowly added with stirring to sulfuric acid (Electronic grade; by Hi-Pure Chemicals, Inc.) (sp.gr. 1.80, 75 c.c.), allowing the temperature to rise, and if necessary raising it to 70°C to ensure complete dissolution. The 2,4-Dinitroaniline (HPLC grade; by Fluka Chemie AG, CH-9470 Buchs) (8.35 g =

0.05 mole) is added over about twenty minutes at 30 ~ 35^{o}C, and then the solution is stirred for two hours while the temperature is allowed to fall to room temperature. This solution can be stored at room temperature before using.

B. Preparation of standard Aniline Solution. (1000 ppm)

Pipet 2 ml of pure aniline (purified grade; by J.T. Baker) into a 100 ml volumetric flask and dilute to volume with acetonitrile.

Pipet 5 ml of this solution in another 100 ml volumetric flask dilute to volume with acetonitrile.

Conc. of aniline = 2 ml / 100 ml x 5 ml / 100 ml

= 1,000 x 10^{-6} ml/ml = 1,000 ppm

In this experiment each time 1 ml is diluted to 25 ml of acetonitrile, a solution containing 40 ppm is produced.

1 ml x 1,000 ppm / 25 ml = 40 ppm

C. The procedure of coupling reaction.

1. Place about 0.03 ml of the diazonium sulfate solution in 25 ml acetonitrile. (Pipet 0.5 ml of diazonium salt solution into a 10 ml volumetric flask and dilute to volume with acetonitrile, then

take out 0.6 ml of this solution which concentration is 0.03 ml of diazonium salt solution.

2. Add deserved amount of aniline standard solution (1000 ppm) into the above diazonium solution to produce a final concentration of 4 to 80 ppm.
3. After mixing, the absorbance is measured at 486 nm by Ultralviolet Spectrophotometer at intervals.

IV. DATA and RESULTS:

A. The effect of diazonium salt solution.

The diazonium salt is formed and stored in concentrated sulfuric acid. The strong acid is necessary to stabilize this solution but has a big influence on the coupling reaction. Too much sulfuric acid will react with aniline which interfere the coupling reaction. Therefore choosing a suitable amount of this solution is very important.

1. Different amounts of diazonium sulfate solution (from 0.005 ml to 0.20 ml) were added to 50 ml flasks containing 25 ml of acetonitrile.
2. 0.6 ml of aniline solution was pipetted into the above solutions, each of which contain 24 ppm of aniline.
3. The absorbance of each solution was measured at

intervals.

The absorbances obtained from two experiments (for convenience of measurement) are shown in Table 1 and 2 and Figigue 1-4.

Table 1

Reaction of 0.005 ml to 0.04 ml of diazonium salt with 24 ppm of aniline in acetonitrile

amount of salt (ml)	0	0.005	0.01	0.02	0.03	0.04
time, 1 (hr)	0.00	0.49	0.36	0.24	0.12	0.13
2	0.00	0.76	0.58	0.45	0.28	0.28
3	0.00	0.97	0.81	0.63	0.44	0.44
4	0.01	1.14	0.98	0.79	0.58	0.59
5	0.01	1.27	1.19	1.00	0.77	0.76
6	0.01	1.40	1.39	1.16	0.93	0.94
8	0.02	1.52	1.65	1.43	1.19	1.20
10	0.02	1.54	1.92	1.90	1.50	1.51
12	0.04	1.53	2.08	2.21	1.78	1.76
14	0.04	1.55	2.14	2.32	1.91	1.84
16	0.05	1.57	2.10	2.30	1.95	1.90
18	0.06	1.55	2.11	2.35	1.93	1.87
20	0.07	1.56	2.12	2.34	1.92	1.86

Table 2

Reaction of 0.05 ml to 0.20 ml of diazonium salt with 24ppm of aniline in acetonitrile

amount of salt (ml)	0	0.05	0.10	0.15	0.20
time, 1 (hr)	-0.01	0.22	0.15	0.13	0.09
2	0.02	0.52	0.38	0.24	0.18
3	0.02	0.70	0.48	0.33	0.24
4	0.01	0.93	0.63	0.44	0.31
5	-0.01	1.12	0.78	0.53	0.36
6	0.01	1.35	0.88	0.60	0.39
7	0.03	1.52	0.96	0.72	0.47
8	0.01	1.70	1.15	0.79	0.42
10	0.01	1.88	1.22	0.86	0.51
12	0.02	2.05	1.31	0.92	0.49
14	0.02	2.01	1.29	0.94	0.53
16	0.03	2.10	1.28	0.95	0.55
18	0.04	1.98	1.35	0.92	0.50
20	0.06	1.96	1.30	0.93	0.51

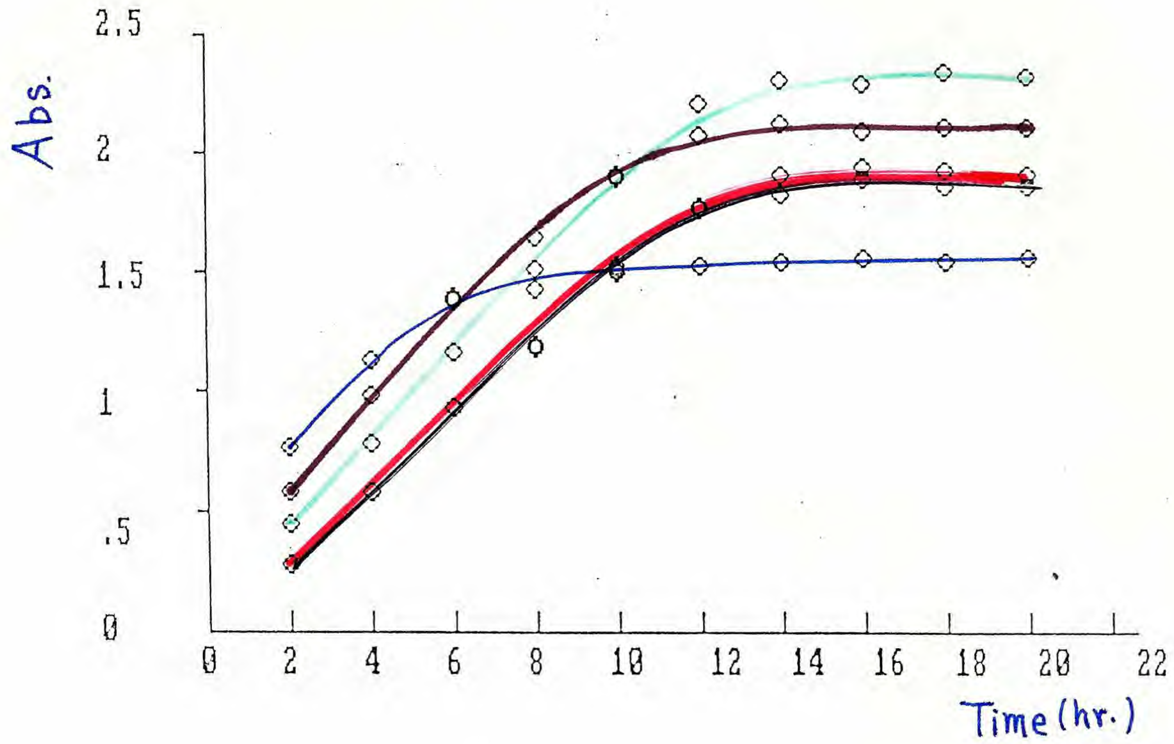


Fig. 1 Reaction with Lower concentration of diazonium salt (Absorption vs. Time)

——— : 0.04 ml of salt

——— : 0.03 ml of salt

——— : 0.02 ml of salt

——— : 0.01 ml of salt

——— : 0.005 ml of salt

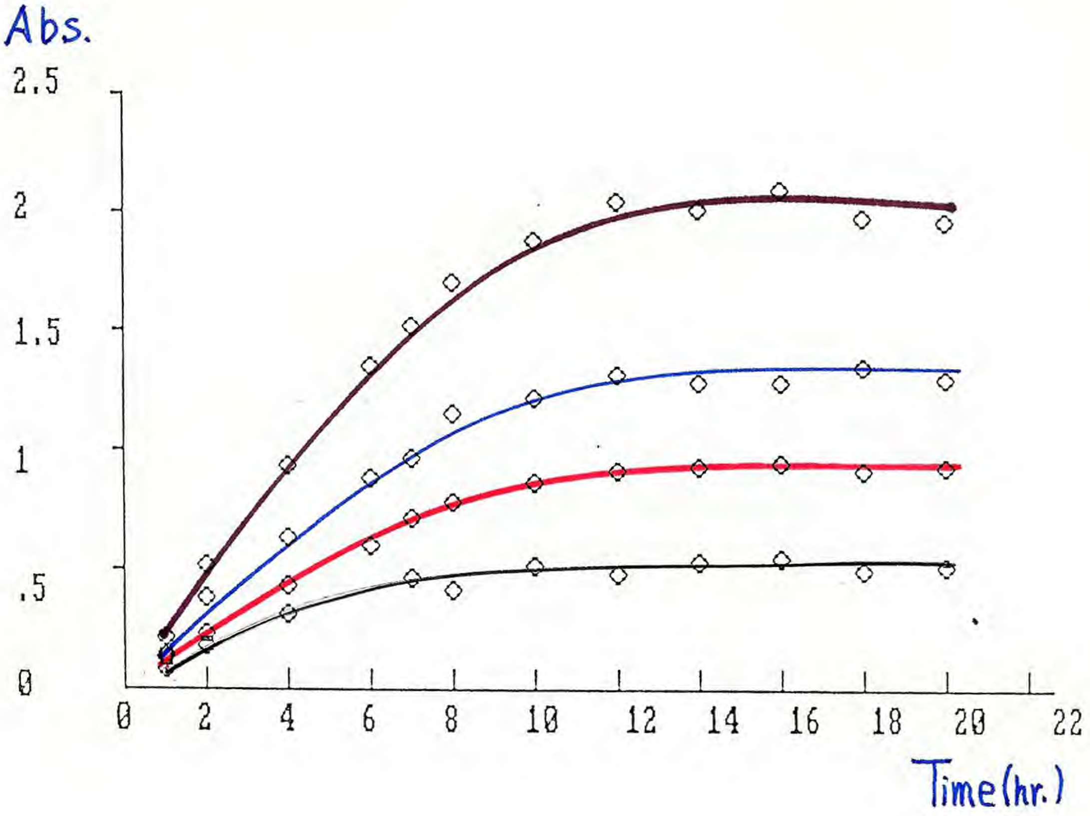


Fig. 2 Reaction with higher concentration of diazonium salt (Absorption vs. Time)

—— : 0.20 ml of salt —— : 0.10 ml Of salt

━━ : 0.15 ml of salt ━━ : 0.05 ml Of salt

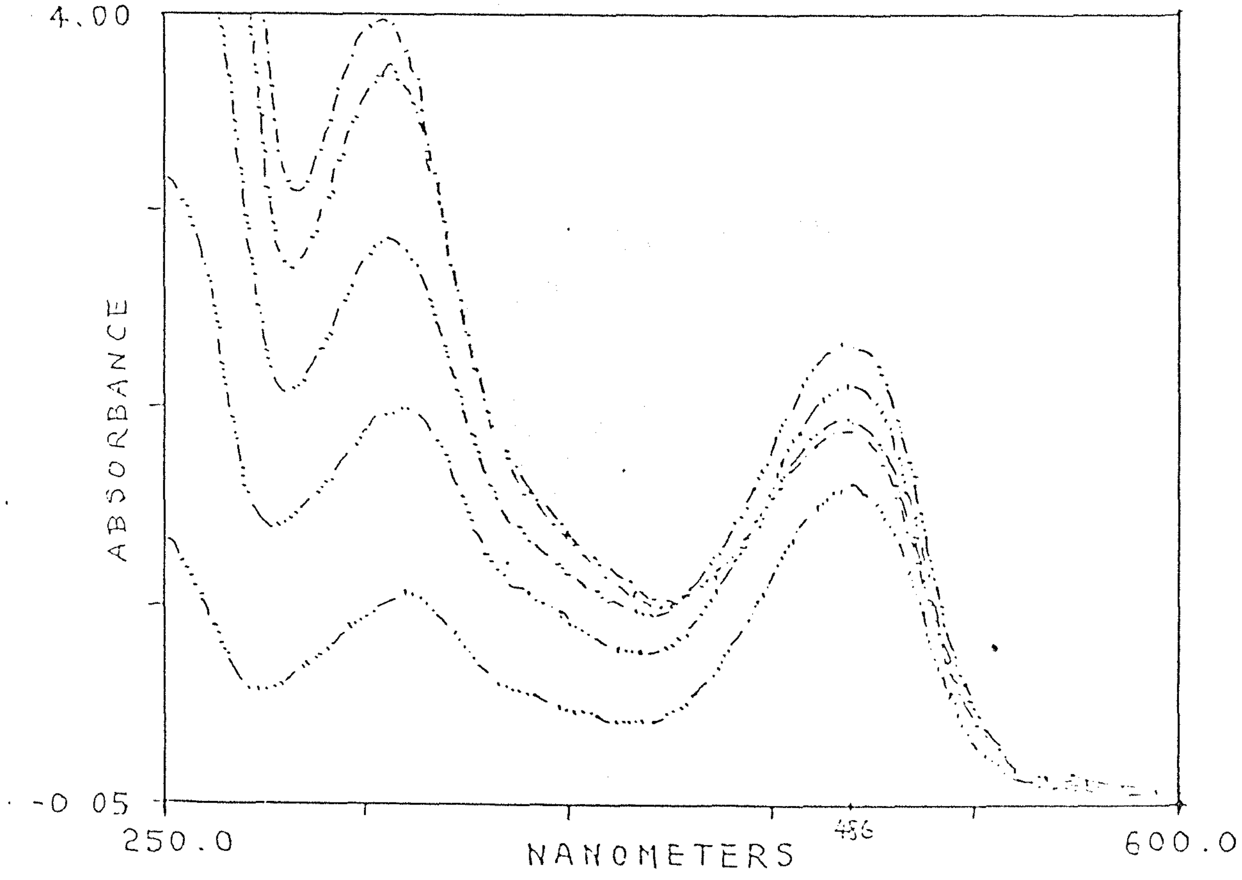


Fig. 3 The UV spectrum of lower concentration of diazonium salt in 0.6 ml of aniline (after 20 hours)

—·—·— 1 : 0.04 ml of salt —····— 4 : 0.01 ml of salt

—··—·— 2 : 0.03 ml of salt —·····— 5 : 0.005 ml of salt

—··—··— 3 : 0.02 ml of salt

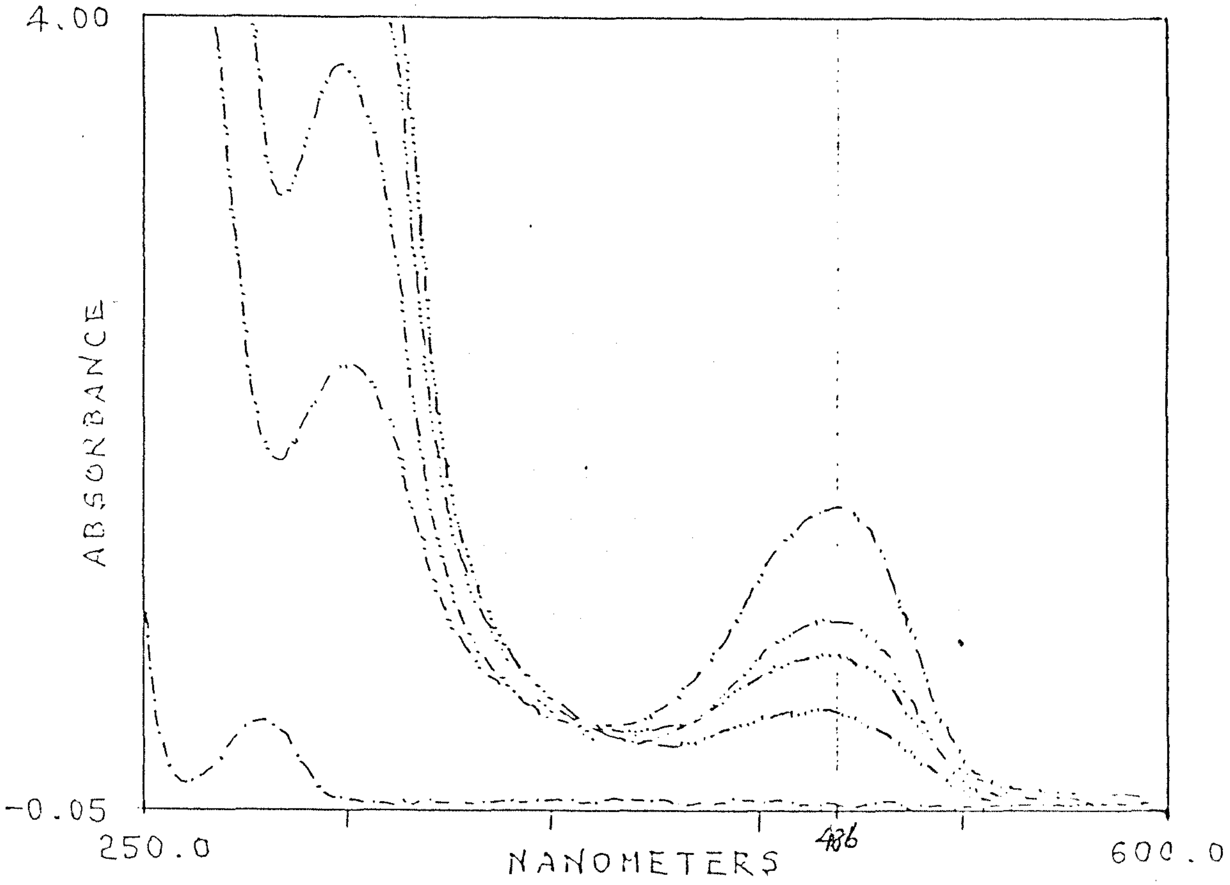


Fig. 4 The UV spectrum of higher concentration of diazonium salt in 0.6 ml of aniline (after 7 hours)

-•-•- 1 : Diazonium salt (without aniline)

-•-•- 2 : 0.05 ml of salt -··- 4 : 0.15 ml of salt

-··-··- 3 : 0.10 ml of salt -····- 5 : 0.20 ml of salt

The data from these two experiments indicate three points:

1. The optimum concentration of diazonium sulfate solution is produced when 0.01 ml to 0.05 ml are used .
2. The absorbance keeps increasing for about 12 hours at room temperature, then becomes nearly constant.
3. The UV spectra indicate an absorption peak at 486 nm for all trials of this reagent pair.

B. The coupling reaction conditions.

The coupling reaction is very sensitive to reaction conditions and selection of the best conditions is important for analysis. There are several condition variables in this experiment which can be optimized.

1. Reaction with temperature difference.

a. Room temperature reaction.

(1) Higher concentration of aniline:

Add 0.05 ml of diazonium sulfate solution in 25 ml of acetonitrile, then pipet 0.5 to 2.0 ml of aniline solution (1000 ppm) into it. The concentrations of these solutions are 20 to 80 ppm. The results are shown in Table 3. and Figs. 5-7

Table 3

High concentration at room temperature

amount of aniline (ppm)	0	20	40	60	80
time 1 hr	-0.01	0.01	0.14	0.34	0.53
2	-0.01	0.08	0.39	0.76	1.16
3	-0.01	0.17	0.74	1.21	1.94
4	-0.01	0.32	0.99	1.59	2.54
5	0.01	0.43	1.18	1.97	2.88
6	0.01	0.50	1.35	2.28	3.16
7	0.01	0.61	1.53	2.58	3.37
8	0.01	0.72	1.74	2.84	3.55
10	0.02	0.99	2.15	3.21	3.71
12	0.02	1.31	2.51	3.33	3.76
20	0.06	1.35	2.68	3.31	3.75

POINT	X	Y
1	20	1.35
2	40	2.68
3	60	3.31
4	80	3.75

```
 Slope =  3.914999E-02  +/-  7.26342E-03
Intercept =  .8150005  +/-  .32483
Correlation =  .9672605
Calculated on points  1  TO  4
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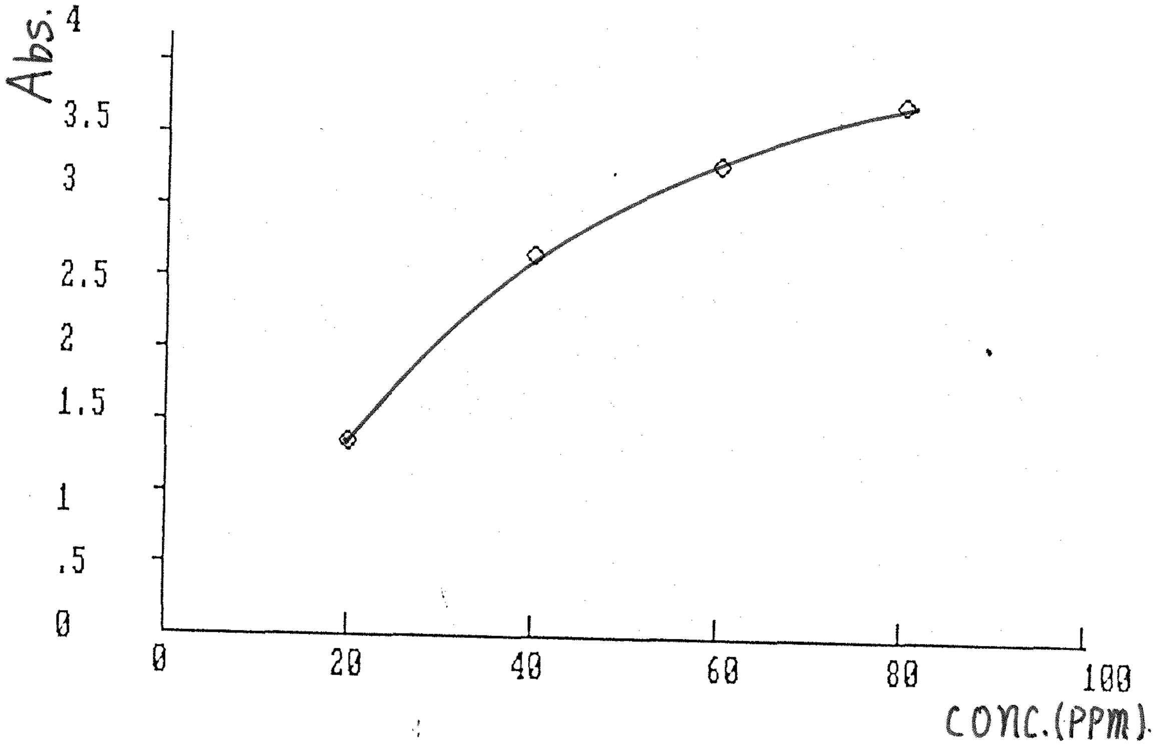

Fig. 5 Higher concentration at room temperature

(after 20 hours)

Absorption vs. concentration

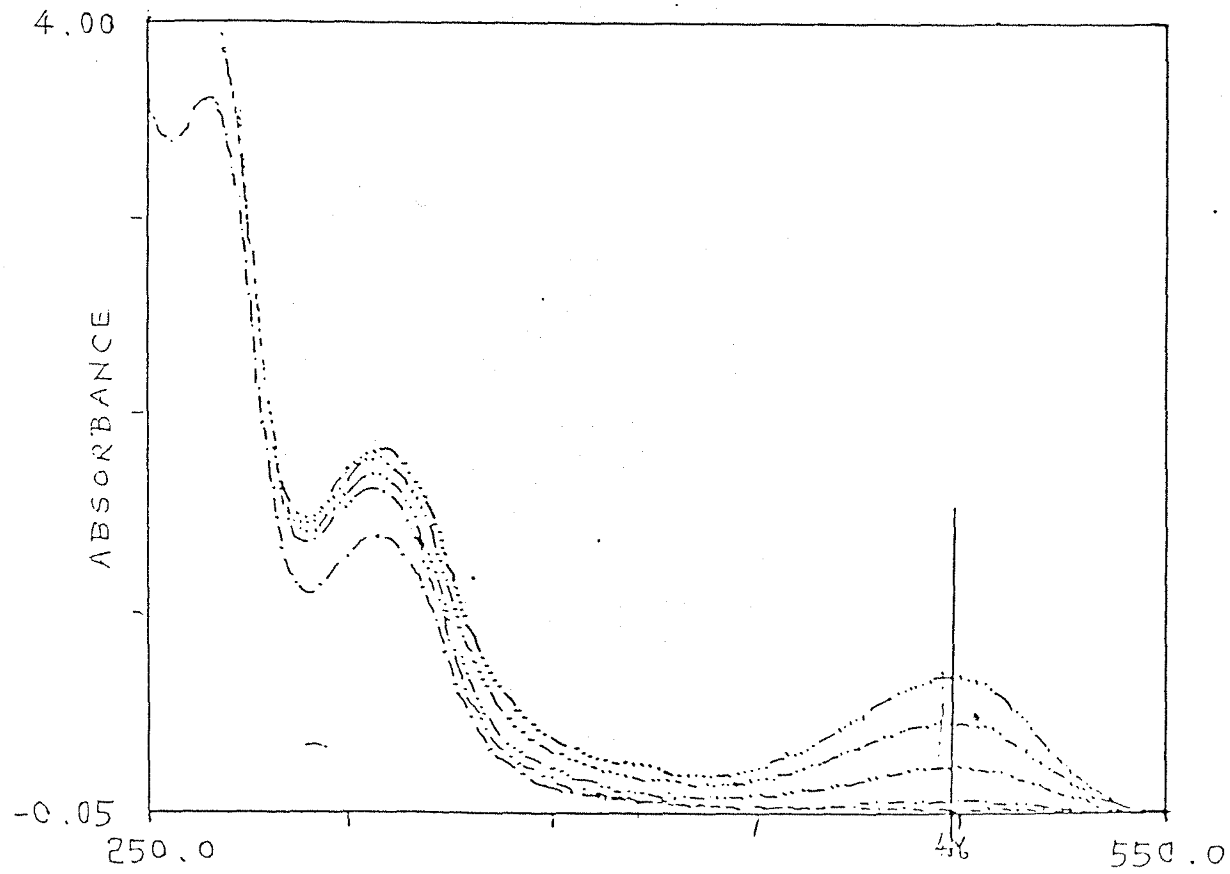

Fig. 6 UV spectrum of higher concentration at room temperature (after 1 hour)

-·-·- 1 : Without aniline

-··-··- 2 : 20 ppm of aniline

-··-··- 3 : 40 ppm of aniline

-····- 4 : 60 ppm of aniline

-·····- 5 : 80 ppm of aniline

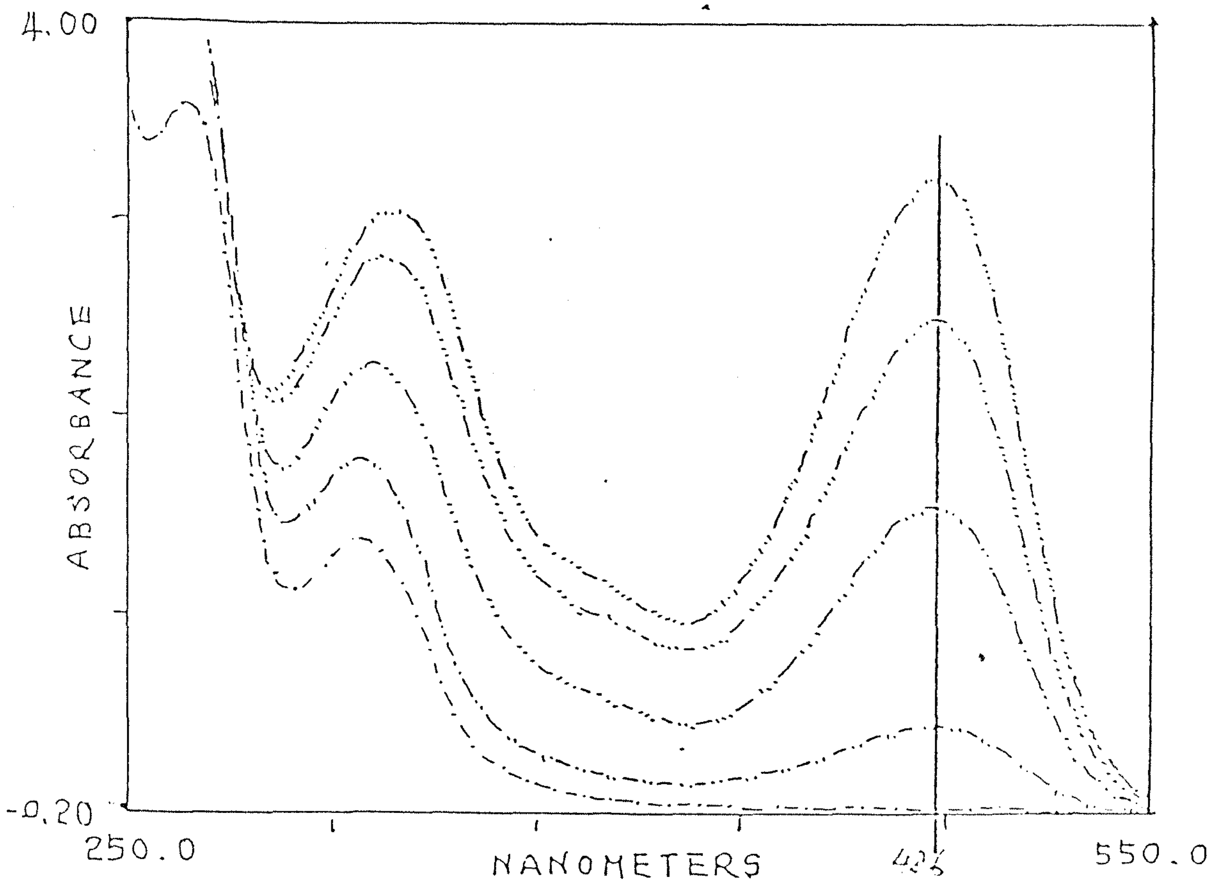

Fig. 7 UV Spectrum of higher concentration at room temrature (after 7 hours)

-·-·- 1 : without aniline

-··-··- 2 : 20 ppm of aniline

-···-···- 3 : 40 ppm of aniline

-····- 4 : 60 ppm of aniline

-·····- 5 : 80 ppm of aniline

(2). Lower concentration of aniline.

Add 0.02 ml of diazonium sulfate solution to 25 ml acetonitrile, then pipet 0.01 to 0.06 ml of aniline solution (1000 ppm) into it. The concentration of these solutions are 4 to 24 ppm. The results are shown in Table 4 and Fig. 8, 9, 10

Table 4

Lower concentration at room temperature

amount of aniline (ppm)	0	4	8	12	16	24
time 1 hr	0.00	0.004	0.01	0.03	0.06	0.24
2	0.00	0.02	0.06	0.11	0.21	0.45
3	0.00	0.04	0.12	0.25	0.33	0.63
4	0.01	0.08	0.18	0.31	0.45	0.78
5	0.01	0.14	0.25	0.41	0.59	1.00
6	0.01	0.15	0.30	0.51	0.72	1.12
7	0.01	0.19	0.40	0.65	0.87	1.31
8	0.02	0.22	0.45	0.72	0.95	1.48
10	0.02	0.21	0.54	0.94	1.16	1.84
12	0.03	0.21	0.67	1.19	1.38	2.17
20	0.06	0.21	0.71	1.24	1.59	2.40

POINT	X	Y
1	4	.21
2	8	.71
3	12	1.24
4	16	1.59
5	24	2.4

```
 Slope =  .1086149  +/-  4.71977E-03
Intercept = -.1602704  +/-  7.262928E-02
Correlation =  .9971795
Calculated on points  1  TO  5
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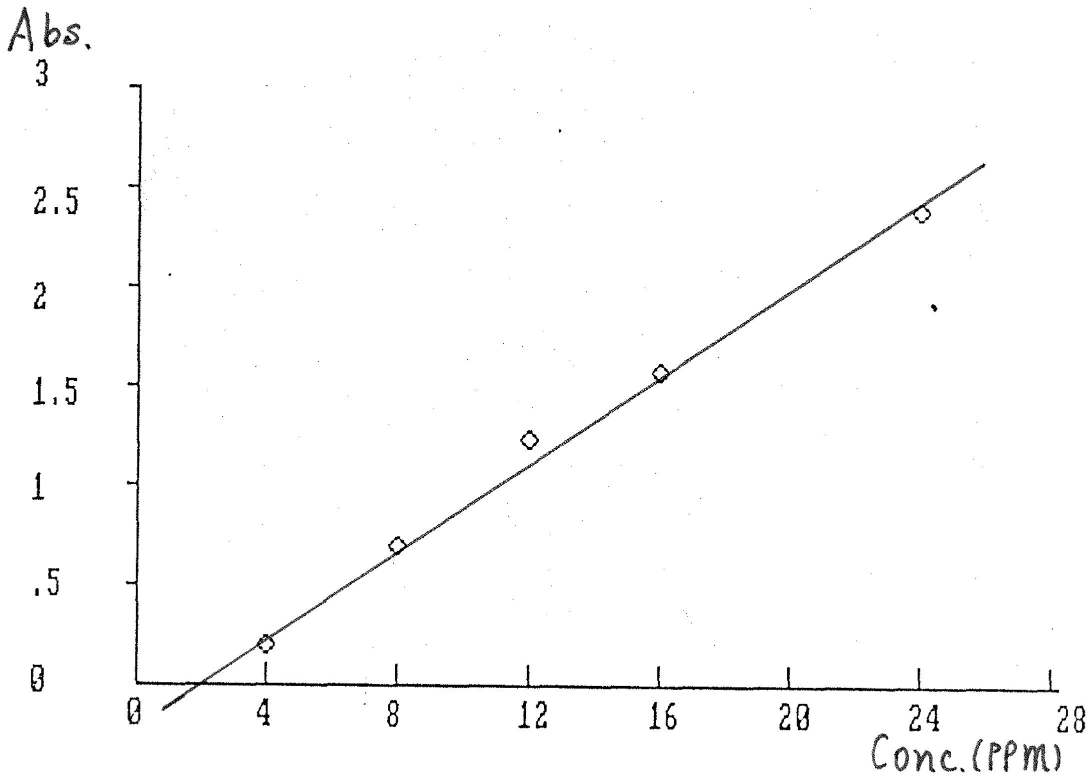


Fig. 8 Lower concentration at room temperature after 20 hours.

Absorption vs. concentration

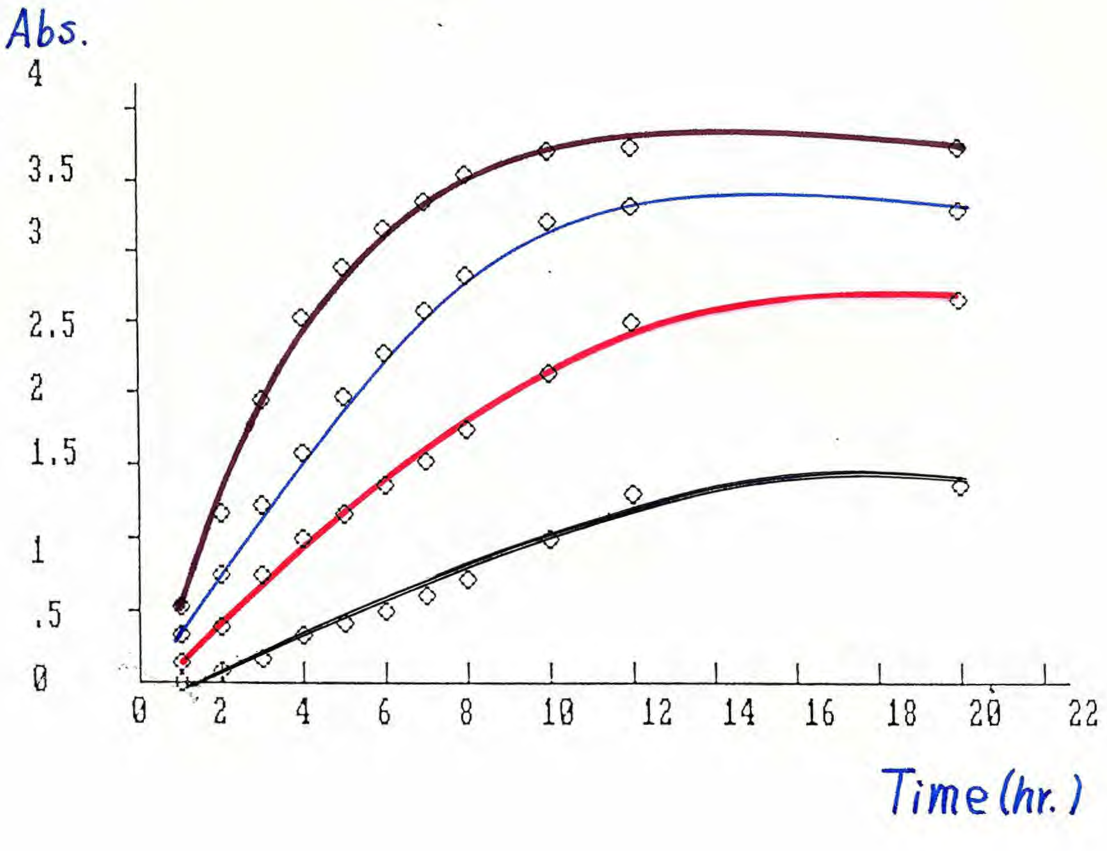
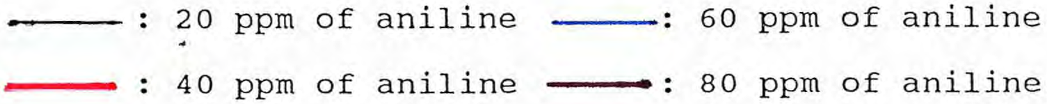


Fig. 9 Higher concentration at room temperature

Absorption vs. Time



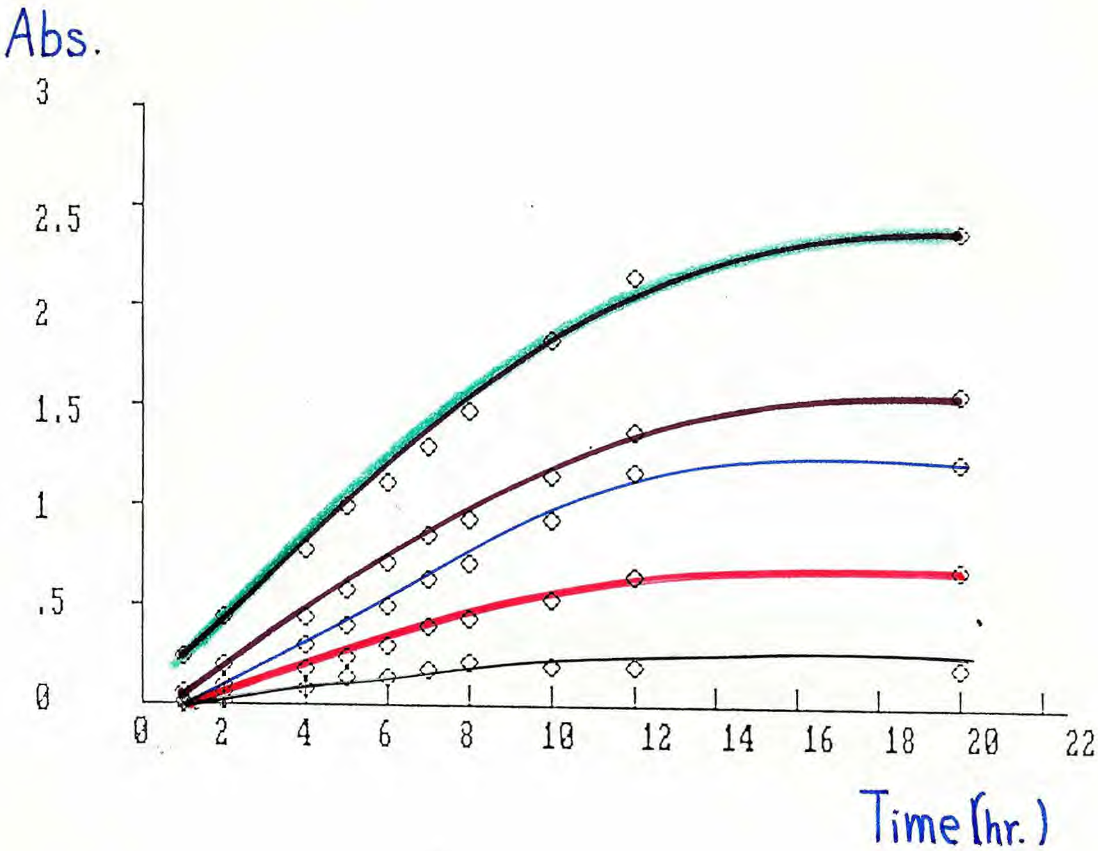


Fig.10 Lower concentration at room temperature

Absorption vs. concentration

— : 4 ppm of aniline

— : 8 ppm of aniline

— : 12 ppm of aniline

— : 16 ppm of aniline

— : 24 ppm of aniline

From Figs. 1,2,9 and 10 we find the coupling reaction takes about 12 hours to reach completion at room temperature. The UV spectra Figs.3,4,6 and 7 indicate an absorption peak at 486 nm. Plotting the absorbance vs. concentration shows a linear relationship between 4 and 60 ppm. Above 60 ppm, the curve becomes nonlinear. The concentration of aniline in the sample can be determined from the calibration curve by measuring its absorbance.

b. Reaction at room temperature then cooled in ice water.

Add 0.05 ml of diazonium sulfate solution to 25 ml of acetonitrile; then pipet different amount of aniline in it. After the coupling reaction has progressed for two hours the solution is cooled in ice water. Then the absorbance of each solution is measured at different times. The results are shown in Table 5 and Fig. 11, 12.

Table 5

Reaction at room temperature (0.05 ml of diazonium salt) then cooled in ice water

amount of aniline (ppm)	0	20	40	60	80
time, 1 (hr)	-0.01	0.02	0.18	0.38	0.61
2	-0.01	0.09	0.36	0.76	1.12
Cooled in ice water					
2.5	-0.01	0.09	0.37	0.78	1.16
3	-0.01	0.10	0.36	0.77	1.14
4	-0.01	0.09	0.38	0.79	1.16
5	-0.01	0.10	0.40	0.83	1.21
6	-0.02	0.10	0.41	0.85	1.25

```
   POINT                 X                          Y
--------------------------------------------------------------
       1                20                         .1
       2                40                         .36
       3                60                         .77
       4                80                         1.14
--------------------------------------------------------------
 Slope =   .01765   +/-   1.098897E-03
Intercept = -.2899999   +/-   4.914418E-02
Correlation =   .9961461
Calculated on points  1  TO  4
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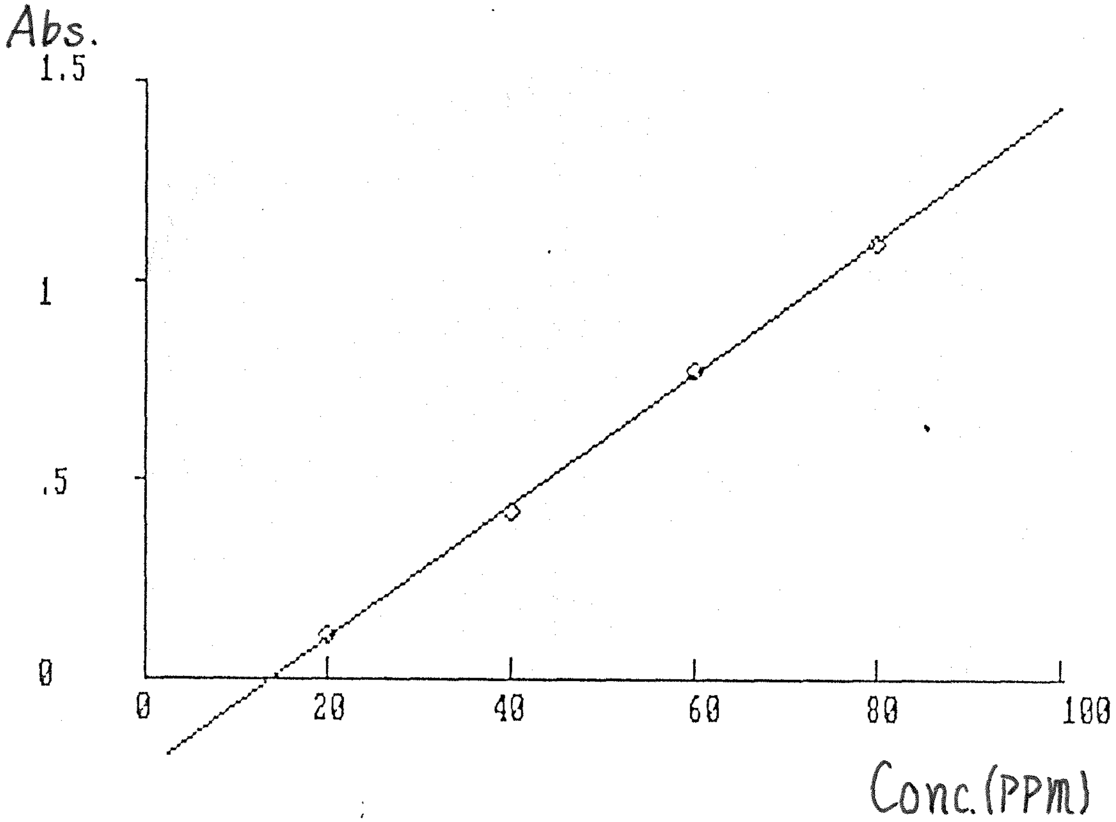

Fig.11 Reaction at room temperature then cooled in ice water

Absorption vs. concentration (after 2 hour)

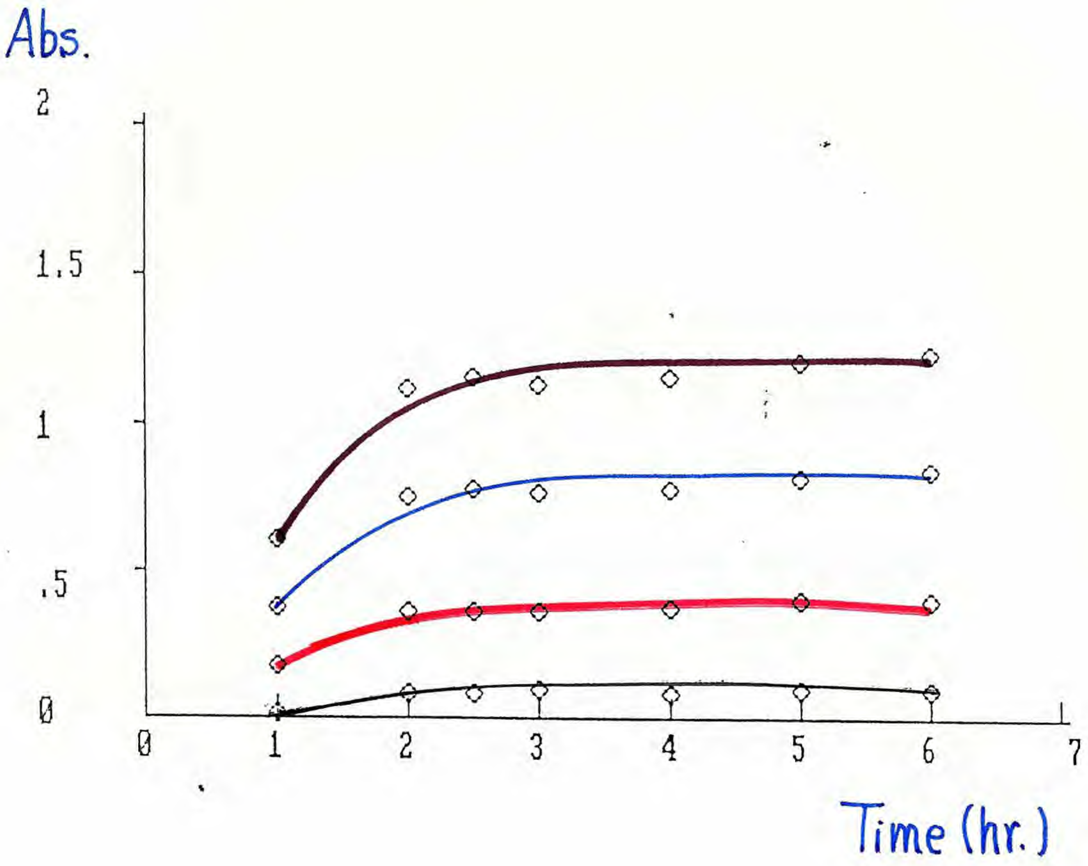

Fig.12 Reaction at room temperature then cooled in ice water

Absorption vs. Time

— : 20 ppm of aniline — : 60 ppm of aniline

— : 40 ppm of aniline — : 80 ppm of aniline

Fig. 12 shows that the coupling reaction becomes very slow when the temperature changes to zero. Plotting absorbance vs. concentration (Fig.11) produces a useful calibration curve. Therefore the unknown sample can analyzed under the same conditions and from the calibration curve, the quantity can be determined by measuring its absorption at 486 nm.

c. Reaction at elevated temperature.

a. Add 0.05 ml of diazonium sulfate solution into 25 ml acetonitrile; then pipet different amount of aniline into it.

b. Slowly increase the temperature (about 5 minutes) to 65°C in a water bath, holding it for 5 minutes. Then take it out of the water bath. After half an hour the absorbance is measured at different times.

The results are shown in Table 6 and Figs. 13-15.

Table 6

Reaction at elevated temperature

amount of aniline (ml)	0	8	12	16	24
time, 0.5(hr)	0.05	0.14	1.16	2.17	3.35
1.5	0.07	0.15	1.17	2.20	3.37
2.5	0.14	0.22	1.19	2.21	3.35
3.5	0.14	0.21	1.20	2.22	3.36
5.0	0.15	0.22	1.19	2.21	3.34
7.0	0.15	0.23	1.21	2.21	3.36

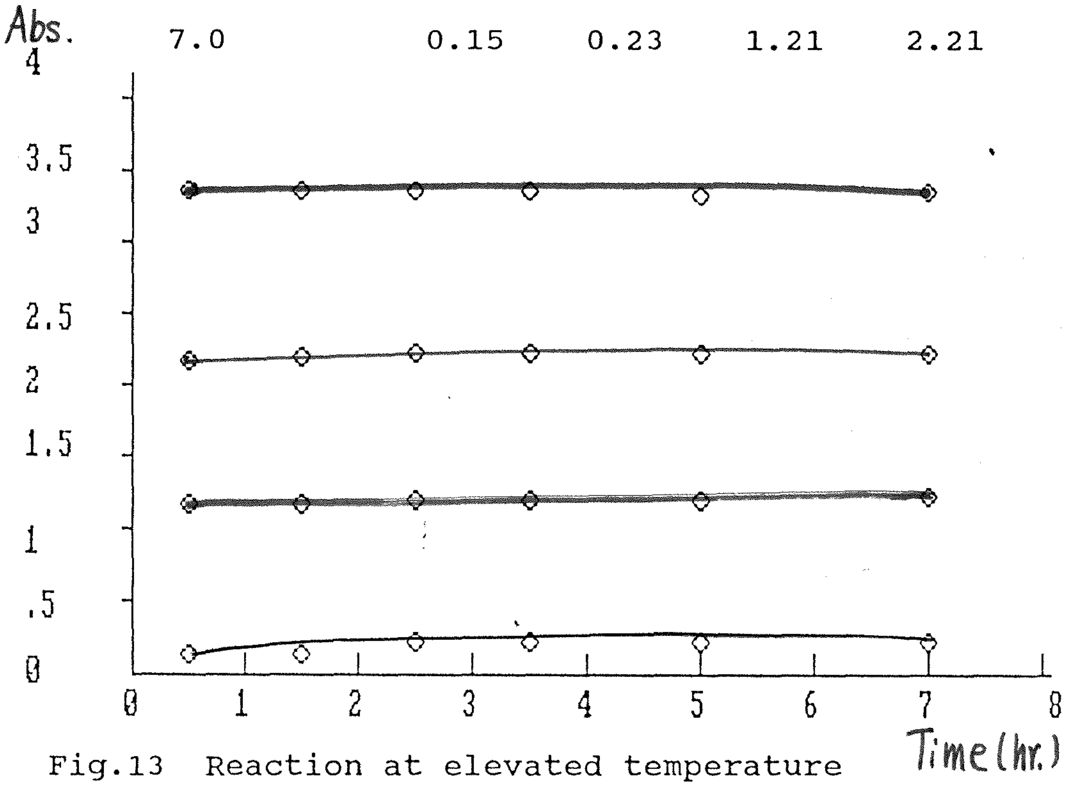

Fig.13 Reaction at elevated temperature

Absorption vs. Time

—— : 8 ppm of aniline —— : 16 ppm of aniline

▬▬ :12 ppm of aniline ▬▬ : 24 ppm of aniline

```
  POINT                X                          Y
-----------------------------------------------------------
      1                8                          .22
      2                12                         1.19
      3                16                         2.21
      4                24                         3.35
-----------------------------------------------------------
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Intercept = -1.177141  +/-  .2468407
Correlation =  .9887066
Calculated on points  1  TO  4
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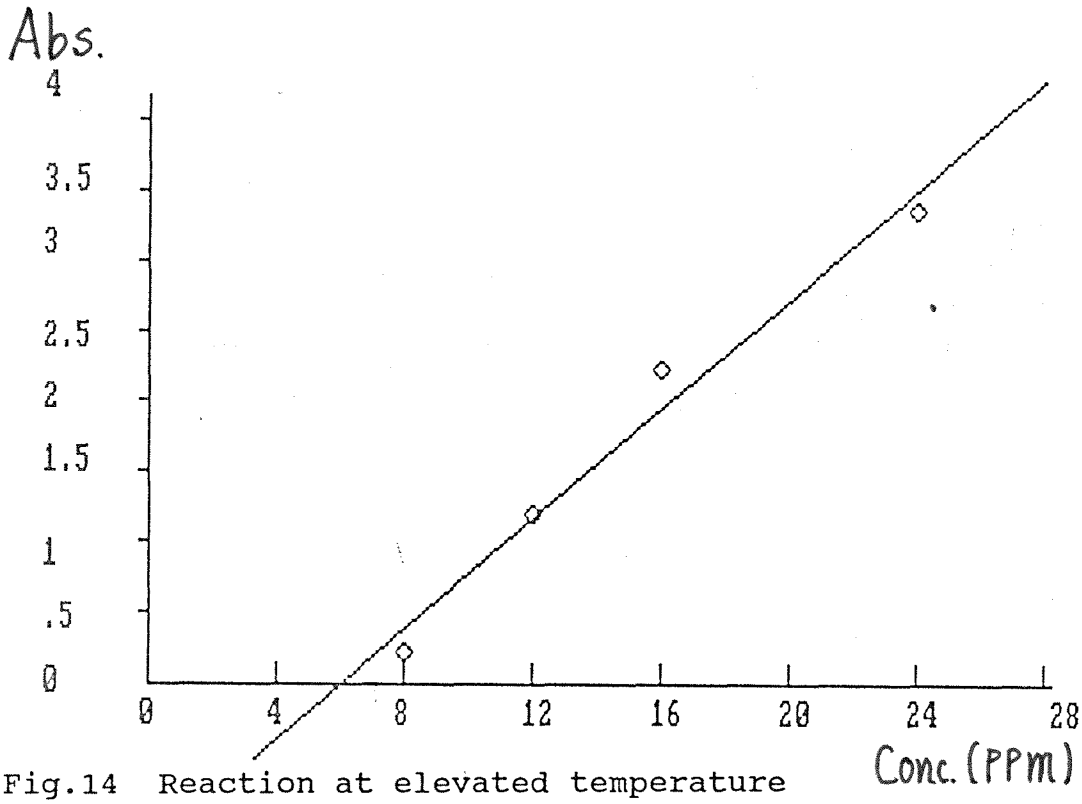


Fig.14 Reaction at elevated temperature

Absorption vs. concentration (after 2 hours)

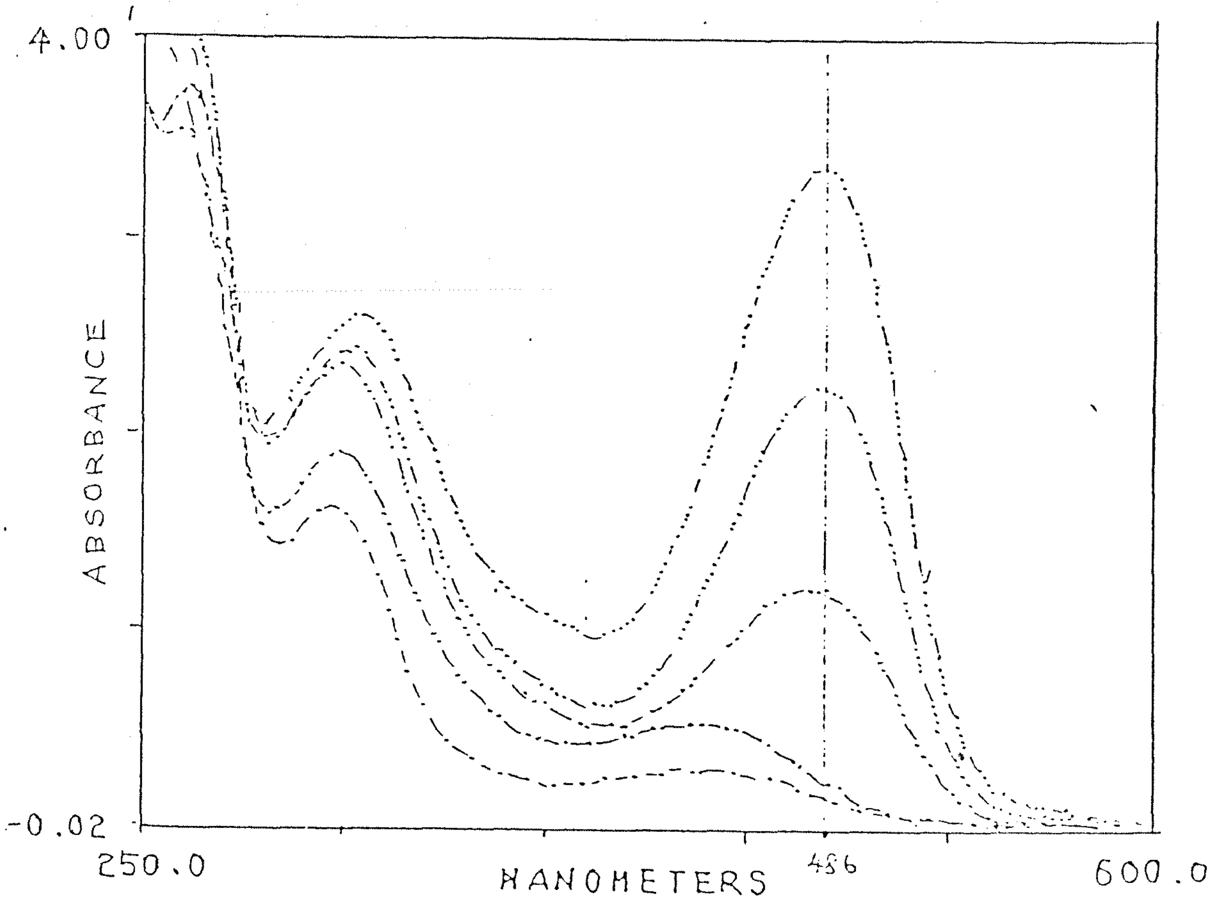


Fig.15 UV spectrum (reaction at elevated temperature) after 3 hours reaction

-·-·- 1 : without aniline
-··-··- 2 : 8 ppm of aniline
-··-··- 3 : 12 ppm of aniline
-····- 4 : 16 ppm of aniline
-····- 5 : 24 ppm of aniline

When the temperature is increased to 65°C for about five minutes, the color becomes deeper and from Fig. 13 one can see that the reaction quickly reaches completion. The UV spectrum (Fig.15) also shows an absorption peak at 486 nm. The plot of absorbance vs. concentration (Fig.14) gives a useful calibration curve. It indicates that the rate of the coupling reaction rises rapidly as temperature increased.

2. Reaction at room temperature quenched by concentrated sulfuric acid added.

Add 0.05 ml of diazonium sulfate solution to 25 ml of acetonitrile; then pipet different amounts of aniline into it. After the coupling reaction has proceeded for two hours, 0.5 ml of concentrated sulfuric acid is added, then the absorbance of each solution is measured at different time.

The results are shown in Table 7 and Fig. 16, 17

Table 7

Reaction at room temperature then with con. H_2SO_4 added

amount of aniline (ml)	0	20	40	60	80
time, 1 (hr)	-0.01	0.03	0.21	0.37	0.53
2	-0.01	0.12	0.41	0.81	1.13
Add 0.5 ml of conc. H_2SO_4					
3	0.00	0.11	0.42	0.78	1.10
4	0.00	0.11	0.43	0.78	1.10
5	0.00	0.10	0.42	0.77	1.12
6	0.00	0.13	0.44	0.80	1.14

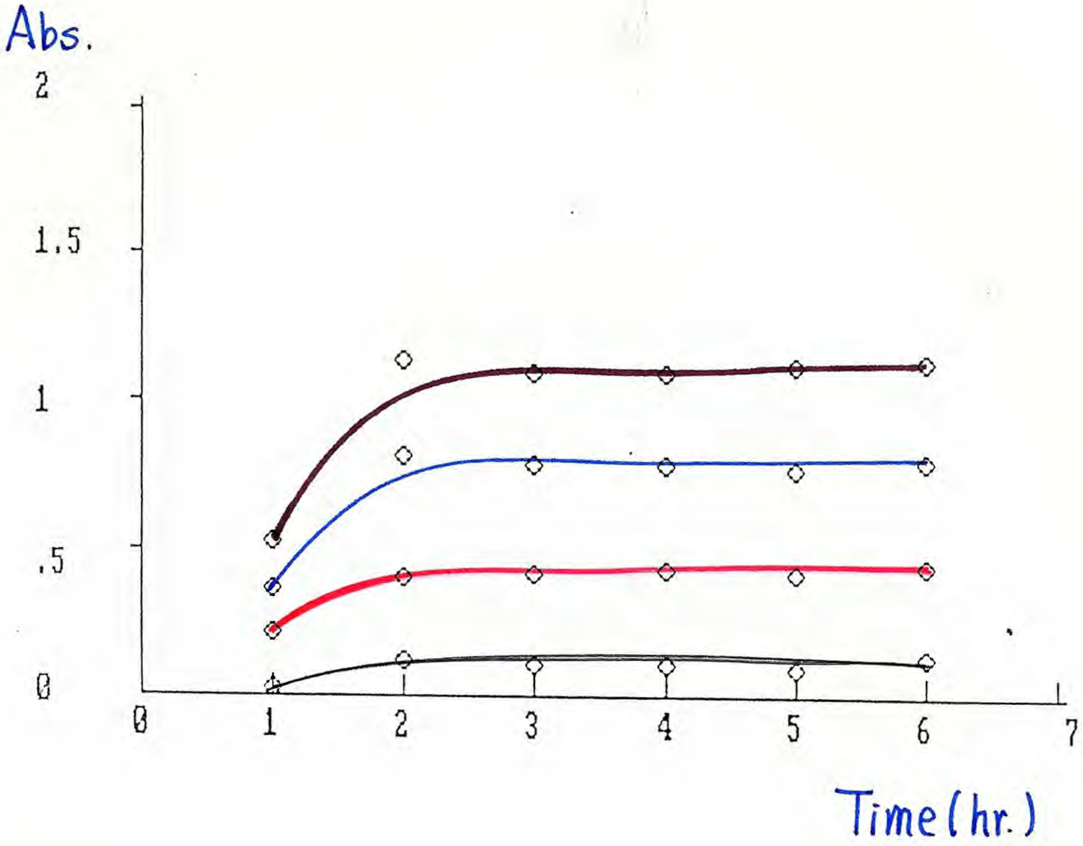


Fig.16 Reaction at room temperature then with concentrated sulfuric acid added

Absorption vs. Time

―― : 20 ppm of aniline ―― : 60 ppm of aniline

―― : 40 ppm of aniline ―― : 80 ppm of aniline

```
 POINT              X                            Y
-----------------------------------------------------------
    1              20                          .11
    2              40                          .42
    3              60                          .78
    4              80                          1.1
-----------------------------------------------------------
 Slope =  1.665001E-02  +/-  3.277366E-04
Intercept = -.2300004  +/-  1.465683E-02
Correlation =  .9996128
Calculated on points  1  TO  4
```

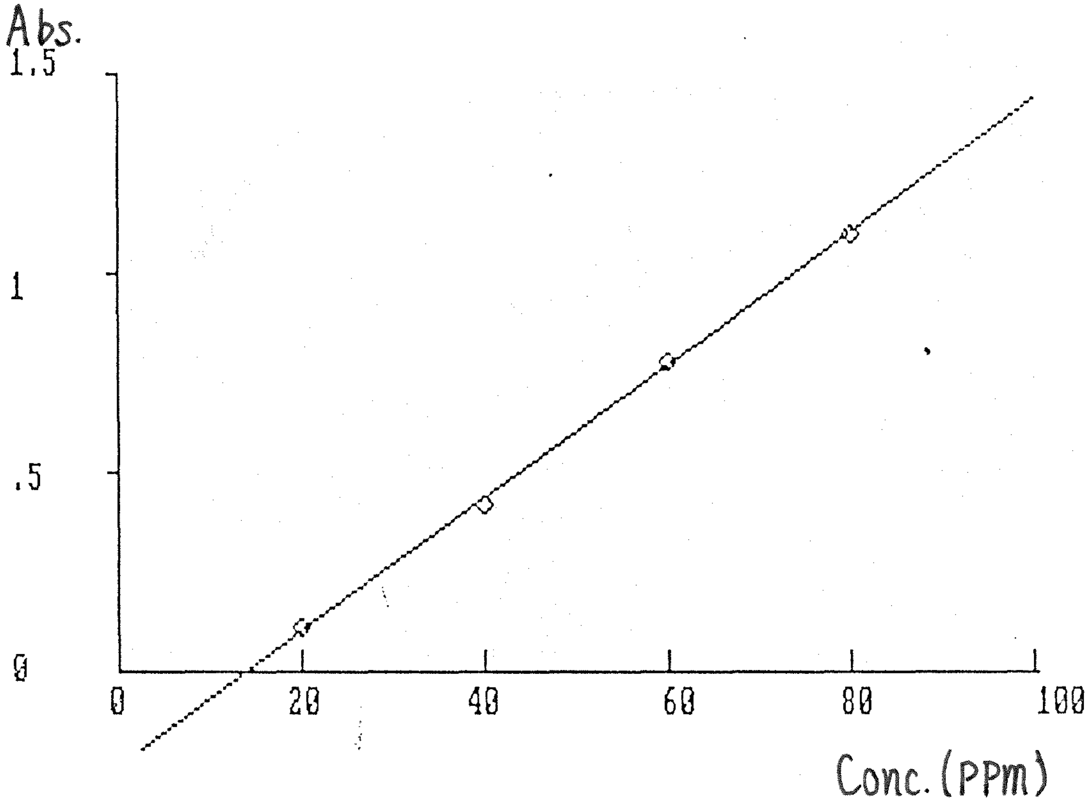


Fig.17 Reaction at room temperature then with concentrated sulfuric acid added

Absorption vs. concentration (after 2 hours)

This experiment (Fig.16) indicates that the coupling reaction can be stopped by adding concentrated sulfuric acid. The plot of absorbance vs. concentration (Fig.17) shows that using this method can determine the concentration of aniline in the unknown sample by measuring its absorbance at 486 nm.

V. Application of this method to the analysis of simulated air samples.

A. Preparation of air sample:

Pipet 250 ml of acetonitrile in 500 ml flask then add 30 ml of aniline to it. Air is passed through at a flow of about 10 ml per second to produce an air sample contaminated with aniline. Fig.18 shows the apparatus.

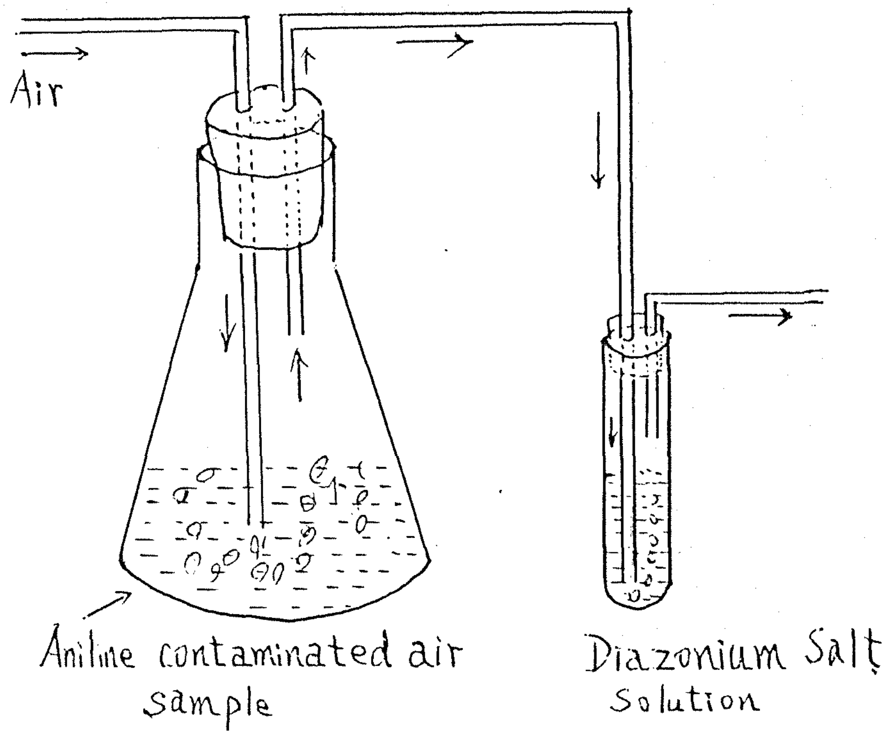


Fig. 18 Generation of air sample

B. Procedure:

1. Put 0.05 ml of diazonium sulfate solution into 25 ml acetonitrile. This solution is used as adsorbant to scrub different amounts of aniline contaminated air samples by changing the adsorption time.

2. The absorbance at 486nm of each solution used to collect different amounts of aniline from air sam-

ples was measured

The results are shown in Table 8, 9 and Fig. 19,-22

Table 8

Standards (Measure the absorbance after 12 hours)

amount of aniline (ml)	8	16	24	32
absorbance	0.63	1.16	2.05	2.81

Table 9

Absorbance of aniline air sample (after 12 hr)

collection time (hr)	1	2	3	4
absorbance	0.12	0.91	1.90	2.71

POINT	X	Y
1	8	.63
2	16	1.16
3	24	2.05
4	32	2.81

```
 Slope =  9.287501E-02  +/-  6.278676E-03
Intercept = -.1950002  +/-  .1123164
Correlation =  .9954609
Calculated on points  1  TO  4
```

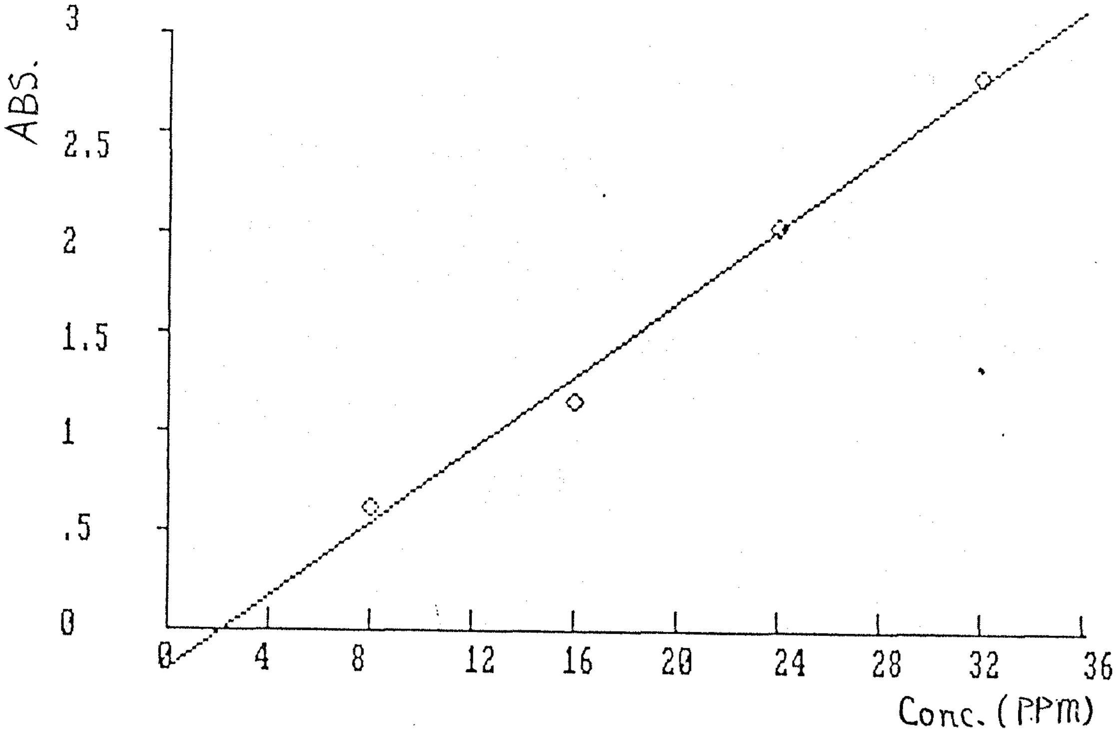


Fig.19 Standards (Reaction at room temperature after 12 hours)

Absorption vs. concentration

```
  POINT                 X                          Y
------------------------------------------------------------------
    1                   1                          .12
    2                   2                          .91
    3                   3                          1.9
    4                   4                          2.71
------------------------------------------------------------------
 Slope =   .8760001   +/-   2.705669E-02
Intercept = -.7800001  +/-   6.050059E-02
Correlation =  .9990474
Calculated on points  1  TO  4
```

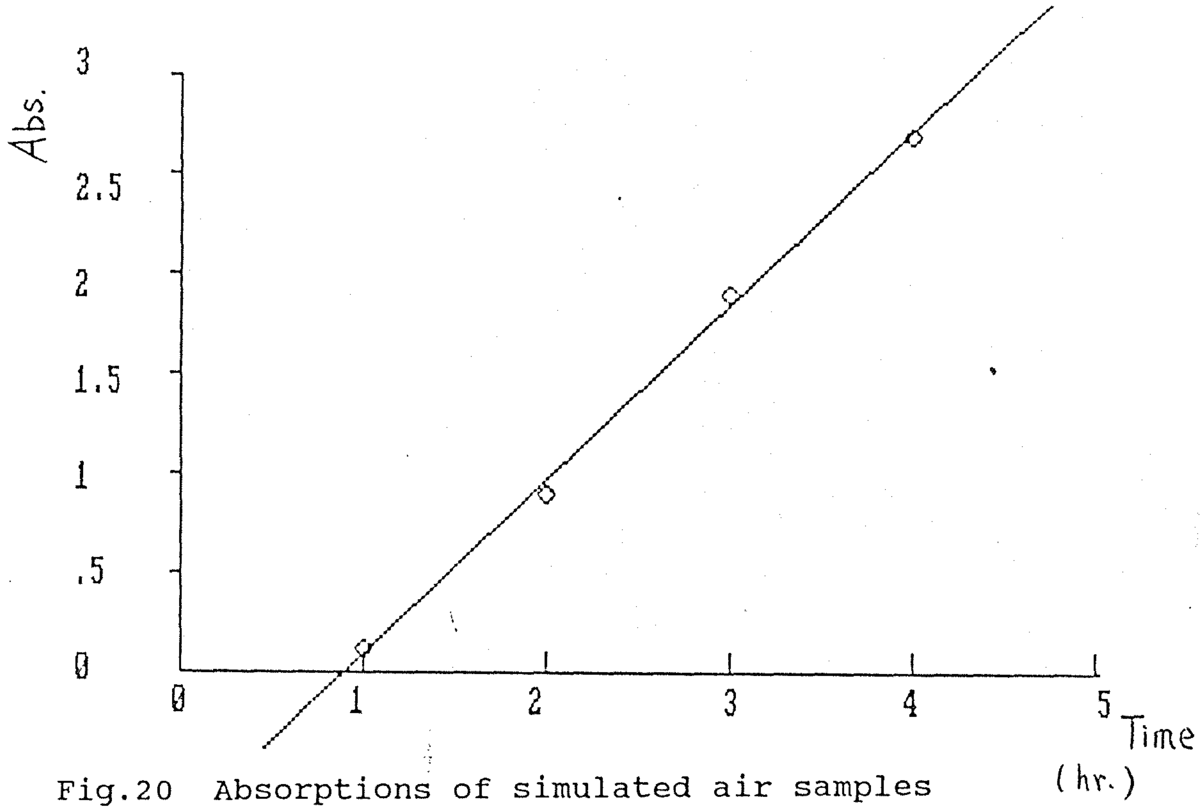


Fig.20 Absorptions of simulated air samples

Absorptions vs collection time

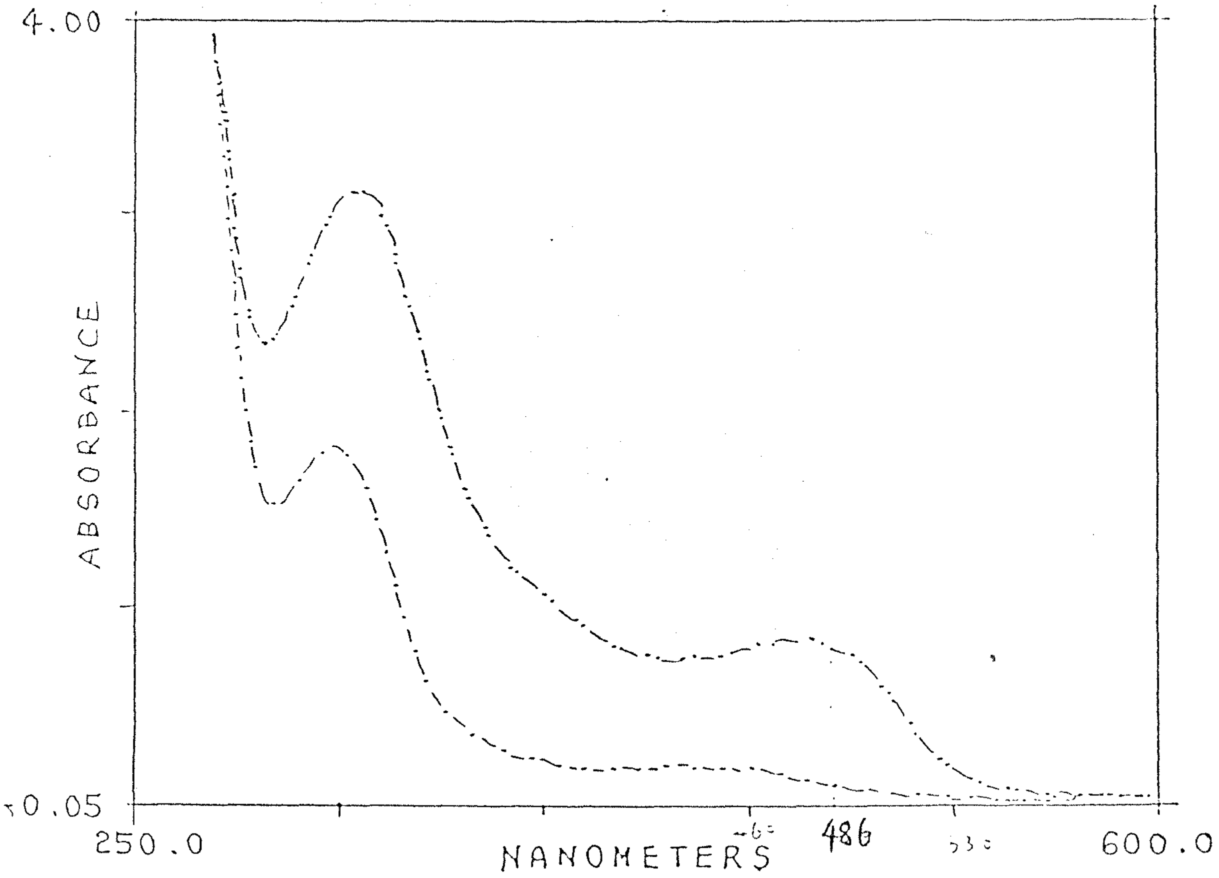


Fig.21 UV spectrum of simulated air samples

-·-·- 1 : one hour collection

-··-··- 2 : two hours collection

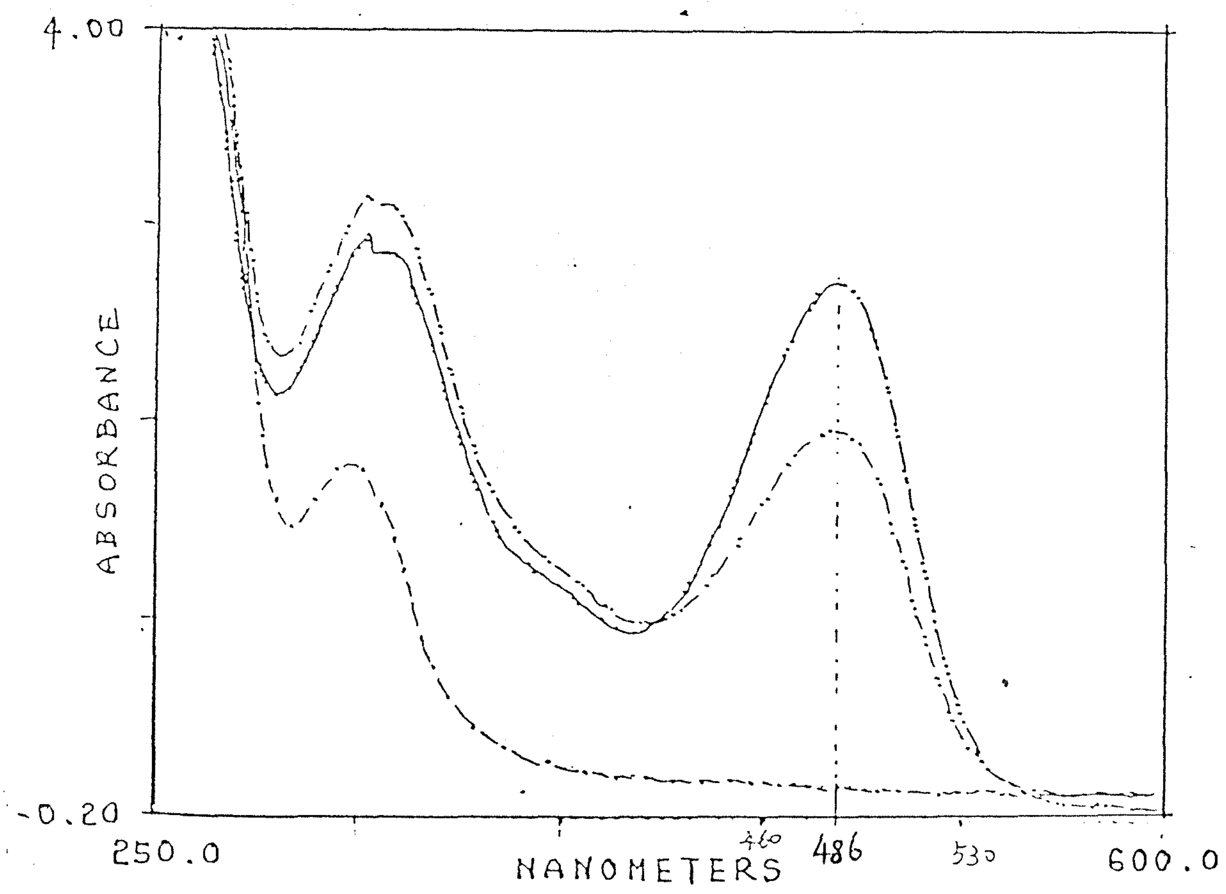


Fig.22 UV spectrum of simulated air samples

-·-·- 1 : Blank -·-·- 2 : Three hours collection

-··-··- 3 : Four hours collection

C. Result:

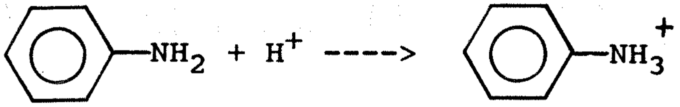
The time for collection of aniline from the air samples plotted vs. the absorbance (Fig.20) gives a linear relation. The UV spectrum (Fig.21, 22) also indicates the same absorption at 486 nm. Using a standard calibration curve (Fig.19) and according to Beer's law the amount of aniline in the air samples can be determined. The results indicate using this method to determine the amount of aniline in air samples seems possible.

VI.DISCUSSION:

A. In this experiment, the coupling reactions under several different conditions shows that a bright yellow color and all the UV spectra indicate a specific absorption peak at 486 nm. Increased concentration of aniline also increases the absorbance at 486 nm. Plotting absorbance vs. concentration produces a linear calibration curve. Therefore this method can be used to detect the existence of aniline and to determine the amount from the calibration curve.

B. When the concentration of aniline in the sample becomes larger than 60 ppm, the linearity of this calibration curve disappears. This happen because the concentration is too high and the color becomes too deep.

C. When the aniline concentration is less than 4 ppm the concentration become too small to measure accurately. The reason is that the reaction is inhibited by sulfuric acid which originally exists in diazonium sulfate solution.



D. In order to perform the analysis in a reasonable time there are three methods which can be used.

1. After a short period of reaction (just until the color of the solution changes) concentrated sulfuric acid is added to quench the reaction before measurement. This requires careful measurement and control of the reaction time before quenching; then a good result can be obtained without the effect of reaction time. The reaction is stopped by adding concentrated sulfuric acid, since the remaining aniline reacts with H_2SO_4 rather than undergoing the coupling reaction.

2. Because the reaction rate depends on temperature, cooling the solution in an ice bath after a measured amount of time will also give a good calibration curve and a useful analysis.

3. Increasing the reaction temperature will speed up the reaction before measuring the absorbance. This allows the reaction to go to completion, and timing is not as critical.

The first two methods are good for higher concentrations (> 30 ppm of aniline) because the reaction rate is proportional to time. Therefore a partial of complete coupling reaction gives sufficient product for an accurate determination. The last method is good for lower concentrations (< 30 ppm). When the concentration of aniline is low, a complete reaction is necessary to increase the sensitivity.

E. In this method, a difference in concentration of aniline in the sample of just 1 ppm gives a change which is easily seen. Therefore, a color chart similar to that used for pH paper could be designed for a quick estimate of the amount of aniline in a sample. This may become another application.

F. This method can be applied to analyze aniline in air samples. Because air sample collection at room temperature takes time, the reactions to prepare the standards should be carried out at room temperature and measured after 12 hours.

G. The recommended threshold value (TLV) of aniline vapor in air is 0.5 ppm by volume for eight hour daily exposure(1). This method is sufficiently sensitive to measure the concentration of aniline in air at levels near the TLV.

VII. FUTURE WORK:

A. Other aromatic amines containing electron releasing groups or electron withdrawing groups can be studied. This method can be applied to them, to see whether they can be determined by this method or if they will cause interferences with the measurement of aniline.

B. Use this method to analyze real air samples can know the contain of aniline and to determine whether it is pratical and accurate or not. Samples should be analyzed by other methods and compared with the present method to assess the accuracy of the method and to determine possible interferents and detection limits.

C. The "Colour Index" list one hundred and sixty-five dyes prepared from aniline itself(32) and many more from its derivatives. Consider another derivatives may improve this method.

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