KKU ENGINEERING JOURNAL 2016;43(S1):137-140 Research Article

KKU Engineering Journal

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# A simple colorimetric method for the determination of aromatic amines

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Received April 2016
Accepted June 2016

**Abstract**

A simple colorimetric of aromatic amines was developed by using sodium nitrate in acid medium for the determination of five aromatic amines including diphenylamine (DPA), 2-aminodiphenyl (2-ADP), 4-aminodiphenyl (4-ADP), *p*-phenylenediamine (*p*-PDA) and *o*-phenylenediamine (*o*-PDA). The effect of various factors such as type and concentration of acid, sodium nitrate concentration and reaction temperature were inspected. Upon the optimized condition, the reaction colors of DPA, 2-ADP, 4-ADP, *p*-PDA and *o*-PDA gave blue, dark pink, red, light pink and brown, respectively. The linear range concentration of DPA, 2-ADP, 4-ADP, *p*-PDA and *o*-PDA were obtained at 1-50, 1-170, 1-20, 1-100 and 1-150 mg.L$^{-1}$ whereas the detection limit were found at 0.052, 0.081, 0.054, 0.001 and 0.009 mg.L$^{-1}$, respectively.

**Keywords:** Aromatic amines, Colorimetric, Spectrophotometer, Sensor

## 1. Introduction

Aromatic amines (AAs) have been known as pollutants in many industrial areas and they are also considered as hazardous chemicals for health and environment. Several AAs have also been detected in cigarette smoke and pesticides; such as, aniline, o-toluidine, 1-naphthylamine (1-NA), 2-naphthylamine (2-NA), 4-aminodiphenyl (4-ADP) and diphenylamine (DPA). Up to date, gas chromatography mass spectrometry (GC-MS) [1-2], high-performance liquid chromatography (HPLC) [3-4], liquid chromatography mass spectrometry (LC-MS) [5-6] and electrochemical method [7] have been known as a standard methods. However, these methods are needed to deal with some expensive and unwieldy equipment for a long time. A simple colorimetric method is a simple and convenient technique which also can be monitored by naked eye without any analytical techniques, can simply and conveniently monitor target ions in the visible range with high sensitivity, low cost, specificity, rapidity and most importantly 'naked-eye' detection of analyte [7-11]. Herein, we reported a colorimetric method for determination of aromatic amines specifically, diphenylamine (DPA), 2-aminodiphenyl (2-ADP), 4-aminodiphenyl (4-ADP), *p*-phenylenediamine (*p*-PDA) and *o*-phenylenediamine (*o*-PDA). The purposed of this study provide a simple, effective, sensitive method based on oxidation reaction of aromatic amine and sodium nitrate in medium acid solution.

## 2. Materials and methods

### *2.1 Materials*

DPA, 2 - ADP, 4-ADP, *p*-PDA and *o*-PDA were purchased from commercial supply with analytical grade and used without further purification. The photophysical absorption was recorded on a UV-2600 spectrophotometer with 1 cm path length quart cell.

General method for absorption studies

All measurements were carried out at room temperature in acid. Stock solutions of aromatic amine were prepared by dissolving aromatic amine in methanol. The UV–vis spectra were obtained in 2 ml conc. $H_2SO_4$, 1 ml of 1x10$^{-3}$ M $NaNO_3$ and 2 ml of aromatic amine solution. The order of addition for each aromatic amine containing 1-50 mg/l, 1-170 mg/l, 1-20 mg/l, 1-100 mg/l and 1-160 mg/l of DPA, 2-ADP, 4-ADP, *p*-PDA and *o*-PDA, respectively.

## 3. Results and discussion

It was known that the dimerization reaction of diphenylamine with an acid and nitrate ion gave the violet color of diphenylbenzidine [12-13] with maxima absorption at 565 nm (Figure 1). With this data in hand, diphenylamine was used for the optimized study including the investigation for acid type and concentration variation, sodium nitrate concentration and reaction temperature.

### *3.1. Study of acid type and acid concentration*

Nitric, sulfuric, hydrochloric and acetic acids were tested to determine the suitable acid for diphenylamine testing (Figure 2a). The result showed that sulfuric acid gave the maximum absorption intensity at 565 nm. Then, a different concentration of $H_2SO_4$ was studied using 0.1, 1, 2, 3, 5 M

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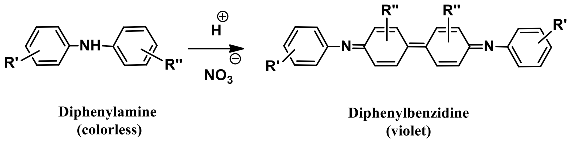
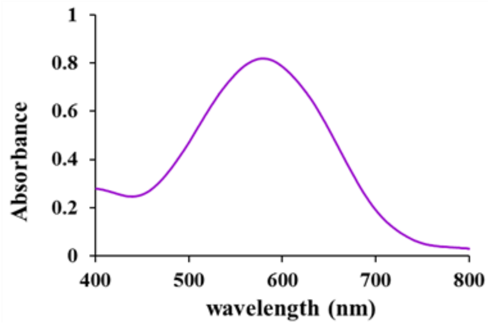
doi: 10.14456/kkuenj.2016.41

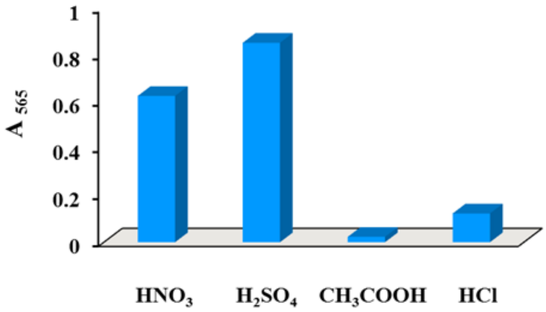



(a)

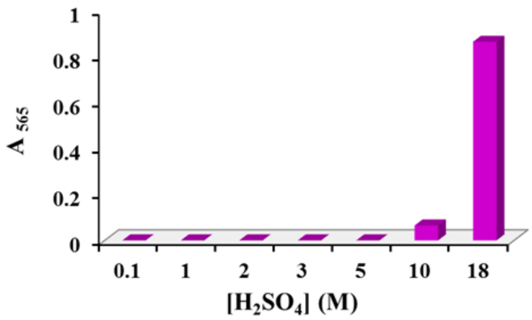



(b)

**Figure 1** (a) The dimerization reaction of diphenylamine with acid and $NaNO_3$ (b) absorption spectrum of the dimerization reaction




(a)



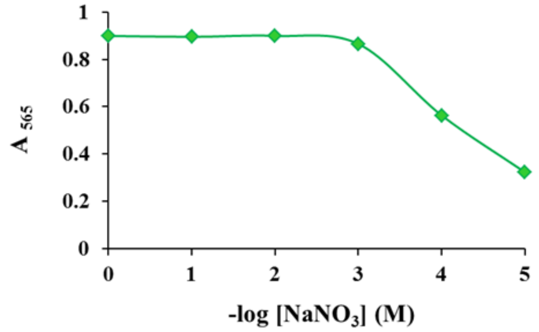

(b)

**Figure 2** Absorption intensity at 565 nm of 50 ppm DPA and $1x10^{-3}$ M $NaNO_3$ (1 ml) with (a) conc. $HNO_3$, $H_2SO_4$, $CH_3COOH$, HCl (b) 0.1, 1, 2, 3, 5 M and conc. $H_2SO_4$

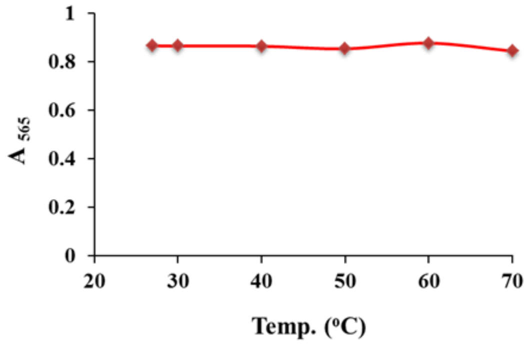
and conc. $H_2SO_4$ (18 M). We found that the highest absorption reaction was obtained from conc. $H_2SO_4$ medium (18 M), Figure 2b.

*3.2 Study of sodium nitrate concentration and reaction temperature*

A varied concentration of sodium nitrate from $10^{-1}$-$10^{-5}$ M were studied (Figure 3a). The suitable $NaNO_3$ concentration was obtained at $1x10^{-3}$ M. Furthermore, there is no effect on the absorption intensity when the reaction temperatures were increased to 70 °C (Figure 3b). We concluded that the optimized condition is 50 ppm amine (3 ml) with conc. $H_2SO_4$ (2 ml) and $1x10^{-3}$ M $NaNO_3$ (1 ml) at room temperature (27 °C).




(a)




(b)

**Figure 3** Absorption intensity at 565 nm of 50 ppm DPA, conc. $H_2SO_4$ (a) with $10^{-1}$, $10^{-2}$, $10^{-3}$, $10^{-4}$ and $10^{-5}$ M $NaNO_3$, (b) $1x10^{-3}$ M $NaNO_3$ at 27, 30, 40, 50, 60 and 70 °C

*3.3 Colorimetric detection of aromatic amine using dimerization reaction*

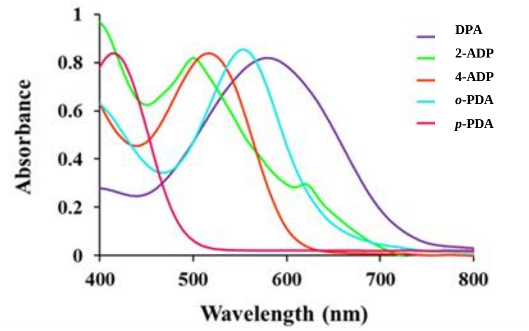
We investigated the colorimetric response with aromatic and aliphatic amines using the optimized condition. We found that the resulting reaction colors and absorption wavelengths were specific to aromatic amine. 2-ADP, 4-ADP, *p*-PDA and *o*-PDA gave dark pink (475 nm), red (523 nm), light pink (512 nm) and brown (425 nm), respectively, which could be easily recognized both by naked eyes and monitored by visible absorption spectra (Figure 4). While aliphatic amines including dibuthylamine (DBA), tributhylamine (TBA), propylamine (PPA), triethylamine (TEA) and diethanolamine (DEA) have no respond using dimerization reaction condition.

*3.4 Study of linearity, detection and quantitation limit of aromatic amine*

The calibration curves were constructed by plotting of the absorbance of aromatic amine (A) at difference concentration (C). The linear calibration graphs were obtained as shown in Figure 5 and summarized in Table 1.

## 4. Conclusions

We have established a simple, rapid and sensitive colorimetric method determination of five aromatic amines



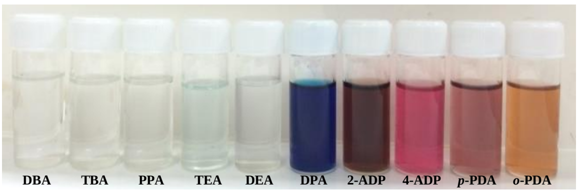




**Figure 4** Absorption spectra and photographic using 50 ppm different amine (3 ml); conc. $H_2SO_4$ (2 ml); $1x10^{-3}$ M $NaNO_3$ (1 ml) at room temperature

**Table 1** Linear equation, correlation coefficient ($R^2$), analytical range and limit of detection (LOD) of dimerization reaction

| Sample | linear equation (n = 3) | $R^2$ | Analytical range (mg.L$^{-1}$) | LOD (mg.L$^{-1}$) |
|---|---|---|---|---|
| **DPA** | A= 0.0156C + 0.1748 | 0.9977 | 1-50 | 0.052 |
| **2-ADP** | A= 0.0054C + 0.0537 | 0.9989 | 1-170 | 0.081 |
| **4-ADP** | A= 0.036C + 0.1714 | 0.9966 | 1-20 | 0.054 |
| ***p*-PDA** | A= 0.0068C + 0.3138 | 0.9989 | 1-100 | 0.001 |
| ***o*-PDA** | A= 0.05C + 0.1184 | 0.9988 | 1-150 | 0.009 |

The correlation coefficients ranged from 0.9968-0.9990 were obtained. Limit of detection (LOD) were calculated from 3SD/*m* where *m* is slope.

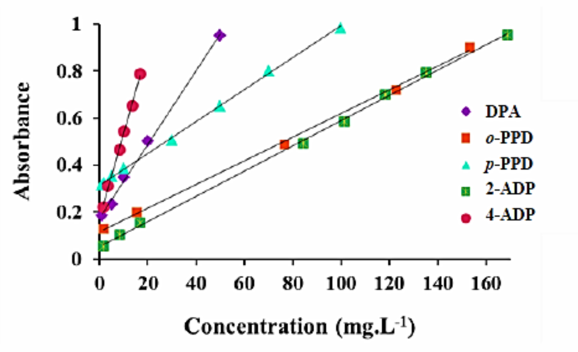



**Figure 5** Linear responses of the aromatic amines with conc. $H_2SO_4$ (2 ml), $1x10^{-3}$ M $NaNO_3$ (1 ml) at room temperature

with good linearity of color and absorbance adjustment. This system could be a novel colorimetric probe via oxidation reaction of aromatic amine significantly changes in the absorption spectra accompanied by a color change. Furthermore, it exhibited an excellent tolerance to coexisting components with other amine. In addition, both good linearity of the color and absorbance in practical applications, this system could be potentially used as a novel for DPA, 2-ADP, 4-ADP, *p*-PDA and *o*-PDA.

## 5. Acknowledgements

The authors would like to thank Ubon Ratchathani University for the financial support.

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