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# Spectrophotometric Determination of Aminophenol Isomers in Aqueous Solution using 1,2-Naphthoquinone-4-sulphonate Reagent

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**Abstract**

A spectrophotometric method was developed for the quantitative determination of aminophenol isomers. The method is based on their reaction with 1,2-Naphthoquinone-4-sulphonate (NQS) reagent in aqueous basic medium forming colored products with maximum absorption at wavelengths 488, 480 and 535 nm for *o*-, *m*- and *p*-aminophenol respectively. Beer's law is obeyed over the concentration range of 0.2-10, 0.08-7.2 and 0.08-18 μg $ml^{-1}$ with molar absorptivity values of 5166.6 ,6613.6 and 7673.6 L $mol^{-1}$ $cm^{-1}$ for the above isomers, respectively. The average recovery was ranged between 99.14 % to 102.5 % and the precision was better than 4.0 %. The limit of detection was in between 0.0348 and 0.05188 μg $ml^{-1}$. The products are formed in ratio of 1:1 and the stability constants are $3.97\times10^7$, $8.58\times10^5$, $2.95\times10^5$ L $mol^{-1}$ for the above isomers, respectively. The method was applied successfully for the determination of o-aminophenol in river, tap, spring and sea waters.

***Keywords:*** NQS; Aminophenol isomers; Spectrophotometry; Aqueous solution.

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## Introduction

Aminophenol isomers are primarily used as intermediates in the manufacture of dyes and pigments. The largest class of dyestuffs is that of the azo colours, which are made by diazotization. These isomers, which are crystalline solids of low volatility, act as skin sensitizers and cause contact dermatitis, which appears to be the greatest hazard arising from their use in industry [1]. These compounds are also the main metabolites of aniline both in vivo and in vitro [2].

Several spectrophotometric methods using various reagents such as 4-aminoantipyrine [3], 2-methyl-5-vinylpyridine [4] and salicylaldehyde [5] are used for determination of *o*-aminophenol. Potassium iodate [6,7], crowned 2,4-dinitrophenolazophenol-barium (Π) complex [8] and 2,4-dinitrofluorobenzene [9] are used for determination of *m*-aminophenol. Resorcinol [10], sodium sulphide [11], 4-nitro- or 2,4-dinitrobenzaldehyde [12] and 5,7-dichloro-4,6-dinitrobenzofuroxan [13] have been described for the determination of *p*-aminophenol. Many spectrophotometric methods based on the oxidative coupling reactions have been reported for determination of *p*-aminophenol produced from the acidic and basic hydrolysis of paracetamol [14-18]. However; most of these methods are either insufficiently sensitive or tedious and required an extraction step. Various analytical techniques have been reported for determination of aminophenol isomers such as thin layer chromatography [19], adsorptive stripping voltammetry [20, 21], liquid chromatography [22-25], potentiometry [26] and fluorimetry [27]. These methods needed of highly sophisticated instruments. The present work describes a simple and sensitive spectrophotometric method for analyses of

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aminophenol isomers. The method is based on the formation of Schiff's base from the reaction of these isomers with 1,2-Naphthoquinone-4-sulphonate (NQS) reagent in aqueous medium.

## Experimental

### *Apparatus*

Shimadzu UV-1650 PC UV-Visible spectrophotometer equipped with a 1.0-cm path length silica cell**,** Philips PW (9421) pH-meter with a combined glass electrode was used for pH measurements**.** All calculations in the computing process were done in Microsoft Excel for Windows.

### *Reagents*

All reagents were of analytical-reagent grade which are provided by BDH, Fluka and Molekula companies. A standard solutions of 100 µg $ml^{-1}$ of *o*-aminophenol (*oA)*, *m*- aminophenol (*mA*) and *p*-aminophenol (*pA)* were prepared separately in 100-ml volumetric flask by dissolving 0.01g in 2.0 ml of ethanol and diluting to the mark with distilled water. The stock solutions were stored in dark and were found to be stable for at least 4 weeks. The working solutions of each isomer were obtained from appropriate dilution of stock solutions daily. $5\times10^{-3}$ M of NQS reagent was prepared by dissolving 0.065 g in distilled water and making the volume up to 50 ml in a volumetric flask, this solution was prepared fresh as a daily procedure. 0.1 M sodium bicarbonate was prepared by dissolving 5.3 g in distilled water and making the volume up to 500 ml in a volumetric flask. 0.1 % of CTAB was prepared in warm distilled water.

### *General procedure*

Appropriate volumes containing 0.2-10, 0.08-7.2 and 0.08-18 µg $ml^{-1}$ of *oA*, *mA* and *pA* standard solutions and 0.4, 0.4 and 0.8 ml of NQS reagent solution were added into separated 25-ml volumetric flasks; respectively, followed by addition of 1.5 ml of sodium bicarbonate and 1.5 ml of CTAB. The solutions were diluted to the mark with distilled water, and were left for 10 min at room temperature. A portion of the solution was transferred into a 1cm silica cell to measure the absorbance at 488, 480 and 535 nm against the respective reagent blank for *oA*, *mA* and *pA*, respectively.

## Results and Discussion

### *Preliminary test*

Aminophenol isomers reacted with NQS reagent and form Schiff bases in the presence of sodium hydroxide with an orange colored solution with maximum absorption at 448 and 460 nm for *oA* and *mA* respectively, while, a red colored was observed with maximum absorption at 530 nm for *pA*.

### *Effect of pH*

The effect of pH on the absorption spectra for solutions of *oA*, *mA* and *pA* (4 µg $ml^{-1}$) was studied. A range between 2.0 and 11.0 pH value in the final volume, by addition of 0.1 M of HCl and NaOH, was examined. It was found that the products were formed in basic medium with maximum absorption in the ranges 10.21-11.07, 10.3-10.8 and 10.20-10.50 at 448, 460 and 495 nm for *oA*, *mA* and *pA* respectively, and beyond these ranges a decrease in absorbance was noticed. Because there was not any significant difference between pH ranges, the pH value of 10.3 was selected in this study.

### *Effect of bases and buffer solutions*

To obtain high sensitivity for the products, the effect of some bases such as sodium bicarbonate, sodium carbonate, potassium hydroxide and ammonium hydroxide have been examined. As shown in Table-1, potassium hydroxide gave maximum absorption at 475, 460 and 525 nm for *oA*, *mA* and *pA*, respectively, but with unstable color absorbance. Sodium carbonate, which was selected in this method, gave more stable color absorbance at 475, 460 and 495 nm for *oA*, *mA* and *pA*, respectively. (Fig. 1) shows that concentration ranges of 1.0-3.0, 1.0-3.5 and 1.5-5.0 ml of 0.1 M sodium carbonate for *oA*, *mA* and *pA* gave maximum absorption. The effect of buffer solution such as ammonium, borate, carbonate and phosphate buffers with pH 10.3 was examined, but either no significant change or decrease in the absorbance of the products was observed. Therefore, 1.5 ml of 0.1M sodium carbonate was selected in the subsequent experiments.

***Table 1.*** **Effect of bases on the absorption of aminophenol isomers.**

| Base 0.5ml of 0.1M | *oA* | | | *mA* | | | *pA* | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max}$ (nm) | Absorbance | | $\lambda_{max}$ (nm) | Absorbance | | $\lambda_{max}$ (nm) | Absorbance | |
| | | *Sample* | *Blank* | | *Blank* | *Sample* | | *Blank* | *Sample* |
| 0.030 | 0.195 | 480 | 0.031 | 0.075 | 480 | 0.030 | 0.163 | 480 | Without |
| 0.018 | 0.273 | 495 | 0.055 | 0.259 | 460 | 0.068 | 0.189 | 448 | NaOH |
| 0.037 | 0.207 | 480 | 0.048 | 0.105 | 480 | 0.045 | 0.184 | 475 | $NaHCO_3$ |
| 0.032 | 0.217 | 495 | 0.082 | 0.204 | 460 | 0.040 | 0.182 | 475 | $Na_2CO_3$ |
| 0.018 | 0.283 | 525 | 0.058 | 0.235 | 460 | 0.071 | 0.198 | 475 | KOH |
| 0.207 | 0.148 | 495 | 0.368 | 0.097 | 460 | 0.192 | 0.119 | 470 | $NH_4OH$ |

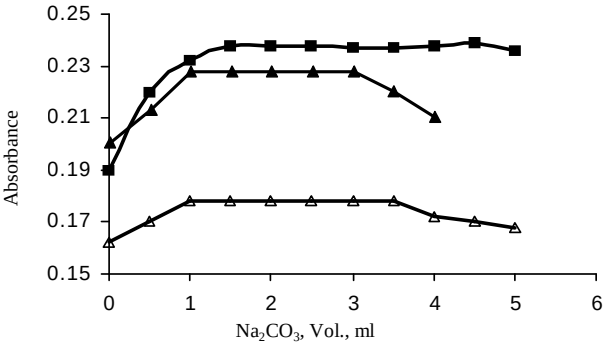



***Figure 1.*** **Effect of $Na_2CO_3$ concentration on the absorption of reaction mixture of 4 µg $ml^{-1}$ for each (∆) *oA* measured at 475 nm, (▲) *mA* measured at 460 nm and (■) *pA* measured at 495 nm in the presence of NQS reagent.**

## *Effect of NQS reagent*

The effect of changing the NQS concentration on the absorbance of solution containing a fixed amount of each isomer was studied. It is evident that the absorbance increases with increasing NQS concentration and reached maximum on using 0.4 of $5\times10^{-3}$ M NQS for *oA* and *mA* and 0.8 ml for *pA*, (Fig.2). Therefore, these concentrations were used in all subsequent work.

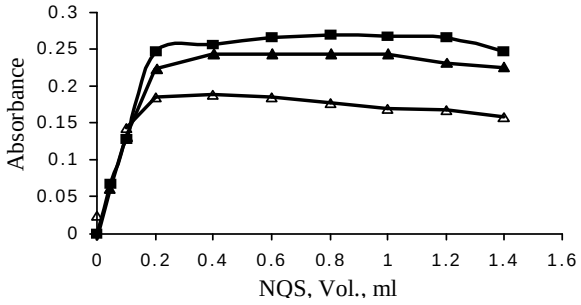



***Figure 2.*** **Effect of NQS reagent concentration on the absorption of reaction mixture of 4 µg $ml^{-1}$ for each (∆) *oA* measured at 475 nm, (▲) *mA* measured at 460 nm and (■) *pA* measured at 495 nm in the presence of $Na_2CO_3$ solution.**

## *Effect of surfactants*

The effect of surfactants; cetyltrimethyl ammonium bromide (CTAB), cetylpyridinium chloride (CPC), Tween-80 (TW-80) and TritonX-100 (TX-100), of 0.1 % concentration, on the absorption spectra of products have been investigated. As shown in Table 2, the cationic surfactants CTAB and CPC shift the maximum absorption to longer wavelength and increased the absorbance of isomer-NQS products, but the anionic SDS, nonionic TX-100 and TW-80 surfactants showed no positive effect. As shown in Table 2, the use of CTAB as a cationic surfactant was most effective in improving absorbance, and the color development was stable and reproducible. However, CTAB was selected in this method. The absorbance increased with an increase in CTAB concentration up to 1.0 ml and remain constant up to 3.0 ml for all isomers (Fig.3). Therefore 1.5 ml of 0.1 % CTAB was selected for further investigation.

***Table 2.*** **Effect of surfactants on the absorption of aminophenol isomer.**

| Surfactant | Aminophenol isomers | | | | | |
|---|---|---|---|---|---|---|
| | *pA* | | *mA* | | *oA* | |
| | Abs. | $\lambda_{max}$ (nm) | Abs. | $\lambda_{max}$ (nm) | Abs. | $\lambda_{max}$ (nm) |
| 0.262 | 495 | 0.220 | 460 | 0.188 | 475 | Without |
| 0.285 | 525 | 0.245 | 480 | 0.189 | 475 | CPC |
| 0.296 | 535 | 0.254 | 480 | 0.193 | 488 | CTAB |
| 0.255 | 495 | 0.225 | 460 | 0.184 | 465 | SDS |
| 0.259 | 500 | 0.220 | 460 | 0.187 | 465 | Trion X-100 |
| 0.259 | 500 | 0.221 | 460 | 0.176 | 465 | Tween 80 |

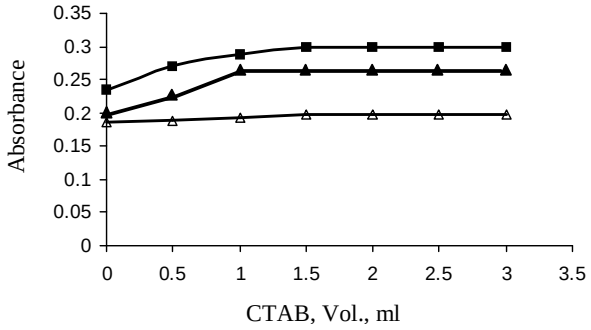



***Figure 3.*** **Effect of CTAB concentration on the absorption of reaction mixture of 4 µg ml$^{-1}$ for each (∆) *oA*, (▲) *mA* and (■) *pA* in the presence of NQS and $Na_2CO_3$ solution.**

### *Effect of temperature and developing time*

The effect of temperature on the rate of reaction for the studied isomers was studied at 25° and 40°C at the previous optimum reaction conditions. The results indicated that products were formed after addition of reagents immediately at room temperature (25°C) and reached its maximum absorbance after 5.0 min at 488, 480 and 535 nm for *oA*, *mA* and *pA*, respectively and remain constant for 120 min for *oA* and 20 min for *mA* and *pA*, where as, a decrease in absorbance with increased time was noticed at 40°C indicating dissociation. Hence, 10 min at 25°C was used in this work.

### *Absorption spectra*

The final absorption spectra of the three isomer products are plotted under the optimum conditions obtained above, (Fig. 4) shows that *oA*, *mA* and *pA* Schiff base products have a maximum absorption at 488, 480 and 535 nm versus their corresponding blank respectively, where as the reagent blank has a maximum absorption at 360 nm versus distilled water.

### *Quantification*

In order to investigate the range in which the colored product adhere to Beer's law, the absorbance of the products were measured at their corresponding $\lambda_{max}$ value after developing the color by following the suggested procedure for individual calibrations for a series of solutions containing increasing amounts of each isomer. The Beer's law limits and molar absorptivity values were evaluated and given in Table 3, which are indicated that the method is sensitive. The linearity was represented by the regression equation and the corresponding correlation coefficient for the aminophenol isomers determined by the proposed method represents excellent linearity. The relative standard deviation (RSD) and accuracy (average recovery %) for the analysis of six replicates of each three different concentrations for each isomer indicated that the method is precise and accurate Table 4. Limit of quantitation (LOQ) is determined by taking the ratio of standard deviation of the blank with respect to water and the slope of calibration curve multiplied by a factor of 10. LOQ is approximately 3.3 times LOD. Naturally, the LOQ slightly crosses the lower limit of Beer's law range. However, LOD is well below the lower limit of Beer's law range.

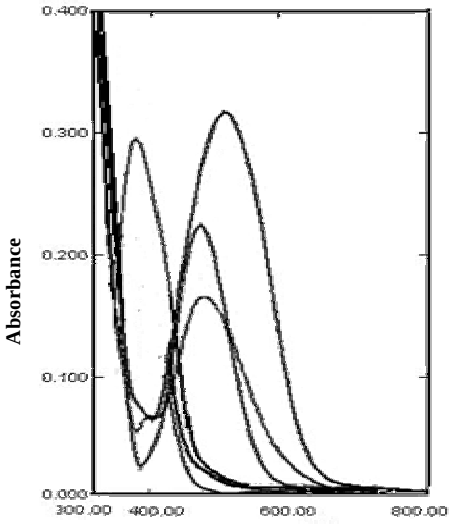



***Figure 4.*** **Absorption spectra of NQS product with 4 µg ml$^{-1}$ of (a) *oA*, (b) *mA*, (c) *pA* Vs reagent blank and (d) reagent blank Vs distilled water at the optimum conditions.**

***Table 3.*** **Summary of optical characteristics and statistical data for the proposed method.**

| Parameter | *oA* | *mA* | *pA* |
|---|---|---|---|
| Beer's law limits (µg ml$^{-1}$) | 0.2-10 | 0.08-7.2 | 0.08-18.0 |
| Molar absorptivity (l.mol$^{-1}$. cm$^{-1}$) | 5167 | 6614 | 7647 |
| LOD (µg.ml$^{-1}$) | 0.05188 | 0.03750 | 0.03480 |
| LOQ (µg.ml$^{-1}$) | 0.1729 | 0.1250 | 0.1160 |
| Average recovery (%)** | 100.23 | 99.14 | 102.50 |
| Correlation coefficient | 0.9994 | 0.9993 | 0.9993 |
| Regression equation (Y)* | | | |
| Slope, *a* | 0.0474 | 0.0607 | 0.0704 |
| Intercept, *b* | 0.0019 | 0.0107 | 0.0145 |
| RSD** | ≤ 2.48 | ≤ 3.12 | ≤ 3.57 |

*$Y = a\,X + b$, where $X$ is the concentration of analyte in µg ml$^{-1}$.
** Average of six determinations.

***Table 4.*** **Precision and accuracy data for aminophenol isomers determination obtained by the proposed method.**

| Isomer | Amount added ($\mu gml^{-1}$) | Recovery* (%) | Average recovery (%) | RSD* (%) |
|---|---|---|---|---|
| *oA* | 0.8 | 99.87 | 100.23 | 2.48 |
| | 4.0 | 101.50 | | 1.73 |
| | 10.0 | 99.34 | | 0.73 |
| *mA* | 0.8 | 95.25 | 99.14 | 3.12 |
| | 4.0 | 102.50 | | 0.87 |
| | 6.4 | 99.68 | | 0.55 |
| *pA* | 1.0 | 102.90 | 102.50 | 3.57 |
| | 10.0 | 103.10 | | 1.51 |
| | 16.0 | 101.75 | | 0.79 |

*Average of six determinations

## *Interferences*

The interference from various organic nitrogen compounds, including primary amines and amides on the determination of 4 µg $ml^{-1}$ of *oA* (as example for aminophenol isomers) in addition to inorganic cations and anions, was examined. It was found that these compounds did not affect the accuracy of the determination of *oA* when present in excess range between 6 folds for butylamine and 20 folds for dibutylamine and formamide and in the presence of 750 folds of cations and anions except of $Fe^{3+}$, $Al^{3+}$ and $Ca^{2+}$ ions which showed interfering effect. An error of 5.0 % in the absorbance readings was considered tolerable. The results are summarized in Tables 5 and 6.

***Table 5.*** **Effect of some primary amines and amides on the assay of *oA*.**

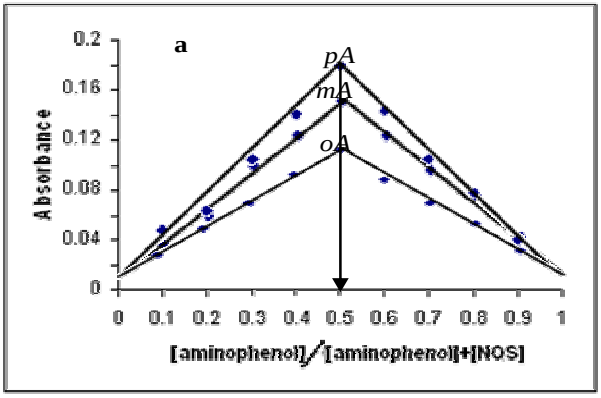
| Foreign compound | Recovery % of 4 $\mu gml^{-1}$ of *oA* per $\mu gml^{-1}$ foreign added | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | ***80*** | ***40*** | ***24*** | ***20*** | ***16*** | ***12*** | ***8*** | ***4*** |
| Butylamine | - | 87.50 | 95.00 | 95.83 | 100.00 | 102.08 | 100.00 | 99.16 |
| Dibutylamine | 100.00 | 95.92 | 96.92 | 96.38 | 96.38 | 100.45 | 95.00 | 97.28 |
| Triethylamine | 94.09 | 96.36 | 97.72 | 99.00 | 98.63 | 101.36 | 101.36 | 100.90 |
| Acrylamide | 112.32 | 109.00 | 105.68 | 102.36 | 101.42 | 100.94 | 98.57 | 98.10 |
| Formamide | 98.64 | 101.35 | 100.45 | 99.54 | 99.09 | 98.64 | 96.84 | 95.49 |

***Table 6.*** **Effect of some cations and anions on the assay of *oA*.**

| Foreign ion | Recovery % of 4$\mu gml^{-1}$ *oA* per $\mu gml^{-1}$ foreign added | | | | |
|---|---|---|---|---|---|
| | ***3000*** | ***2000*** | ***1000*** | ***500*** | ***100*** |
| $Na^{+}$/ NaCl | 102.71 | 102.71 | 100.80 | 103.20 | 101.63 |
| $K^{+}$/ KCl | 99.50 | 99.00 | 100.50 | 97.50 | 97.00 |
| $Mg^{+2}$/ $MgCl_2.6H_2O$ | 97.58 | 98.06 | 99.51 | 101.93 | 104.34 |
| $Ca^{+2}$/ $CaCl_2.2H_2O$ | 121.50 | 145.50 | 154.50 | 126.00 | 127.50 |
| $Al^{+3}$/ $AlCl_3$.9H2O | 82.07 | 87.26 | 91.50 | Turbid | 83.34 |
| $Fe^{+3}$/ $FeCl_3$ | 301.00 | 319.00 | 384.00 | 390.00 | 374.50 |
| $Cl^{-}$/ NaCl | 107.76 | 101.45 | 99.51 | 101.45 | 112.13 |
| $NO_3^{-}$/ $NaNO_3$ | 105.80 | 104.30 | 100.40 | 100.97 | 102.90 |
| $SO_4^{-2}$/ $MgSO_4.7H_2O$ | 100.00 | 100.00 | 99.52 | 97.12 | 102.39 |

### *Stoichiometry and stability constant*

The stoichiometry of the reaction of aminophenol isomers with NQS reagent was studied by the molar ratio [28] and Job [29] methods, using solutions of $1x10^{-3}$ M for each isomer and NQS reagent. As shown in (Fig. 5 a & b), the results indicate that 1:1 aminophenol to reagent was formed using both above methods. This indicates that amino group present in the isomer is responsible for the formation of the Schiff base products.



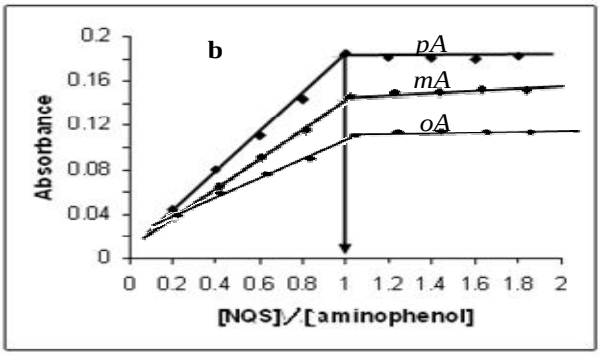




***Figure 5.*** **Determination of the isomer-NQS products by (a) Job and (b) mole ratio methods.**

According to the results obtained from above stoichiometry**,** the apparent stability constant was estimated by comparing the absorbance of a solution containing stoichiometric amounts of the each aminophenol isomer and NQS (As) to one containing an excessive amount of NQS reagent (Am). The average conditional stability constants of the complexes are calculated by the following equation :

$$Kc=1-\alpha/\ \alpha^{2}\ C$$

$$\alpha = Am-As/Am$$

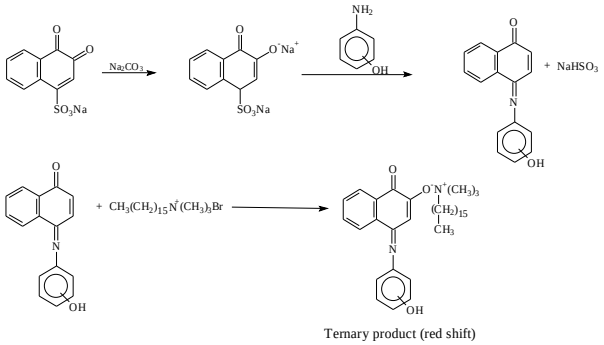
where Kc is the association constant ($l.mol^{-1}$), α the dissociation degree and C the concentration of the product which is equal to the concentration of aminophenol. The results shown in Table 7 indicate that the products are relatively stable.

***Table 7.*** **Association constants of the NQS-aminophenol isomer products.**

| Isomer | Volume (ml) | Con. (M) | Absorbance $A_m$ | Absorbance $A_s$ | α | Average $K_{st}$ ($Lmol^{-1}$) |
|---|---|---|---|---|---|---|
| *oA* | 1.0 | $1x10^{-3}$ | 0.217 | 0.225 | 0.03550 | $3.97x10^{7}$ |
| | 1.5 | | 0.329 | 0.329 | 0.03340 | |
| | 2.0 | | 0.420 | 0.440 | 0.04540 | |
| *mA* | 1.0 | $1x10^{-3}$ | 0.255 | 0.324 | 0.21290 | $8.58x10^{5}$ |
| | 1.5 | | 0.385 | 0.430 | 0.10460 | |
| | 2.0 | | 0.399 | 0.453 | 0.11920 | |
| *pA* | 1.0 | $1x10^{-3}$ | 0.275 | 0.352 | 0.21875 | $2.95x10^{5}$ |
| | 1.5 | | 0.400 | 0.512 | 0.21875 | |
| | 2.0 | | 0.545 | 0.697 | 0.21807 | |

### *Reaction mechanisms*

A characteristic orange colored products of λmax 475, 460 and 495 nm for *oA*, *mA and pA* respectively are formed when they allowed to react with NQS in the presence of $Na_2CO_3$ in aqueous medium. Under the experimental conditions, the light yellow alkaline solution of the *o*-quinoidal NQS reacts with compounds containing one removable hydrogen atom [29] attached to one nitrogen atom, to yield an anionic orange colored paraquinoid imide condensation product with the elimination of $NaHSO_3$ [30]. When CTAB is added to these products, an intense orange colored products of λmax 488, 480 nm for *oA* and *mA* respectively and red colored product of λmax 535 nm for *pA* are formed as ternary products [29]. A reaction mechanism based on the above reaction is shown in Scheme 1.




Scheme 1: Probable product formation

### *Application of the method for determination of oA in real water samples*

To evaluate the applicability of the proposed method to real samples, it was applied to the determination of *oA* in real water samples including river, tap, well and sea waters. The samples tested were found to be free from *oA* and other isomers, thus, synthetic samples were prepared by adding known amounts of *oA* to the filtered water samples. Following the general procedure, the absorbance was measured at 488 nm and the results are given in Tables 8. The recoveries are indicating that there is no serious interference in such water samples except of the presence of high concentration of *oA* in sea water. However; the proposed method is suitable for determination of *oA* in water samples.

***Table 8.*** **Determination of *oA* in water samples.**

| ***oA*** **added** **($\mu gml^{-1}$)** | **Recovery (%)** | | | |
|---|---|---|---|---|
| | **Sea water** | **Well water** | **Tap water** | **River water** |
| 99.00 | 98.20 | 97.00 | 103.50 | 2.0 |
| 101.00 | 100.45 | 97.40 | 97.45 | 4.0 |
| 118.75 | 100.00 | 101.75 | 102.25 | 8.0 |

## Conclusion

The proposed method is simple, rapid, selective, sensitive and economical compared to reported methods and does not require any pretreatment or extraction procedure and has good accuracy and precision. In terms of simplicity and expense, the method could be considered superior in comparison with the previously reported methods, especially those needed of highly sophisticated instruments. Hence, this method is best suited for the determination of aminophenol isomers to assure high standard of quality control.

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