Spectrophotometric method for designation of nitrobenzene by using o-chloranil so application in Diyala River and waterproof case

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Abstract. A reproducible, critical and simple spectrophotometric method for assay of RNB was investigated is based on (charge transfer complex) formation reaction of RNB with O-Chloranil reagent in the presence of sodium bicarbonate in ethanol to give a highly coloured species with maximal absorption at 440 nm, As well Beer’s law was obeyed in the range of (5-50) µg.mL with a molar absorptivity of 1.21×10^4 L.mol⁻¹.cm⁻¹ and the limit of detection and quantitation were 0.059 and 0.242 µg.mL respectively. The (average recovery rate) was 101.65% and relative standard deviation (RSD) was better than 0.55%. In addition, it was ratio of 1:1. The method was successfully applied to assay of RNB in Diyala river water and waterproof case.

Keyword: RNB, Surfactant, o-Chloranil, Charge transfer complex

Introduction

Nitrobenzene is a simplest aromatic compound using in industries pharmaceutical, pigments and explosives1,2, as described to preparation of analytical chemistry determination of Ca the method is depended on the transfer of Ca ions from water to nitrobenzene3. But at higher concentration of nitrobenzene depressed respiration, bluish-grey skin disturbed vision and came may occur, no information is available on the reproductive, developmental or carcinogenic effects of nitrobenzene in humans4.

Different various analytical techniques have been recorded for determination RNB, several spectrophotometric procedures have been implemented for determination it using different reagents such as SnCl2 with Marshalls reagent 5. Electrochemical conduct of nitrobenzene to a bismuth-film modulate carbon pasta electrode (Bif/cpe) in the present of cetyltrimethyl ammonium bromide (CTAB) 6, as well determination it by preparation and characterization of attapulgite-silver nano composites7. The voltmeter method using to determination it 8. Shu-Xuan Liang describing electric method of estimation it 9. Also it determination in wastewater samples with (accuracy) (95%-102%), by the difference pulse based on an adsorptive stripping technicality10 and by ultrasound-supported magnetic solid-phase extraction depends on ionic liquid-coated film (Fe3O4) for the estimation of nitrobenzene compounds in ecological water sample11.
Experimental Apparatus

UV-VIS spectrophotometer 1650 shimadzu cell 1. cm path length Silica cell, PW 9421 pH-meter with a common glass electrode was employed for pH measurements. The reagent is supplied by BDH, Fluka and Molekula companies. A standard solution of 100 of RNB was prepared by dissolving 0.01g in 2mL of ethanol Zn-powder 0.5g with HCl (conc) was added and continuous shaking of solution for 10 min, 5×10^{-3}M of o-chloranil was prepared Via dissolving 0.123g in ethanol and doing the Volume up to 50mL in a volumetric Flask. 0.1 M sodium bicarbonate was maked by dissolving 0.84g in distilled water in volumetric Flask 100mL, 0.1 M sodium hydroxide was maked Via dissolving 1gm in 250 mL in distilled water, Solution are made by dissolving 0.1 gm. of this in 100mL of warm distilled water.

Results and Discussion

Study of optimal condition for interaction To prove the sensitivity of proposed method, the reagent amount must be optimized, the best solvent, effect of base such as sodium hydroxide, sodium bicarbonate sodium carbonate potassium-hydroxide and ammonium hydroxide and pH, test of buffer solutions such as sodium hydroxide, sodium bicarbonate, sodium carbonate, potassium–hydroxide and ammonium hydroxide. Effect of surfactant such as cetyl trimethyl ammonium bromide (CTAB) cetyl pyridinium chloride (CPC), tween 80 (Tw80) and triton X-100 (Tx-100). The temperature effect; the interaction time was determined by trailing the color evolution at room temperature and in the water – bath at different temperature up to 55°C to test the sensitivity of proposed method the order of addition of reagent were tested under the optimal conditions Obtain the final absorption spectra of RNB-o-chloranil product study the stoichiometry via the molar ratio^{12} also job method^{13}, employing solutions of 3×10^{-3} M for each RNB and o-chloranil, and application study determination of nitrobenzene in diyala river water and tap water.

Effect of dissolve and diluting:

To test the sensitivity of proposed method. The sample in and reagent. Were dissolved in different solvent table [1] shows the effect of solvent solution.

Table [1]: Effect of dissolve and diluting

| No | Nitrobenzene in | O-Chloranil in | Absorbance |
|----|----------------|---------------|------------|
| 1  | Water          | Water         | 0.09       |
| 2  | Ethanol        | Ethanol       | 0.203      |
| 3  | Ethanol        | Water         | 0.198      |
| 4  | Methanol       | Methanol      | 0.142      |
| 5  | Methanol       | Water         | 0.09       |
| 6  | Water          | Acetonitrile  | 0.08       |
| 7  | Acetonitrile   | Acetonitrile  | 0.101      |
| 8  | Acetone        | Acetone       | 0.08       |

As shown in table [1] The Ethanol, solvent, solution increased the absorbance of product therefore which is recommended in this study.

Test of types bases:
To obtain high sensitivity for the product the sodium carbonate gave maximum absorption at 440nm. As shown in figure [1]

![Fig 1: Effect of type bases](image1)

**Effect of amount base and pH**

The effect of sodium bicarbonate amount and found that 1ml gave maximum absorbance at pH 8.5 fig [2], which is recommended in this work.

![Fig 2: Effect of amount base and pH](image2)

**Effect of buffer solution**

The effect of buffer solution with pH 8.5 was examined, but decrease in the absorbance of the product was observed.

**Effect of O-Chloranil amount**

The absorbance increase with amount 1ml of 5×10⁻³ M Of o-Chloranil and reached to a maximum. Which is recommended in a study Figure [3] show a maximum absorbance on using 1ml of 5×10⁻³ M Of o-Chloranil.
Effect of Surfactants:

The surfactants decrease the absorbance of the product was observed Table [2], show the results obtained.

Table [2]: Effect of surfactants on the absorption o-Chloranil – RNB product

| Surfactant     | Absorbance |
|----------------|------------|
| No addition    | 0.321      |
| CPC            | 0.231      |
| SDS            | 0.262      |
| Triton X – 100 | 0.192      |
| Tween 80       | 0.241      |

Effect of temperature and developing time:

It was noted that the absorbance reached maximal after 10 min at 50 C° and remain constant for 15 minutes. Whereas, a diminution in absorbance with growing time and temperature was noticed indicating dissociation. Table [3] show the results obtained.
Table [3]: Effect of temperature and developing time

| Temp °C | Absorbance at time (min) |
|--------|---------------------------|
|        |  5 | 10 | 15 | 20 | 25 | 30 | 40 | 50 | 60 |
| 25     | 0.232 | 0.245 | 0.251 | 0.253 | 0.24 | 0.242 | 0.201 | 0.198 | 0.192 |
| 35     | 0.300 | 0.321 | 0.321 | 0.330 | 0.320 | 0.310 | 0.262 | 0.160 | 0.158 |
| 45     | 0.321 | 0.350 | 0.349 | 0.330 | 0.301 | 0.28 | 0.231 | 0.198 | 0.193 |
| 50     | 0.330 | 0.371 | 0.291 | 0.250 | 0.233 | 0.210 | 0.190 | 0.162 | 0.120 |

Effect of order addition:

Table [4]: Effect of order addition on the absorption of 8µg.mL (RNB)

| No | The addition                  | Absorbance |
|----|-------------------------------|------------|
| I  | RNB + O-Chlor + base          | 0.370      |
| II | RNB + base + O-Chlor          | 0.292      |
| III| Base + RNB + O-Chlor          | 0.332      |
| IV | O-Chlor + base + RNB          | 0.203      |
| V  | O-Chlor + RNB + base          | 0.169      |
| VI | Base + O-Chlor + RNB          | 0.148      |

Absorption Spectra: The final absorption spectra of $\alpha$-Chloranil – RNB product are plotted under the best conditions reached above. Figure[4] establish that (Charge Transfer Complexes – CT-Complex) product have maximum absorption at 440 nm versus reagent blank, while the reagent blank has faint absorbance at this wavelength and have a maximal absorption at 370 nm versus solvent.
The absorbance of the product was measured at 440 nm after evolving the colour via following the general execution calibration graph for a collection of solutions containing rising amount of RNB. The Beer’s law border and molar absorptivity rates were estimated and given in Table [5], which indicated the attitude is critical. The excellent linearity was appeared by the regression equation and the corresponding correlation coefficient. Therefore, (LOD) and (LOQ) is in the acceptable range below the minimum of Beer’s law range.

Table [5]: Summery of optical characteristics and statistical dates for the proposed method

| Parameter                        | RNB |
|----------------------------------|-----|
| Beer’s law limit s (µg.ml⁻¹)     | (5 – 50) |
| Molar absorptivity L.mol⁻¹.cm⁻¹   | (1.21×10⁴) |
| LoD (µg.ml⁻¹)                   | 0.059 |
| LoQ (µg.ml⁻¹)                   | 0.242 |
| Average Recovery                 | 101.65 |
| Correlation Coefficient          | 0.998 |
| Slope                            | 0.0373 |
| RSD                              | ≤0.44 |

The stoichiometry of the reaction of RNB with o-Chloranil reagent was studied by the molar ratio¹² and Job methods¹³. Utilizing solutions of 5×10⁻³ M for each sample and o-Chloranil reagent. As explained in Figure [5] a&b the outcomes indicate that 1:1 whereby the results acquired from above stoichiometry, the ostensible stability constant was evaluated by comparing the absorbance of a solution contains stoichiometric amount of the RNB and o-Chloranil (As) to one contains an excrement amount of o-Chloranil reagent (Am). The average conditional immutability constant of the product was calculated via the following equation: 

\[ K_c = \frac{1}{\alpha C} \] 

Where \( K_c \) is the association constant (L.mol⁻¹) the dissociation degree while \( C \) the centration of the product. The average \( K_C \) is 3.32×10⁷ indicate that the product is stable.

![Absorbance vs. Concentration](image)
Reaction Mechanisms

A characteristic product of $\lambda$ max 440nm for RNB was formed when it allowable to react with O-Chloranil at the presence of Na$_2$Co$_3$ in organic milieu under the experiential conditions. Schemed [1]Shows the probable product formation mechanism.

Schemed 1: probable product genesis mechanism

The determination of Aromatic Nitrobenzene in the water

Water contamination is defined as the presence of any extraordinary organic or non-organic matters, which attempts at decreasing the quality of the water and annihilating all its contents $^{16}$. Through many studies on the Tigris and Euphrates $^{17-18}$, it became clear that there is a low concentration of dissolved Oxygen due to an increase in the concentration of the oxidative organic matters. Nitroaromatic compounds are prescribed from the contaminative organic matters to the surface water $^{19}$. Therefore, I held an application to determine the aromatic nitrobenzene compound on various water sources such as the tap water and diyala river water under the application of optimal conditions.
The determination of nitrobenzene in tap water: - A sample of the tap water has been taken then 0.05 gram of Nitrobenzene was weighed and dissolved within an amount of ethanol then stirring them by adding 0.5 gram of Zinc dust (Zn dust) to complete the reduction process and adding amounts of tap water. The size was reached to 100 ml by adding the tap water. The output equals 500 mg/ml of reduced Nitrobenzene which is made of the tap water, then 100 µg/ml are produced of it to make tests on it table [6] shows the outcomes that have been reached to.

The determination of nitrobenzene in diyala river water: - A sample of diyala river water has been taken which lies near by Baquba down town on which the water drainage tunnels are directed where the Nitroaromatic compounds exist. The amount of the Nitrobenzene within this sample has been determined by following the same method used in the previous paragraph.

Table [6]: The outcomes that have been reached

| Nitrobenzene added (µg/ml) | Recovery (%) |
|---------------------------|--------------|
|                           | Tap Water    | River Water  |
| 1                         | 102.5        | 105.2        |
| 1.5                       | 103.2        | 109.31       |
| 2                         | 100.1        | 111.21       |
| 3                         | 99.82        | 106.2        |
| 4                         | 101.3        | 110.4        |
| 5                         | 102.5        | 108.3        |
| 6                         | 104.1        | 112.02       |

The table shows the possibility of estimating the nitrobenzene compound in the tap water while the presence of the positive interference in the determination of diyala river water led to water contamination. Hence, the study is accomplished by the addition of amounts of the river water to 8 µg/ml of reduced nitrobenzene and the mitigation with the distilled water instead of the river water.

Table [7]: The determination of nitrobenzene in the diyala river water

| Recovery % of nitrobenzene per ml of diyala river water |
|---------------------------------------------------------|
| 0.1mL | 0.3mL | 0.5mL | 1mL | 2mL | 3mL | 3.5mL |
|-------|-------|-------|-----|-----|-----|-------|
| 102%  | 100.2%| 101.2%| 103.1%| 100.5%| 99.5%| 93.95%|

It can be noticed from the table that there is a lack of interference within limits during the use of amounts reach 3mL of the river water. Therefore, this method can be used to make a field study on contamination.

Conclusion

An indirect spectral method has been developed to determine the aromatic nitrobenzene compound. The nitro group has been reduced in the compound by adding 0.5 gm of (Zn dust) and concentrated hydrochloride acid to transfer it into amino group that reacts with the detector to form the charge-Transfer complex through which the determination became more accurate compatible. The average recovery is about 101.65% and the relative standard deviation is less than 4%, the limit of uncovering 0.059 µg/mL. It was also found that the reaction of o-chlo with the studied compound is calculated 1:1, which proves the involvement of the reduced nitro group in forming the outcomes. The method was applicable in the determination of nitrobenzene within the tap water and the Diyala river water with good average recovery rates.
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