Spectrophotometric Determination of Phenols in Aqueous Solution via Oxidative-Coupling Reaction with 4-Amino-N,N-diethylaniline and Potassium Dichromate

M.Q. Al-Abachi
College of Science
Baghdad University

M.M.Al-Sharook
College of Education
Mosul University

Shayma I. Al-Najafi
College of Education
Mosul University

Received 23/5/2005 **Accepted** 24/10/2005

الخلاصة

طورت طريقة طيفية حساسة لتقدير الفينول تعتمد على تفاعل الاقتران التأكسدي للفينول مع 4-امينو-N،N-ثنائي اثيل انيلين بوجود ثنائي كرومات البوتاسيوم عاملا مؤكسدا في وسط دالته الحامضية 6 لتكوين صبغة زرقاء مخضرة ذائبة ومستقرة لها اعلى امتصاص عند 670 نانوميتر. بين رسم المنحنى القياسي للامتصاص مقابل التركيز ان حدود تطبيق قانون بير كان 2.5-250 مايكروغرام في حجم نهائي مقداره 25 مللتر (0.1-10 جزء من مليون) وبامتصاصية مولارية 3.95×10^4 لتر.مول$^{-1}$.سم$^{-1}$ وبنسب استرجاع (98.10-100.75%) وانحراف قياسي نسبي افضل من ±0.4% اعتمادا على مستوى التركيز، وصفت الظروف المثلى للطريقة المقترحة واستخدمت لتقدير مركبات فينولية اخرى.

ABSTRACT

A simple and sensitive spectrophotometric method for the determination of phenol has been developed. The method is based on the oxidative-coupling reaction of phenol with 4-amino-N,N-diethylaniline in the presence of potassium dichromate at pH 6 solution to form an intense bluish-green water-soluble dye that is stable and has a maximum absorption at 670nm. A plot of absorbance versus concentration shows that Beer's law is obeyed over the concentration range of 2.5-250 µg of phenol in a final volume of 25ml.(i-e 0.1-10ppm) with a molar absorptivity of 3.95×10^4 l.mol^{-1}cm^{-1}, a percentage recoveries of 98.10-100.75% and a relative standard deviation of better than ±0.4%, depending on the concentration level. The optimum conditions for full colour development are described and the proposed method is extended to some other phenolic compounds.

INTRODUCTION

Phenolic compounds have been extensively used as pesticides, herbicides and fungicides and will therefore be present in waste water(1). A number of methods including titrimetric (2), spectrophotometric (3), polarographic (4) gas chromatographic (5) and high-performance liquid chromatography (6) methods for the determination of phenol have been described.

Oxidative coupling organic reaction seems to be one of the most popular spectrophotometric methods for the determination of several phenolic compounds and drugs such as catecholamines (7), paracetamol (8) and sulfonamides (9).

The objective of the investigation reported in this paper is to evaluate a spectrophotometric method for the determination of phenol based on the reaction of phenol with 4-amino-N,N-diethylaniline in the presence of potassium dichromate as oxidizing agent and at pH 6 with citrate buffer solution. A stable water-soluble bluish-green coloured product is formed which can be measured at 670nm.

EXPERIMENTAL

Apparatus:

All spectral and absorbance measurements are carried out on a Shimadzu UV-visible-210 digital double beam recording spectrophotometer using matched 1-cm silica cells.

Reagents:

All chemicals used are of analytical reagent grade.

Phenol stock solution, (100 μg ml^{-1}).

A 0.0100 g amount of phenol is dissolved in distilled water; the solution is then made up to 100 ml in a volumetric flask with distilled water. More dilute solutions are prepared by dilution with distilled water.

Potassium dichromate solution, (2.5×10^{-2} M).

Prepared by dissolving 0.7350 g of potassium dichromate in distilled water and made up to 100 ml volumetric flask with distilled water. More dilute solutions were prepared by simple dilution with distilled water.

4-Amino-N,N-diethylaniline solution, (5×10^{-3} M).

Prepared by dissolving 0.1093 g of 4-amino-N,N-diethylaniline hydrochloride in 100 ml of ethanol.

Citrate buffer (pH 6).

Prepared from 0.1 M citric acid and 0.1 M sodium hydroxide.

Procedure

Into a series of 25ml calibrated flask increasing volumes of phenol ($25\mu gml^{-1}$) solution are transferred, 4 ml of pH 6 citrate buffer, 3.5 ml 4-amino-N,N-diethylaniline solution and 3 ml of potassium dichromate solution are then added. The solutions are diluted to the mark with distilled water and allowed to stand for 30 min. in water bath at 30 °C. The absorbance at 670 nm against a reagent blank prepared in the same way but containing no phenol are measured. The colour of the formed dye is stable for about 120 min.

For the optimization of conditions and in all subsequent experiments, a solution of 50 μgml^{-1} phenol used and the final volume was 25 ml.

RESULTS AND DISCUSSION

Absorption spectra:

When a very dilute aqueous solution of phenol is mixed with 4-amino-N,N-diethylaniline and potassium dichromate in the presence of citrate buffer of pH6, an intense bluish-green colour forms after 5 min, which becomes stable after 30 min. at 30 °C. The colour has a maximum absorption at λ_{max} 670 nm (Fig. 1).

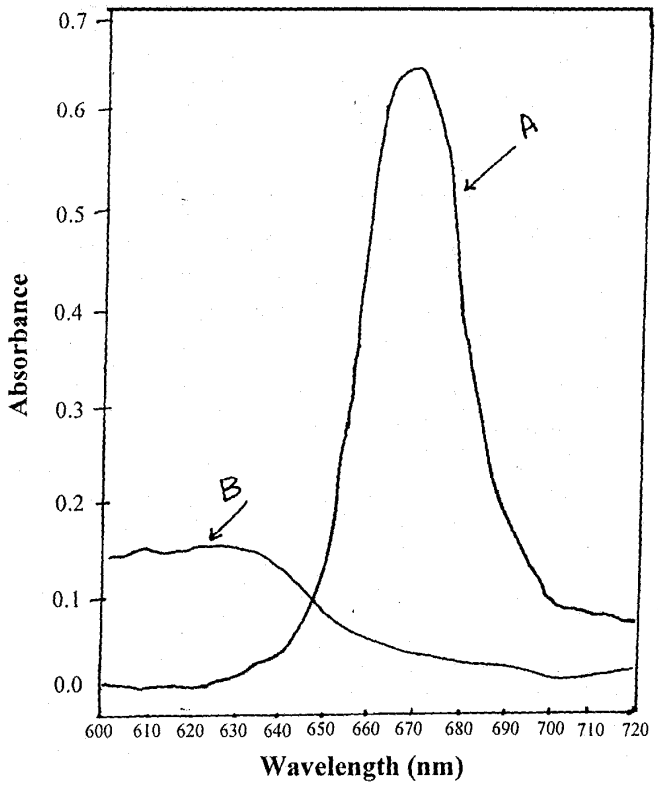


Fig. (1): Absorption spectra of the bluish green colour formed (A) and of the reagent blank (B)

Study of the optimum reaction conditions:

The effect of various parameters on the absorption intensity of the dye formed has been studied and the reaction conditions are optimized.

Effect of pH:

The effect of pH is investigated in the range of 4-11. The obtained results indicate that the dye product is stable at pH 6. The type of the buffer(acetate, phosphate,citrate) has also been studied and found that 4ml of citrate buffer of pH 6 gives high sensitivity and minimum blank value.

Effect of reagent concentration:

When various amounts of 4-amino-N,N-diethylaniline solution are added to a fixed amount of phenol, 4ml of (5×10^{-3}M) solution has been found enough to develop the colour to its full intensity and gives a minimum blank value and is considered to be optimum.

Effect of oxidant concentration:

The dye formation reached a maximum colour with about 3.5ml of (2.5×10^{-2}M) of potassium dichromate solution, therefore, a 3.5 ml of potassium dichromate solution is used in the procedure since it gives high sensitivity, minimum blank value and ensures a quantitative determination at the upper limit of the calibration graph.

Effect of reaction time:

The colour intensity reached maximum after phenol has been reacted with 4-amino-N,N-diethylaniline and potassium dichromate for 30 min, at 30 °C. Therefore, a 30-min development time is selected as optimum in the general procedure. The colour obtained is stable for 90 min.

Effect of the order of the addition:

To obtain optimum results, the order of addition of reagents should be followed as given under the procedure, otherwise a loss in colour intensity and stability is observed.

Effect of temperature:

The effect of temperature on the colour intensity of the dye has been studied. In practice , higher absorbance is obtained when the colour is developed at room temperature (30 °C) than when the calibrated flasks are placed in an ice-bath at (0 °C) or in a water-bath at (50 °C). Therefore, it is recommended that the colour reaction should be carried out at room temperature (30 °C).

Calibration graph:

Employing the conditions, described in the above procedure, a linear calibration graph for phenol is obtained (Fig.2),which shows that Beer's law is obeyed over the concentration range of (0.1-10μg/ml) with a correlation coefficient of 0.9999.The molar absorpitivity of the dye product (with respect to phenol) is 39446 $l.mol^{-1}.cm^{-1}$.

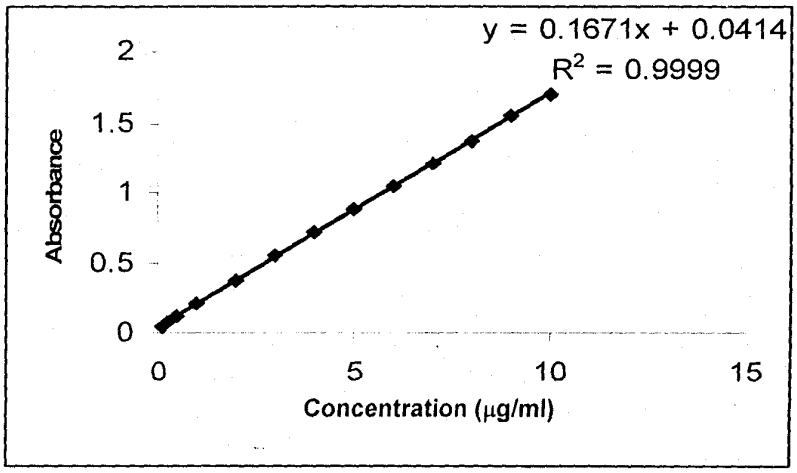


Fig. (2): Calibration graph for the determination of phenol

Accuracy and precision:

To determine the accuracy and precision of the calibration graph, phenol is determined at three different concentrations.The results obtained are shown in Table (1). It indicates that a satisfactory precision and accuracy could be obtained for the calibration graph with the proposed method.

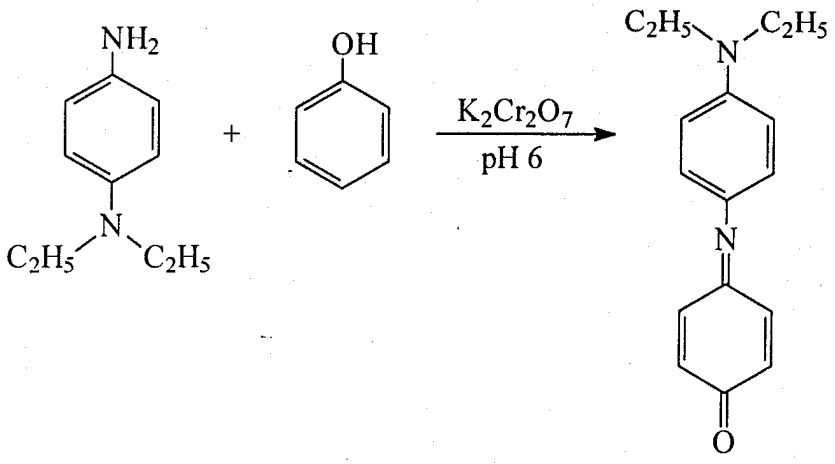
Table (1): Accuracy and precision

Phenol(μg/ml)	Recovery,%*	RSD, %*
3	97.40	± 0.39
5	100.2	± 0.25
7	100.3	± 0.35

* Average for five determinations.

Structure of the dye:

The stoichiometry of the reaction has been investigated using Job's method and mole-ratio method (10). The results obtained (Fig.3) shows a 1:1 phenol to reagent at 670 nm. The formation of the dye may probably occur as follows:



The dye formed is soluble in water. The apparent stability constant has been calculated by comparing the absorbance of a solution containing stoichiometric amounts of phenol and 4-amino-N,N-diethylaniline with that of a solution containing five-fold excess of 4-amino-N,N-diethylaniline. The average conditional stability constant of the dye in water under the described experimental conditions is 6×10^{4} l.mole^{-1}.

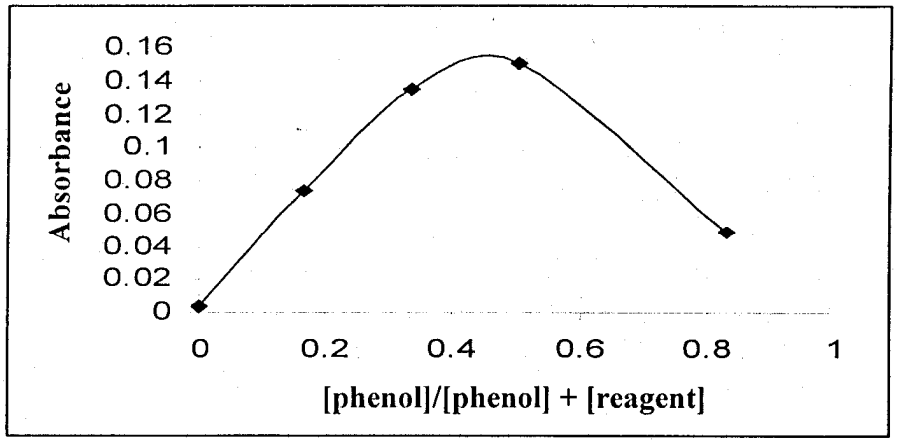


Fig. (3): Study of the stoichiometry of the reaction between phenol and 4-amino-N,N-diethylaniline

Using the same experimental conditions stated above, many substituted phenolic compounds can be analyzed similarly. Table (2) shows some of the analytical parameters for the phenolic compounds studied.

Table (2): Some analytical parameters for the determination of some substituted phenols measured at λ_{max} 670 nm

Compounds	Beer's law range (ppm)	Molar absorptivity ($l.mol^{-1}.cm^{-1}$)	Stability constant ($l.mol^{-1}$)
Phenol	0.1-10	39446	6.0×10^4
o-Aminophenol	0.2-8	10940	5.9×10^4
m-Aminophenol	0.1-6	19200	6.2×10^4
p-Bromophenol	0.1-12	7917	4.0×10^3
Resorcinol	0.1-9	11720	4.8×10^4
o-Cresol	0.2-8	29315	2.0×10^4

Effect of interferences:

In order to asses the possible analytical applications of the proposed method, the effect of some cations and anions frequently found with phenol samples is studied by analyzing synthetic samples solutions containing 50 μg/ml of phenol and excess amounts (10-fold excess) of each interference such as nitrate, nitrite, carbonate, bicarbonate, calcium, magnesium, zinc and aromatic amine such as sulfonamide. The experimental results obtained indicated that all cations and anions studied caused an interference of 3%, where as the aromatic amine interferes seriously.

REFERENCES

1. Environmental Protection Agency of China, The Analytical Methods of Environmental Monitoring. Environmental Science Press of China, Beijing, pp. 158-167(1986).
2. Salem F.B., Talanta, 34, 810-812(1987).
3. Kang C., Wang Y., Zhou L., Zhang B., Microchem. J., 64, 161-171(2000).
4. Gutes A., Cespedes F., Alegret S. and Valle M., Biosensors and Bioelectronics, 20, 1668-1673(2005).
5. Chen J.L. and Liu C-Y., Anal. Chim. Acta, 28, 83-88(2005).
6. Kilinc E., Talanta, 65, 876-881(2005).
7. Nagaraja P., Murthy K.C., Rangappa K.S. and Gowda N.M., Talanta, 46, 39-44(1998).
8. Al-Ward H.S.J., M.Sc. Thesis, Baghdad University, pp. 43-88(2002).
9. Al-Abachi M.Q. and Al-Talib S.M., J. Edu. Sci., 22, 119-131(1995).
10. Delevie R., "Principle of quantitative chemical analysis," McGraw-Hill International Edition, Singapore, p. 498(1997).