

## Spectrophotometric determination of Resorcinol in aqueous solutions and some Bulk Samples by coupling with Diazotized 4- Methoxy aniline

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**Key words:** Spectrophotometric determination, Diazotization and coupling, Resorcinol, 4-Methoxy aniline.

### Abstract

A simple, rapid and sensitive spectrophotometric method for determination of microgram amounts of Resorcinol in aqueous solution and some bulk samples was described. The method is based on a diazotization and coupling reaction between resorcinol and diazotized 4-bromo Methoxy aniline in basic medium to form an intense brown water-soluble dye that is stable, which shows maximum absorption at 448nm. Beer's law is obeyed over the concentration range of (0.4-4.4)  $\mu\text{g}\cdot\text{ml}^{-1}$  of resorcinol, with a molar absorptivity of  $2.7844 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ , and Sandell sensitivity index of  $0.0039 \mu\text{g}/\text{cm}^2$ . The method does not resort to temperature control or to solvent extraction. The optimum conditions for all colour development are described and proposed methods were successfully applied to the determination of resorcinol in aqueous solution and some bulk samples.

التقدير الطيفي للرزورسينول في المحاليل المائية وبعض العينات الخام بالاقتران مع الكاشف 4- ميثوكسي انيلين المؤزوت

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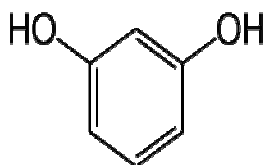
مفتاح الكلمات: التقدير الطيفي, الاقتران والازوتة, رزورسينول, 4- ميثوكسي انيلين .

### الخلاصة

تم وصف طريقة طيفية سهلة وسريعة وحساسة لتقدير كميات مايكروغرامية من الرزورسينول في المحلول المائي وبعض العينات الخام. تعتمد الطريقة على تفاعل الازوتة والازدواج بين الرزورسينول و4- ميثوكسي انيلين في وسط قاعدي لتكوين صبغة ذات لون قهوائي غامق ذائبة في الماء ومستقرة، والتي تعطي اعلى امتصاصية عند 448 نانوميتر. وجد ان قانون بير ينطبق ضمن مدى التراكيز (0.4 - 4.4) مايكروغرام. مل<sup>-1</sup> من الرزورسينول وان الامتصاصية المولارية  $2.7844 \times 10^4$  لتر.مول<sup>-1</sup>سم<sup>-1</sup> ودلالة ساندل للحساسية 0.0039 مايكروغرام/سم<sup>2</sup>. الطريقة لا تحتاج الى السيطرة على درجات الحرارة او الاستخلاص بالمذيب. وتم دراسة الظروف المثلى لتكوين المركب الملون وطبقت الطريقة المقترحة بنجاح لتقدير الرزورسينول في المحلول المائي وبعض العينات الخام.

## Introduction

Resorcinol is a meta-di hydroxyl benzene and recording (IUPAC) Benzene-1,3-diol,  $C_6H_6O_2$ , whereas its chemical structure is<sup>(1)</sup>



Resorcinol is a colourless or slightly pinkish-gery crystalline powder or crystals, turning red on exposure to light and air, very soluble in water and in alcohol<sup>(2)</sup>.

Resorcinol is one of essential naturally phenols found in (Argan oil)<sup>(3)</sup>, and can be obtained it from fusion some Ratenges such as (galbanum) with potassium hydroxide and can be prepared industrially by fusion (3-iodo phenol or phenol-3-sulphonic acid or benzene-1,3-di sulphonic acid) with potassium carbonate by act netroze acid<sup>(4)</sup>.

Resorcinol inter in many fields such as medical for external use as antiseptic and also used 5 into 10% in an ointments to treat skin diseases and also consider it antidundruf factor in shampo or cosmetics<sup>(5)</sup>. A number of analytical methods have been reported for the determination of resorcinol, these included flow injection<sup>(6)</sup> and reversed-phase ion-pair chromatography<sup>(7)</sup>.

In the present work, the stable diazotized 4-methoxy aniline reagent has been proposed to determine resorcinol in aqueous solution and some bulk samples by the azo-coupling reaction in alkaline medium. The brownish product was spectrophotometrically measured at 448 nm. The analytical procedure is simple, rapid and accurate. It has been satisfactorily applied for the determination of resorcinol in aqueous solution and some bulk samples

## Experimental

### Apparatus

- all spectral and absorbance measurements were carried out on UV-Visible 160 digital double beam recording spectrometer .
- sencetive balance (Sartorius BL210S) (Germany).
- Water bath

### Material and reagents

All Chemicals used are of the highest purity available, and without further purification.

Resorcinol ( $110 \mu\text{g}\cdot\text{ml}^{-1}$ ) solution:

This solution is prepared by dissolving 0.011g of resorcinol (SDI) in (100)mL distilled water, then transferred to a dark bottle where it is stable for at least 1 month, and the bulk samples solutions of resorcinol 98% (BDH) and Resorcinol 99% (Merch) are prepared by the same method.

Diazotized 4- methoxy aniline ( $1 \times 10^{-3}\text{M}$ ) reagent solution:

prepared by dissolving 0.003 gm of pure 4- methoxy aniline (Fluka) in amount of distilled water then added 1 mL of 1 M HCl (BDH) shaken well and followed by 2 mL of 0.025 M sodium nitrite (BDH) shake thoroughly, then the volume is diluted to 25 mL then cooled to about  $5^\circ\text{C}$  for 30 min, This solution is transferred to a darkbottle and kept in a refrigerator where it is stable for 2 weeks.

Hydrochloric acid (BDH) (1M):

prepared by diluting (8.33) mL of (37% HCl) to 100 mL with distilled water

Sodium hydroxide (BDH) (1M) :

prepared by dissolving 4.0 gm of NaOH in 100 mL volumetric flask and complete the volume to the mark with distilled water.

### **Procedure :**

A series of 25mL volumetric flasks, increasing volumes of  $110 \mu\text{g}\cdot\text{mL}^{-1}$  resorcinol working standard solution were transferred to cover the range  $(0.4-4.4)\mu\text{g}\cdot\text{mL}^{-1}$  in final dilution, 0.1mL of sodium hydroxide (1M) solution and 2 mL of diazotized 4- methoxy aniline reagent ( 0.001M) solution are then added and diluted to the mark with distilled water, mixed well and left for 15 min at room temperature, the absorbance of the brownish dye formed was measured at 448 nm against a reagent blank containing all materials except resorcinol. A calibration curve was constructed.

### **Procedure for assay of resorcinol in some bulk samples.**

25 mL of resorcinol solution 98% and resorcinol solution 99% are transferred to a 100 mL volumetric flasks and diluted to the mark with distilled water. An aliquot of 1mL of this solution is put in 25 mL volumetric flask, 0.1 mL (1M NaOH), 2 mL of 0.001M diazonium agent were added and the volume make up to the mark with distilled water, set a side for 15 minute then the absorbance is measured at 448 nm. The concentration of resorcinol is obtained by using the calibration curve already made and described above .

## **RESULTS AND DISCUSSION**

Study of the optimum reaction conditions : The effects of various parameters on the optical properties of the azo dye have been Studied and the reaction conditions are optimized.

**1 – Effect of Reagent volume:** The effect of diazonium reagent ( 0.001M) volume (0.1-5 mL) on the intensity of the absorbance, has been studied and 2 mL was found to be optimum.

**2- Effect of Acid:-** It was found that the presence of acid led to increase the intensity of the produced product, therefore some acids such as HCl,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  are examined and was found that all these acids gave almost equal intensity, so, HCl was selected which was found that ( 1 mL) of 1M HCl give a high sensitivity compared with other acids, so which selected in subsequent experiments.

**3- Effect of Base:** The absorbance of the dye formed became more intense and stable in alkaline medium, therefore, the effect of different alkaline solutions on the colored product were studied such as sodium hydroxide, ammonium hydroxide, potassium hydroxide, sodium acetate and sodium carbonate. Maximum sensitivity and stability were obtained only when the reaction was carried out in the presence of sodium hydroxide solution. The effect of different concentrations of NaOH were studied, (0.1-4 M) and 1 M seems to be optimum. The effect of (1 M) NaOH volumes were also studied from 0.05 to 4 mL and 0.1mL was found optimum.

**4- Effect of Order of Addition :-** It was found that the best order of addition that gives the highest absorption (  $R_s+B+R$ ) where (  $R_s$ = resorcinol substance ,  $B$ =base and  $R$ =reagent ) which selected in subsequent experiments.

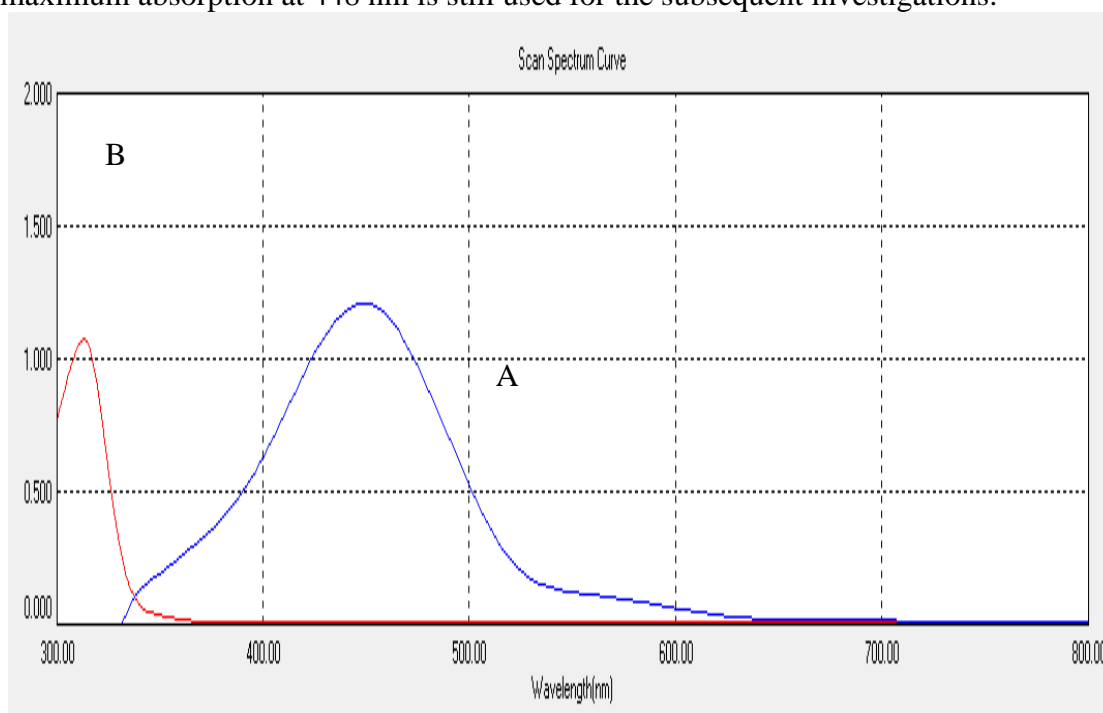
**5- Effect of Temperature:-** The resulting product of the proposed method were studied at different temperatures. The results indicate that the absorbance values remain nearly constant in the temperature range (0-80)°C, whereas, at higher temperatures the absorbance value decrease, indicating the dissociation of the product on prolonged heating. The coloured product was stable at room temperature (25 )°C. Therefore room temperature is selected in this method.

**6- Effect of Reaction Time:-** The colour intensity reached its maximum after the Resorcinol had been reacted immediately with the reagent solution became stable after 15minute . therefore 15 minute development time was selected as optimum in the general procedure. The colour obtained was stable for at 3 hours.

The optimum experimental conditions for the determination of resorcinol were established. Diazonium reaction occurred in an acidic medium <sup>[8]</sup> and hydrochloric acid of concentration of 1M was selected <sup>[9]</sup>, and the absorbance of the dye formed became more intense and stable in alkaline medium <sup>[10]</sup>.

### Absorption spectra

When a dilute solution of resorcinol, under the above-established conditions, is mixed with diazotized 4- methoxy aniline in the presence of sodium hydroxide, the brownish colored dye immediately formed. This shows maximum absorption at 448nm in contrast to the colored reagent blank which shows no absorption.( Fig. 1) Shows the absorption spectra. The wavelength of maximum absorption at 448 nm is still used for the subsequent investigations.



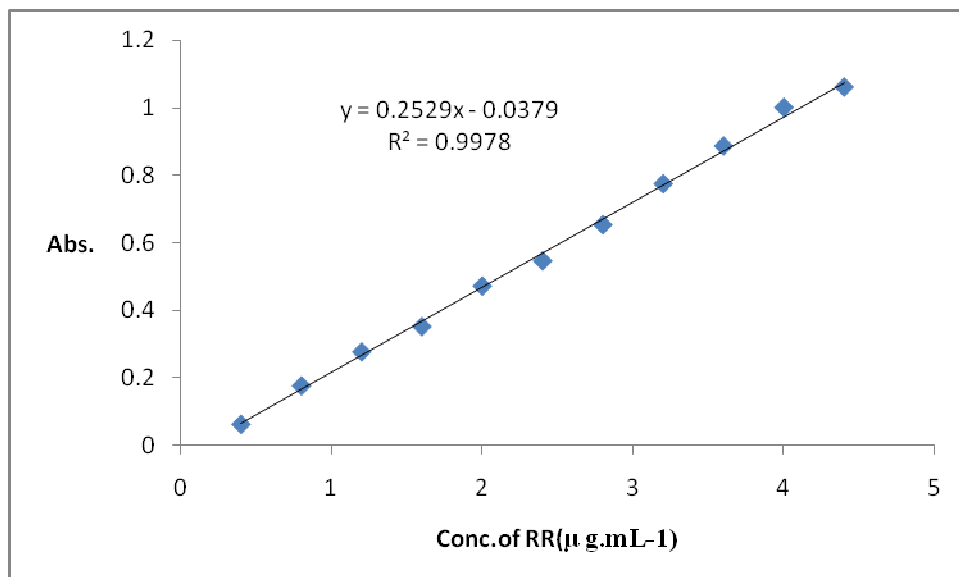
**Fig (1) : Absorption spectra :**

**A : Resorcinol ( $4.4 \mu\text{g} \cdot \text{ml}^{-1}$ ) +4- methoxy aniline ( $1 \times 10^{-3}$ ) product versus reagent blank.**

**B : Reagent blank versus distilled water.**

**Calibration curve:**

Under the optimum experimental conditions linear relation between the absorbance and the concentration of resorcinol was observed over the concentration range 0.4- 4.4 $\mu\text{g}.\text{mL}^{-1}$  (Fig 2) with a correlation coefficient of 0.9978 and intercept of 0.0379. A negative deviation from Beer's law was observed above 4.4  $\mu\text{g}.\text{mL}^{-1}$  concentration of resorcinol. The molar absorptivity was  $2.7844 \times 10^4 \text{ l}.\text{mol}^{-1}.\text{cm}^{-1}$ .



**Fig (2) : calibration curve of resorcinol**

### Accuracy and precision

To determine the accuracy and precision of the calibration graph, resorcinol was determined at three different concentrations. The results shown in Table( 1) indicate a satisfactory precision and accuracy.

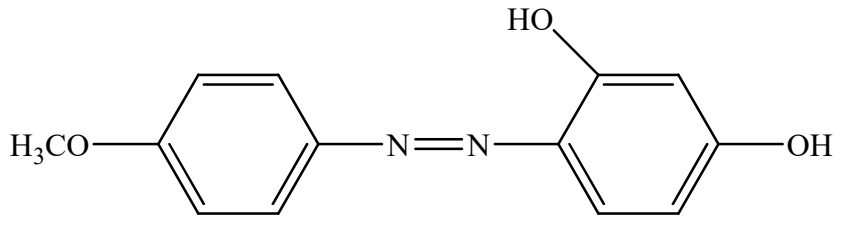
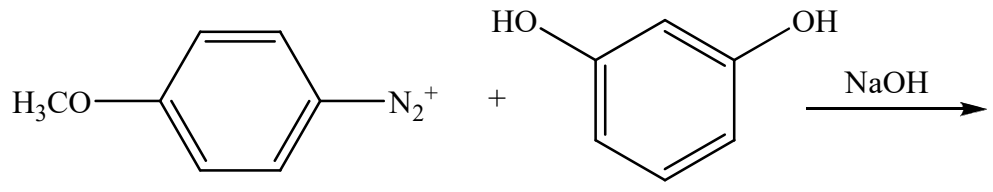
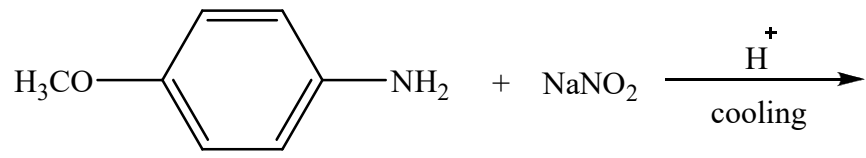
Table (1): Accuracy and precision of proposed method

No.	Conc. of resorcinol mg per 25ml		Error %*	Recovery*	R.S.D %*
	present	found			
1	0.800	0.796	-0.394	99.606	1.650
2	2.800	2.850	+1.785	101.785	0.750
3	3.600	3.660	+1.660	101.660	0.660

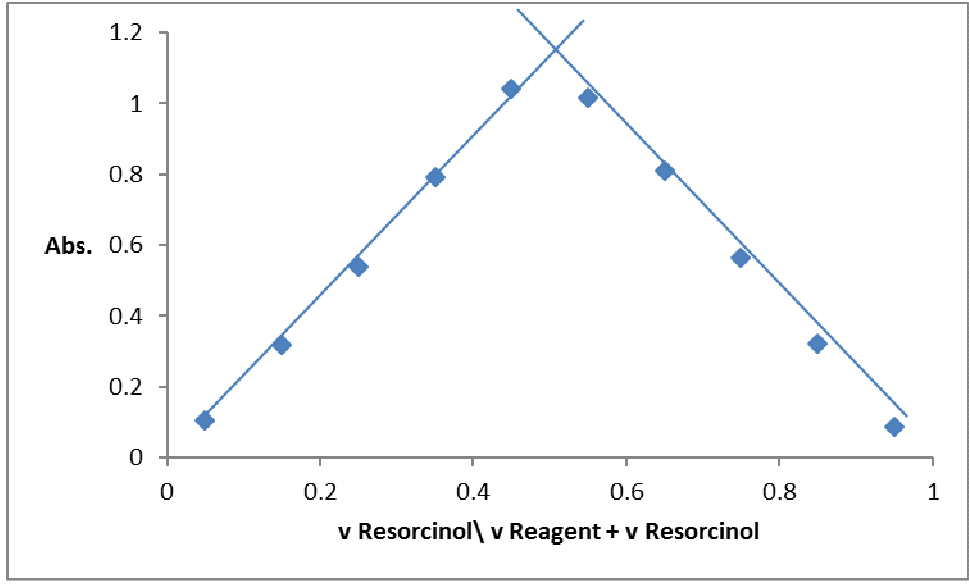
\* Average for five determinations

### Nature of product and reaction mechanism

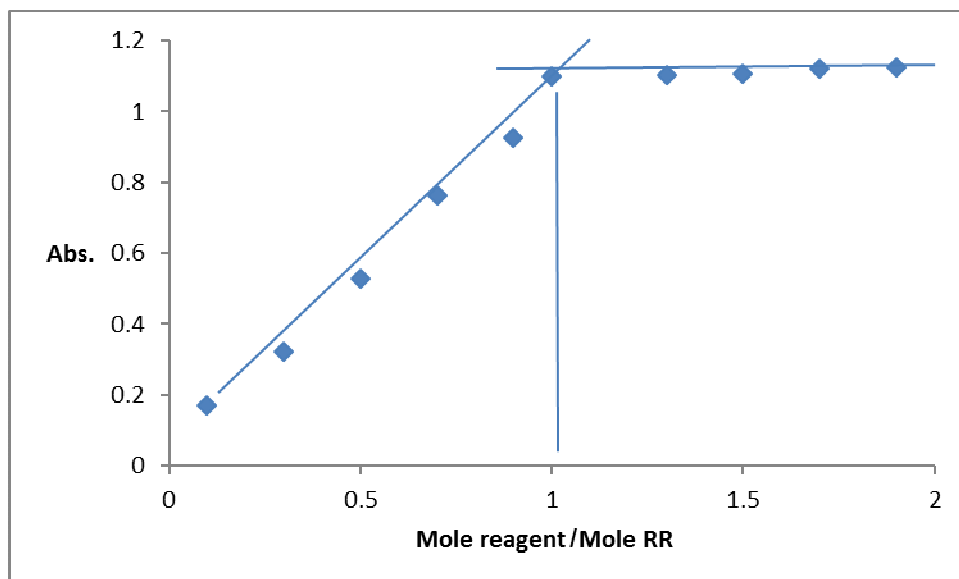
To establish the composition (ratio of resorcinol to diazotized 4-methoxy aniline reagent) of the brownish azo dye formed, Job's method of continuous variations and mole-ratio method have been used. The resulting data reveal that the dye has been formed by the reaction of resorcinol with diazotized 4-methoxy aniline reagent in a ratio of 1:1, Fig(3&4), indicating a mono azo dye with probably of the following scheme:



Colored Azo dye



Fig(3) Continuous variation plot



**Fig (4) Mole ratio plot**

The apparent stability constant of the azo dye in aqueous solution, under the conditions of experimental procedure, has been calculated, and found to be  $2.16 \times 10^8 \text{ l.mole}^{-1}$ . The regression equation obtained, and the analytical features of the procedure are summarized in (Table 2).

**Table 2: Analytical characteristics of the procedure developed for the determination of Resorcinol**

Parameters	Present method
Regression equation	$Y=0.2529x- 0.0379$
Linear range( $\mu\text{g ml}^{-1}$ )	0.4-4.4
Correlation coefficient, $r^2$	0.9978
Limit of detection ( $\mu\text{g ml}^{-1}$ )	0.019
( Average of RSD) %	1.02
Average of recovery %	101.017
Molar absorptivity ( $\text{l mol}^{-1} \text{cm}^{-1}$ )	$2.7844 \times 10^4$
Sandell's sensitivity ( $\mu\text{g cm}^{-2}$ )	0.0039

### Application of the method

The suggested methods were applied to the quantitative determination of resorcinol in aqueous solutions and two samples of bulks containing resorcinol were analyzed and they gave a good accuracy and precision as shown in (Table 3). The proposed method was compared successfully with the official method <sup>(2)</sup>.

**Table 3: Application of the proposed and official methods for the determination of resorcinol in some bulk samples**

Pharmaceutical preparation	Rec.* % proposed method	Rec.* % standard method
Resorcinol pure	100.017	100.454
Resorcinol 98%	99.780	100.318
Resorcinol 99%	99.750	99.546

\* Average for five determinations

### **CONCLUSION:-**

A simple, rapid, precise and sensitive spectrophotometric method has been developed for the determination of trace amounts of resorcinol in aqueous solution based on its diazotized coupling reaction with 4-methoxy aniline and also the method does not resort to temperature control or to solvent extraction.

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