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Micro Determination Study and Organo physical properties of 2-Aminophenol and Catechol with 4-aminoantipyrine in the Presence of Potassium Iodate.

Hussain J. Mohammed , Hayfaa J. Mohammed & Huda S. Hassen
Dept. Chemistry / College of Education for Girls / Kufa University / Iraq
Email : ibrahiem _af@yahoo.com.

Abstract: A simple, sensitive and selective method has been developed for the determination of 2-aminophenol and catechol with 4-aminoantipyrine. The method is based on the reaction of 2-aminophenol and catechol with 4-aminoantipyrine and potassium iodate at pH 3.7 and 3.3 respectively. The reactions gave an intense water soluble color products that have maximum absorption at 427, 378 nm and $\varepsilon_{max}0.1910^4$ and 0.1210^4 for 2-aminophenol and catechol respectively .

A linear correlations (1-9 μg ml^{-1}) for both compounds were found between absorbance at λ_{max} and concentration. The results obtained are both precise (RSD were better than 1.3 % and 2.2 % respectively) and accurate (relative error were better than 0.03 % and 0.4 %) . The colored products were found to be 1:1 for 2-aminophenol:4-aminoantipyrine and catechol : 4-aminoantipyrine . The stability constants and the rate constants of the reactions under optimized conditions and at room temperature were 0.1×10^3 L.$mole^{-1}$, 1.8×10^{-2} min^{-1} and 3.5×10^4 L.$mole^{-1}$, 2.6×10^{-2} min^{-1} respectively.

Key words: 4-Aminoantipyrine, Catechol and[2-Aminophenol, Spectrophotometry .

دراسة تقديرية دقيقة للخواص (الفيزيائية والعضوية) لـــ:2- أمينوفينول والكاتيكول مع 4- امينوانتيبايرين في وجود يودات البوتاسيوم

ملخص: تم تطوير طريقة سريعة وانتقائية وذات حساسية عاليـــة فـــي تقـــدير٢- امينوفينـــول والكاتيكول مع ٤- امينوانتيبايرين ويودات البوتاسيوم عند دالة هيدروجينية٣,٧ و٣,٣على التوالي. أعطت التفاعلات نواتج ملونة ذائبة في الماء ولها أقصى امتصاص عند طول موجي٤٢٧ و٣٧٨ نانومتر لكل من ٢- امينوفينول والكاتيكول على التوالي ومعاملات امتصاص مولاري٠,١٩×١٠^{٤} و٠,١٢×١٠^{٤} لتر مول$^{-١}$ سم$^{-١}$ وكانت العلاقة بين الامتصاص عند الطـــول المـــوجي الأقصـــى والتركيز خطية في مدى التركيزات بين (١- ٩مايكرو غرام/مل) لكلا المركبين وأعطت نتائج ذات تكرارية (الانحراف النسبي أفضل من ١,٣ و٢,٢%) ودقة (نسبة الخطأ أفضـــل مـــن ٠,٠٣% و٠,٤ %) عاليتين ، لقد كانت النسبة المولية للنواتج الملونة هي ١:١ لكل من ٢- امينوفينول : 4- امينوانتيبايرين وكاتيكول: 4- امينوانتيبايرين بلغت ثوابت الاستقرارية لنواتج التفاعلات وثوابت معدل السرعة تحت الظروف المثلى ودرجة حرارة الغرفة هي ٠,١×١٠^{٣} لتر مول$^{-١}$ ، ١,٨×١٠$^{-٢}$ دقيقة$^{-١}$ و٣,٥×١٠^{٤} لتر مول$^{-١}$ ، ٢,٦×١٠$^{-٢}$ دقيقة$^{-١}$على التوالي.

Introduction:

Phenol compounds are noted more as water pollutants than as air pollutants [1]. In the food industry, phenols are interest becase they are essential compounds of beer and wines [2]. Also phenols are used in industry in

variety of aromatic compounds such as paints, rubber and petroleum industries [3,5]. Catechol and 2-aminophenol are important environmental pollutants because they are toxic to humans and difficult to degrade. Furthermore, due to structures and properties, they usually coexist in products . Therefore, it is very important to develop simple and vapid analytical methods for them.

Oxidative coupling reactions have been long used for the determination of many drugs such as amoxicillin[6], folic acid[7], sulphonamide[8] and phenols[9,10]. Spectrophotometric methods often suffer form limitations in sensitivity and selectivity but are widely used due to both the resulting experimental rapidity and simplicity. Therefore the objective of the investigation reported in this paper was to evaluate a spectrophotometic determination of 2-aminophenol and catechol with 4-aminoantipyrine in the presence of potassium iodate **.**

Experimental :

Apparatus:

All spectral and absorbance measurements were carried out on a shimadzu UV-visible 1700 double beam spectrophotometer using 1 cm glass cells. A digital pH meter was used for pH measurements .All Kinetic measurements were made on TRUV 754 UV-visible spectrophotometer.

Reagents:

All chemicals used were of analytical grade supplied from B.D.H and Fluka companies. Standard 2-aminophenol solution (100 µg/ml) was prepared by dissolving 0.02 g of 2-aminophenol in 10 ml of ethanol and made up to 200 ml with distilled water. Standard solution of 2-aminophenol were prepared by simple dilution of the appropriate volume of the standard 2-aminophenol (100 µg/ml) with distilled water .

Catechol (100µg.ml^{-1}) :

0.02 g pure catechol was dissolved in 10 ml of ethanol and made up to 200 ml with distilled water **.**

4-aminoantipyrine (1x10^{-3} M):

0.05 g of 4-aminoantipyrine was dissolved in 10 ml of ethanol and made up to 250 ml with distilled water.

Potassium Iodate solution (0.01 M):

3.5 g of potassium Iodate was dissolved in 250 ml of hot distilled water .

Foreign ions (1 mg. ml^{-1}):

These solutions were prepared by dissolving, an amount of the compound in distilled water and completing the volume in volumetric flask.

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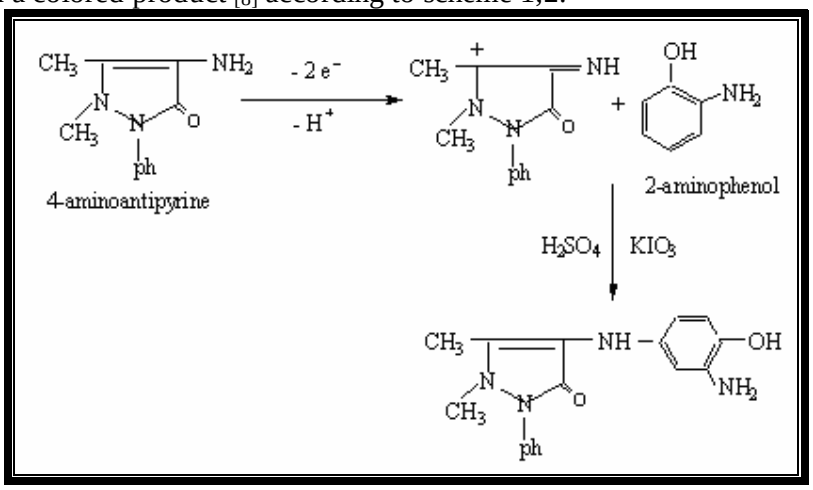
General procedure:

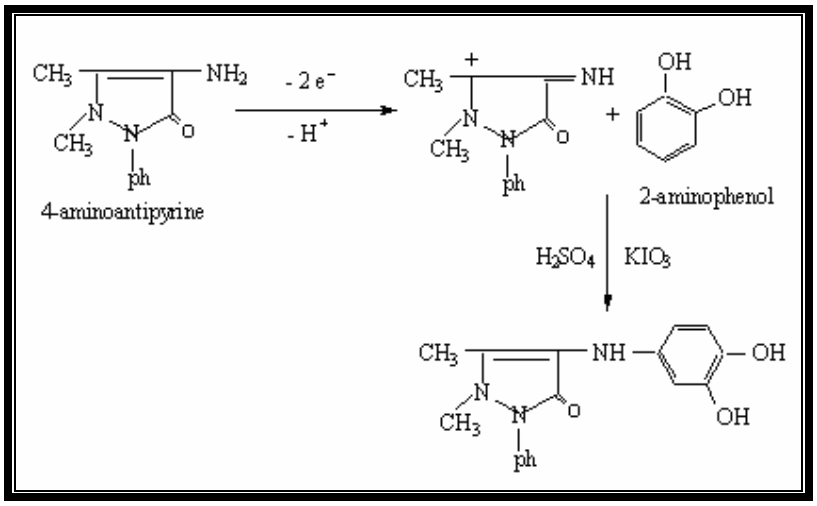
An aliquot of samples containing 10-100 μg of 2-aminophenol and catechol were transferred into a series of 10 ml standard flasks. A volume of 2.5 ml (1×10^{-3} M) 4-aminoantipyrine solution, 2.5 ml of 0.01 M of potassium iodate and 1 ml of H_2SO_4 were added for 2-aminophenol. A volume of 1 ml (110^{-3} M) 4-aminoantipyrine solution, 2.5 ml of 0.01 M of potassium iodate and 2 ml of H_2SO_4 were added for catechol .The contents of the flasks were diluted to the mark with distilled water, mixed well and left for 10 min. The absorbance was measured at 427 nm for 2-aminophenol and at 378 nm for catechol against reagent blanks containing all materials except 2-aminophenol for determination of 2- aminophenol and catechol for determination of catechol .

Reaction mechanism of the method :

2-aminophenol and catechol forms colored products with 4-aminoantipyrine in the presence of potassium iodate in acidic medium . Under the reaction conditions, 4-aminoantipyrine upon oxidation with potassium iodate loses two electrons and one proton, forming an electrophilic intermediate which is an active coupling species. The intermediate undergoes electrophilic substitution with the phenolic moieties of 2-aminophenol and catechol to from a colored product [8] according to scheme 1,2.



Scheme 1 : proposed mechanism of the reaction 2-aminophenol with 4-aminoantipyrine .



Scheme 2 : proposed mechanism of the reaction catechol and 4-aminoantipyrine

Results and discussion:

The result of this investigation indicated that the reactions between 2-aminophenol with 4-aminoantipyrin and catechol with 4-aminoantipyrine in the presence of potassium iodate and sulphuric acid in the pH 3.7 and 3.3 yield highly soluble colored condensation products which can be utilized as a suitable assay procedures for 2-aminophenol and catechol respectively. These colored products have maximum absorption at 427 nm and at 378 nm respectively. The blank at these wave lengths shows zero absorbance Fig (1) .

The influence of various reaction variables on the color development was tested to establish the most favorable conditions .

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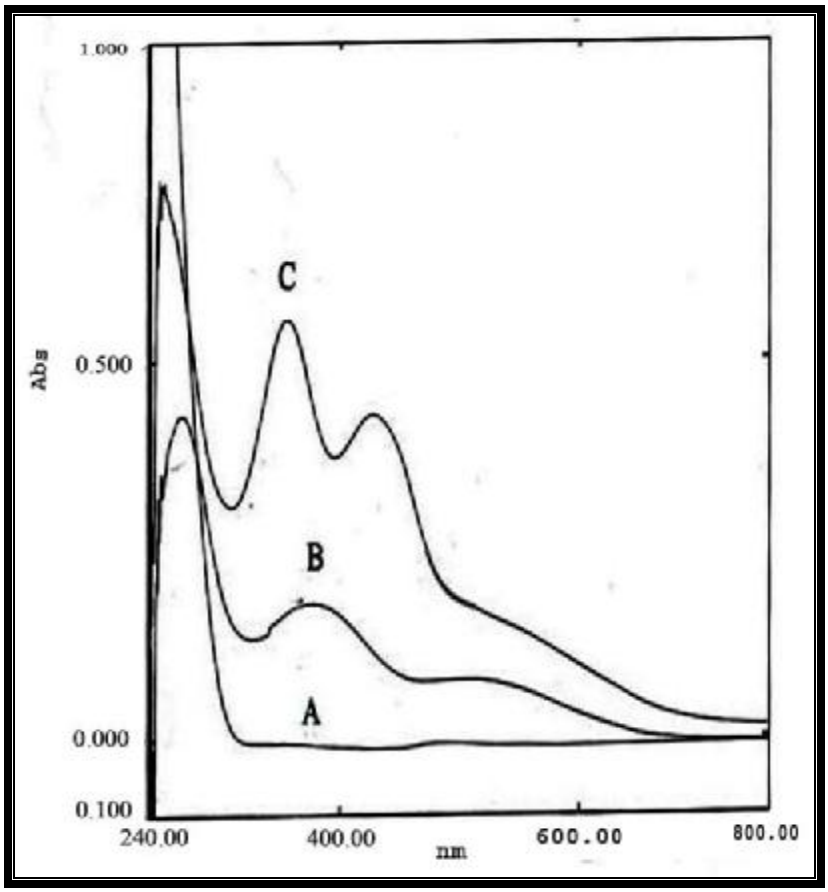

Fig.1:Absorption spectra of (C) 2-aminophenol complex in the presence of potassium iodate (B) catechol complex in the presence of potassium iodate (A) reagent blank with potassium iodate.

Optimization of reagent concentration:

The effect of various concentrations of 4-aminoantipyrine were investigated. 2.5 ml of (1×10^{-3} M) for 2-aminophenol and 1 ml for catechol was found necessary for developing the colored products and increase their stability Fig 2 .

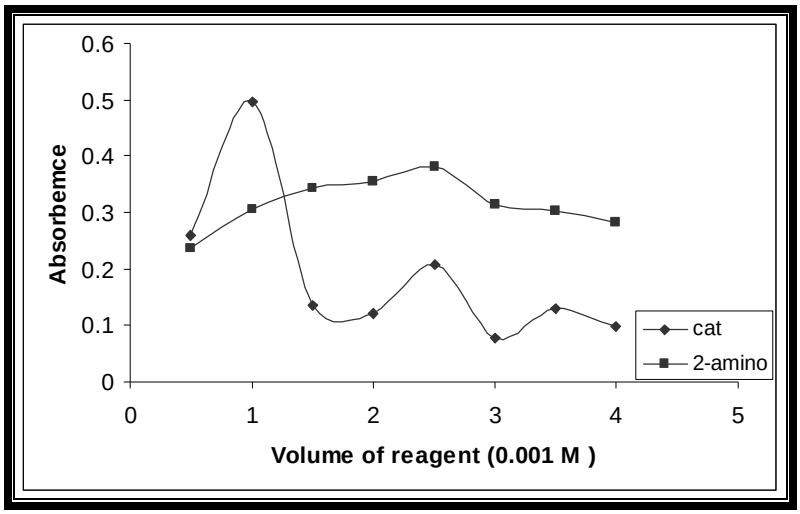

Fig 2: Effect of the reagent volume .

Effect of oxidant concentration :

Various concentrations of potassium iodate solutions were added to a fixed amount of 2-aminophenol or catechol, 2.5 ml of (0.01 M) potassium iodate was used in the procedure since it gives high sensitivity Fig 3 .

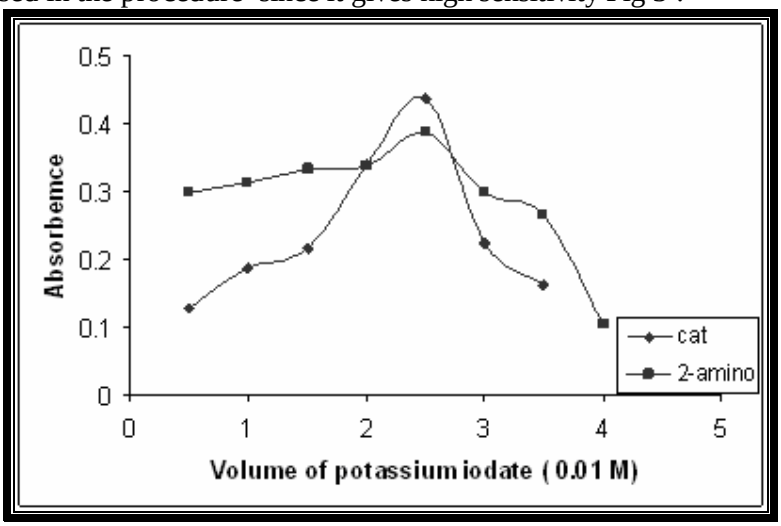

Fig 3: Effect of the oxidizing agent volume.

Effect of acid:

It was found experimentally that the colored products were formed only in acidic medium. The effect of the amount of sulphuric acid was also tested and 1 ml of (0.05 M) for 2-aminophenol and 2 ml for catechol was selected and used in determination of 2-aminophenol and catechol Fig 4.

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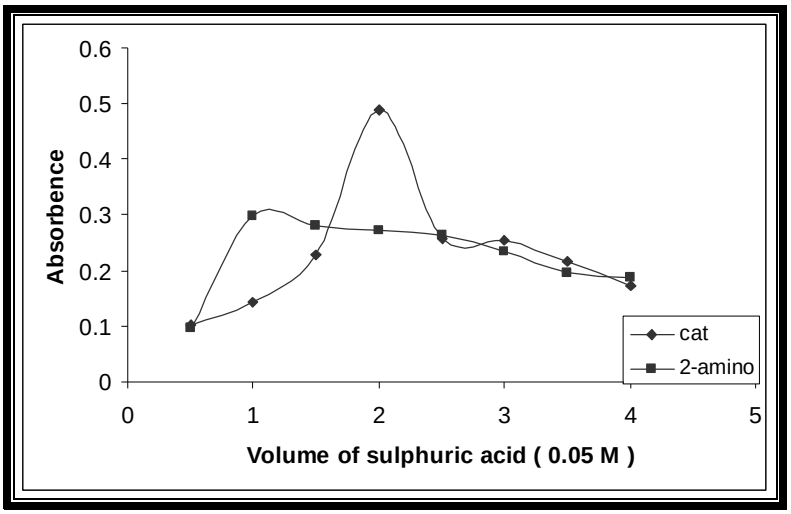

Fig 4 : Effect of acid volume in the 2-aminophenol and catechol .

Calibration carves :

The calibration curves were constructed at their respective absorption maxima and these were linear over concentration range at optimum conditions as listed in Table.1 for phenolic compounds. The molar absorptivity are given in table. 1.

Table .1 : Analytical data of determinations of 2-aminophenol and catechol

Characteristic	2-aminophenol	catechol
Absorption maxima (nm)	427	378
pH	3.7	3.3
Beer's 1aw range (µg/ml)	(1-9)	(1-9)
Molar absorptivity ($L.mol^{-1}cm^{-1}$)	0.19×10^4	0.12×10^4

Development time and stability period :

The color intensity reached maximum after 2-aminophenol or catechol had been reacted with 4-aminoantipyrine in the presence of potassium iodate solutions for 10 min . The color obtained was stable for at least 2hr and this stability, period was sufficient to allow several measurements to be performed sequentially.

Order of addition of reagents :

To obtain the optimum results, the order of addition of reagents should be followed as given by the procedures, otherwise, a loss in color intensity and stability are observed .

Accuracy and precision :

To determine the accuracy and precision of the method, 2-aminophenol and catechol were determined at three different concentrations. The results shown in Table 2 indicate that satisfactory precision and accuracy could be attained with the proposed method .

Table.2 : Accuracy and precision of the method .

Amount af 2-aminophenol or catechol taken ppm	%E of 2-aminophenol	%E of catechol	%RSD of 2aminophenol	%RSD of catechol
4	+ 0.03	+ 0.2	1.3	2.2
6	- 0.33	+ 0.04	1.28	1.3
9	- 0.17	+ 0.4	0.17	0.59

Composition of the complexes :

The composition of the complexes were studied by the mole ratio method[11]. A break of 1:1 suggested the formation of 2-aminophenol with 4-aminoantipyrine complex and catechol with 4-aminoantipyrine complex Fig 5 .The apparent stability constants were calculated by comparing the absorbance of solution containing stoichiometric amounts of 2-aminophenol or catechol with 4-aminoantipyrine that of a solution containing a five-fold excess of reagent. The average conditional stability constants of the dyes in water, under the described experimental conditions are 0.1×10^3 and 3.5×10^4 for 2-aminophenol and catechol complexes .

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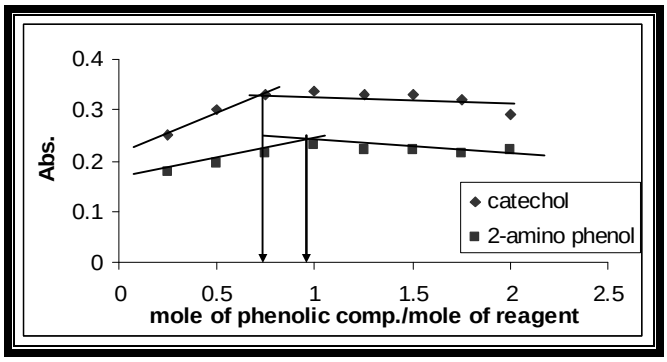

Fig 5: Mole ratio of the 2-aminophenol and catechol Complex .

Rate of reactions :

Rate of reactions were determined spectrophotometrically by measurement of the change in absorbance of the reaction mixture with time. All experiments were curried out under pseudo-first order conditions by keeping concentrations of two reactants in twenty fold excess over that of the third one. The solutions were thermo stated at 25_{+}^{-} 0.1 ºC and the change in absorbance was measured until the reaction was complete. Rate constant was determined by the first order plot using the equation :

$$\mathbf{kt = 2.303 \log A_\infty / A_\infty - A_t}$$

Where A_∞ is the final absorbance and A_t the absorbance at any time t, after addition of reagent and appearance of the color. The validity of this interpretation was checked by plotting log $A_\infty/A_\infty-A_t$ against t, straight line was obtained and the pseudo- first order rate constant is determined from the slope and were found to be 1.8×10^{-2} min $^{-1}$ and 2.6×10^{-2} min^{-1} for 2-aminophenol and catechol respectively

Interferences :

The effects of diverse metal ions on the determination of these phenolic compounds were studied in detail. The tests of diverse ions were determined by the general procedure, in the presence of their respective foreign ions . Each of 2-aminophenol and catechol can be determined with serious interferences in the presence of a 10 fold excess of cations Tables 3.

Table (3) : Effect of foreign ions.

Foreign ions	Amount added ppm	aminophenol-2 E%	catechol E%
Co^{+2}	100	- 38.09	- 26.23
Cd^{+2}	100	- 45.63	- 17.59
Mn^{+2}	100	- 44.84	- 20.06
Zn^{+2}	100	- 39.68	- 5.55
Pb^{+2}	100	+ 79.76	+ 112.03
Cr^{+2}	100	- 40.47	- 10.8
K^{+}	100	- 30.9	- 0.308
Sr^{+2}	100	- 39.92	- 5.24
Hg^{+2}	100	- 48.01	21.91
Ag^{+}	100	+ 18.65	+ 33.64

Conclusions :

The present study demonstrates an excellent approach for the development of spectrophotometric method for determination of 2-aminophenol and catechol, high selectivity and excellent sensitivity for the oxidative coupling reaction of 2-aminophenol and catechol areachieved with 4-aminoantipyrine .

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