Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Spectrophotometric Determination of Catechol and Resorcinol By Oxidative Coupling With 2,4-Dinitrophenyl Hydrazine

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Abstract

A new, simple and sensitive spectrophotometric method for the determination of catechol and resorcinol has been developed. The method is based on the reaction of catechol and resorcinol with2,4- di nitrophenyl hydrazine to yield orange-colored products respectively. catechol and resorcinol showed maximum absorbance at385 nm and 404nm with linearity was observed in the concentration range of (1- 40 µg/mL) for catechol, and (1- 25 µg/mL) for resorcinol with correlation coefficient (0.9982) for both compounds, Sandell's sensitivity 0.0216 (µg cm^{-2}) and 0.025 (µg cm^{-2}) respectively.
Key word: Spectrophotometric , catechol , resorcinol , oxidative coupling , 2,4- di nitrophenyl hydrazine

1. Introduction

Catechol and resorcinol are phenolic compounds and are widely used in tanning, cosmetics, the pharmaceutical industry and in developing photo-graphs [1][2].

These compounds are harmful to humans and animals even in very low concentration.

Therefore, it is very important to develop a highly sensitive and selective analytical method for the determination of catechol and resorcinol in food [3] [4]. As environmental pollutants in the ecological system, it is very important to develop simple and rapid analytical methods for determination of, CC and RC. Because of their similar chemical structure and difficulty in separation and detection simultaneously, it is important to develop simple, rapid, and efficient methods to simultaneously monitor trace dihydroxybenzene isomers. Up to now [5][6].

Many analytical methods have been established to determine dihydroxybenzene isomers, such as HPLC[7], fluorescence[8], chemiluminescence[9], spectrophotometry[10], GC-MS [11], and electrochromatography [12]. Among them, electrochemical methods have attracted ever-growing attention due to the advantages such as fast response, low cost, simple operation, faster analysis, high sensitivity, and excellent selectivity[13].

The present research aims to developing a sensitive, simple and accurate spectrophotometric method for the determination of resorcinol, and Catechol based on their coupling with 2,4-Di-nitrophenylhydrazine to give intense bright colored

2. Materials And Methods

2.1. Apparatus

A Shimadzu UV-visible spectrophotometer model 1800 with 1 cm matched quartz cell was used for the absorbance measurements.

2.2. Chemicals and Reagents

2.2.1. Standard catechol solution (100µg/mL)

The solution was prepared by dissolving 0.01 grams of the compound as pure with distilled water and completed the size to the mark in a 100 ml volume bottle and kept in a dark bottle.

2.2.2. Standard resorcinol solution (100µg/mL)

0.01 gram of pure resorcinol was dissolved in distilled water and completed the size to the mark in a 100 mL calibrated flask".

2.2.3.

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Receive Date: 16 January 2021, Revise Date: 11 February 2021, Accept Date: 22 April 2021
DOI: 10.21608/EJCHEM.2021.57506.3253

2.2.4. *Potassium periodate solution (5×10-3 M)*

The solution was prepared by dissolving 0.1150 g of pure material in 3 ml of diluted sulphuric acid and completed with distilled water in a 100mL volume flask.

2.2.5. *Dinitro pheneyl Hydrazine Solution (2×10-3 M)*

The solution was prepared by dissolving 0.1981 grams of material in 5 mL of diluted sulphuric acid and completed the volume with distilled water in a volume bottle of 100 mL and then taken from the diluted preparation solution 20 mL and completed the volume using distilled water in 100 mL of a volumetric flask.

2.3. Optimization of experimental conditions

2.3.1. *Effect of Reagent Concentration*

The effect of the amount of reagent was carried out on the intensity of the absorption of the colored product, in addition to increased volumes of 2, 4-dinitro phenyl hydrazine with a concentration of 2×10-3M to a set of volumetric flasks with a capacity of 25 mL containing 4 mL of catechol or resorcinol solution with a concentration of 100 µg/mL and 1ml of potassium periodate solution at a concentration of 5×10-3 M, then complete the volume with distilled water to the mark and measure the absorption of these solution at a wave length of 385 nm and 404 nm respectively against their blank solutions and the results are shown in Fig. (1)

From fig (1) 2 mL gave highest absorbance for products

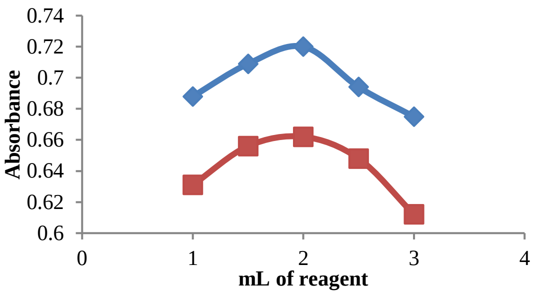

Figure (1): Effect of 2.4-dinitrophenyl hydrazine on absorbance

2.3.2. *Effect of potassium periodate solution (5×10-3M)*

The effect of the oxidative agent in absorption was studied at a concentration of 5×10^{-3}M by adding different volumes to 4 mL of catechol and resorcinol solution at a concentration of 100 µg/mL with a 2 mL of 2,4- di nitro phenyl hydrazine 2 x 10-3M in a volumetric flask of 25 mL and complete with distilled water, after which the absorption of all solutions is measured at a wavelength of 385 nm and 404 nm respectively against the image solution and the results are shown in Figure (2).

Figure (2): Effect of potassium periodate concentration on absorbance intensity of catechol and resorcinol with 2,4- di nitro phenyl hydrazine product.

2.3.3. *Effect of surfactants*

A-For catechol: The results reveal that the presence of **(SDS**) increase the intensity on the color product.

B- For resorcinol: The effect of surfactant on the color intensity has been examined. The results given in Figure 3 reveal that the presence of the Cetyl trimethyl amonium bromide (**CTAB**) increase the intensity of the color product.

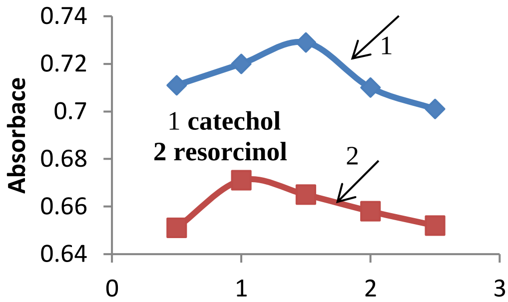

Figure (3): Effect of surfactants amount on the intensity of Complex product

2.3.4. *Effect order of addition*

In order to choose the best addition sequence of the reactants, a number of different laboratory experiments were conducted to find out the effect of the addition sequence to the solutions. The results shown in Table (7, 8) show that the preferred addition sequence is (I), to form the colored product and accordingly it was approved in the subsequent experiments.

Table (7): The effect of order of addition on absorbance the color product

Order of addition	Order number	Absorbance
S+R+O+ CTAB	I	0.729
O+R+ CTAB +S	Π	0.567
S+O+R+ CTAB	Ш	0.626
R+S+O+ CTAB	IV	0.413
R) =2,4-DNPH ‹(O) =KIO4 ‹(=S catechol.		

Table (8): The effect of order of addition on absorbance the color product

Order of addition	Order number	Absorbance
S+R+O+SDS	I	0.671
O+R+ SDS +S	П	0.553
S+O+R+ SDS	III	0.526
R+S+O+ SDS	IV	0.313
.Resorcinol =S ، (KIO_4) =O ،(2,4-DNPH) =R		

2.3.5. *The effect of time on the stability of the reaction product"*

The effect of time on the stability of the colored product was studied, depending on the optimal conditions obtained from previous experiments, using a volumetric flask of 25 mL and completing the volume with distilled water. After that, the absorbance of colored solutions were measured at different time at wavelengths 385nm for catechol and 404 nm for resorcinol. The results are shown in Figure (4).

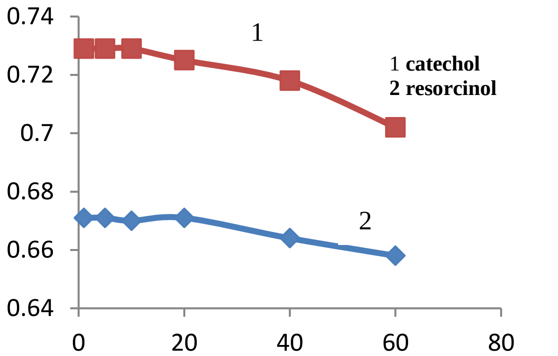

Figure (4): Effect of time for catechol reaction product

2.3.6. *Final absorption spectra for catechol.*

The final absorption spectrum of catechol was plotted for the resulting product at optimum conditions where the absorption spectrum diagram showed the maximum absorption intensity at wavelength 385 versus the blank solution.

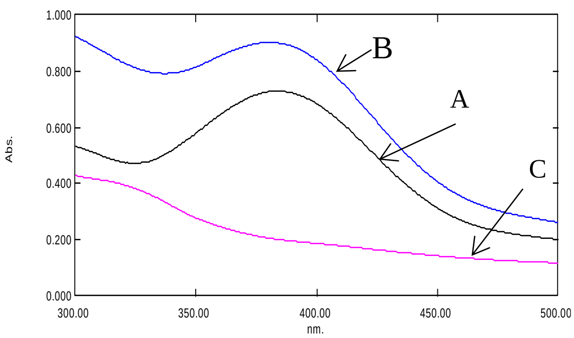

Figure (5): Absorption spectrum of 16µg / ml of catechol (according to optimal conditions and measured against the blank solution). (B) Catechol solution versus distilled water. (C) solution versus distilled water

2.3.7. *Final absorption spectra for resorcinol:*

The final absorption spectrum of resorcinol was drawn for the resulting product and according to the optimal conditions established. The absorption spectrum drawing showed the maximum absorption intensity at a wavelength of 404 nm versus blank

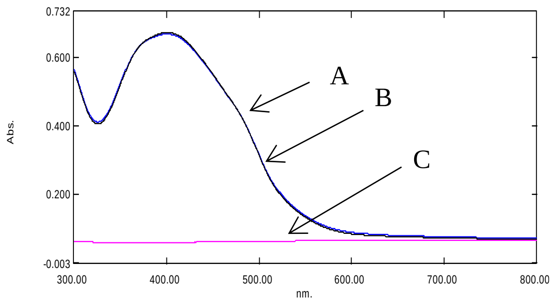

Figure (6): Absorption spectrum of 16µg / ml of resorcinol (according to optimal conditions and measured against the blank solution). (B) resorcinol solution versus distilled water. (C) solution versus distilled water

2.3.8. *Recommended procedure and Calibration graph*

A. for catechol

Aliquots of 100 µg/mL catechol solution (0.25 - 10 mL) were pipetted into a series of 25-mL an standard volumetric flasks. A 2 mL of 2,4- di nitro phenyl hydrazine 2 x 10^{-3}M , 1 mL of(5×10^{-3}M) potassium periodate and 1.5 mL of (0.1%) CTAB were added to each volumetric flask and the content was diluted to volume with distilled water. The absorbance was measured at385 nm against blank solution

B. for resorcinol

Aliquots of 100 µg/mL catechol solution (0.25 – 10 mL) were pipetted into a series of 25-mL an standard volumetric flasks. A 2 mL of 2,4- di nitro phenyl hydrazine 2 x 10^{-3}M , 3 mL of(5×10^{-3}M) potassium periodate and 1 mL of (0.1%) sodium dodecyl sulfate were added to each volumetric flask and the content was diluted to volume with distilled water. The absorbance was measured at404 nm against blank solution.

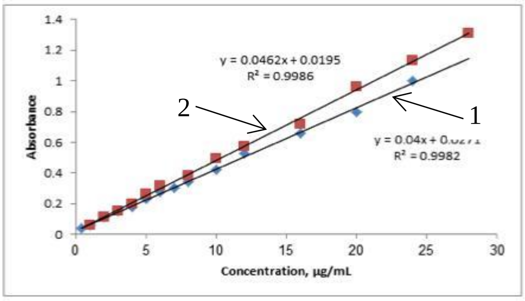

Figure (7): the standard curve for determination of (1) catechol and (2) resorcinol

Table 3. Optical Characteristics and Statistical Data for the Regression Equation of the Proposed Methods

Parameter	Catechol	Resorcinol
Beer's law limits (µg/mL)	1- 40 µg/ml	1- 25 µg/mL
Molar absorptivity ($l.mol^{-1}$ cm^{-1})	5.0866 × 10^3	4.404×10^3
maximum absorbance	385 nm	404 nm
Sandell's sensitivity ($\mu g\ cm^{-2}$)	0.0216	0.025
Regression equation (Y)#		
Slope, *a*	0.0462	0.04
Intercept, *b*	0.0192	0.0271
Correlation coefficient (R^2)	0.9982	0.9982
RSD##		

#$Y = aX + b$, where X is the concentration of amikacin sulphate in µg ml^{-1}.
Average of six determinations

2.3.9. Study The Nature Of The Product Formed:

The nature of "the formed" product was" studied by "applying the "Job's method ""to know the molar composition ratio between the drug (**catechol and resorcinol**) with the reagent (2,4-DNPH), where the solutions of the drug and the reagent were prepared in an equal concentration (2×10^{-4}M), from which a number of solutions were prepared by mixing different volumes of **catechol and resorcinol** and the reagent so that the final volume of the two components is constant which is (3 mL), and by following the optimal conditions and dilution to the mark limit in a volumetric flasks of 25 mL was measured The intensity of absorption of the solutions versus their blank solutions at the wavelength 385 nm, 404 respectively and it is observed in Figure (8) that the ratio of the conjugation between **catechol and resorcinol** with the (2,4-DNPH) reagent is (1: 1).

2.4. Applications

In order to evaluate the analytical applicability, precision and accuracy of the methods, A certain quantity of each of the compounds was added to the river water and the proposed methods determined their concentrations. The results are listed in the table(4) Shows the success of the proposed method

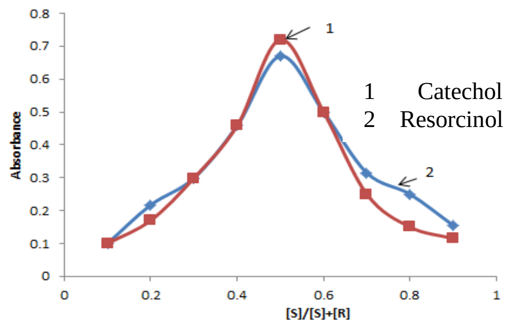

Figure (8): "Job's method" For catechol and resorcinol with 2,4- DNPH

Table (4): Determination of catechol and resorcinol in river water

Compound	Added(µg/mL)	Found (µg/mL	Relative error(%	Relative standard deviation %
Catechol	4	3.98	2	1.4
	8	8.05	2.5	1.1
	12	12.1	2	1.92
Resorcinol	5	4.35	1.71	1.42
	10	9.98	0.04	0.06
	15	14.84	0.46	2.31

2.4.1. Comparison of the methods

The results of comparison between the analytical variables of the present method with (other spectrophotometric methods show that the present method is sensitive for the determination of catechol and resorcinol (Table 5)

Analytical Parameter	Present method		Literature method [14].	
	Catechol	**Resorcinol**	**Catechol**	**Resorcinol**
λ_{max}.	385 nm	404 nm	530 nm	530 nm
Beer's law limits (µg/mL)	1- 40 µg/mL	1- 25 µg/Ml	0.25–2.0 mg/mL	0.1–2.0 mg/mL
Sandell's sensitivity ($\mu g\ cm^{-2}$	0.0216	0.025	——	—
Slope, *a*	0.0462	0.04	–0.0592	–0.160
Correlation coefficient	0.9982	0.9982	0.9994	0.9992
RSD			1.40	1.21

3. Conclusion

The reagents utilized in the proposed methods are cheap, readily available and the procedures do not involve any critical reaction conditions or tedious sample preparation. Moreover, the methods are free from interference of the new procedures for routine quality control was well established by the assay of catechol and resorcinol in pure form and in river water.

4. Acknowledgments

The authors wishes to express gratitude to collage Of Education" For Girls Department of Chemistry, To provide the workplace and equipment

5. References

[1] W. Xu, Z. Huang, X. Ji, and J. P. Lumb, "Catalytic Aerobic Cross-Dehydrogenative Coupling of Phenols and Catechols," *ACS Catal.*, vol. 9, no. 5, pp. 3800–3810, 2019, doi: 10.1021/acscatal.8b04443.

[2] L. Zhao, B. Lv, H. Yuan, Z. Zhou, and D. Xiao, "A sensitive chemiluminescence method for determination of hydroquinone and catechol," *Sensors*, vol. 7, no. 4, pp. 578–588, 2007, doi: 10.3390/s7040578.

[3] B. B. Al-mosulli, A. S. Al-jomaili, and H. S. Al-janabi, "Determination of hydroquinone in pure form and pharmaceutical preparations using Batch and FIA-Merging Zone techniques with spectrophotometric detection," *Iraqi J. Sci.*, vol. 56, no. 1, pp. 265–274, 2015.

[4] P. L. García, M. I. R. M. Santoro, A. K. Singh, and E. R. M. Kedor-Hackmann, "Determination of optimum wavelength and derivative order in spectrophotometry for quantitation of hydroquinone in creams," *Rev. Bras. Ciencias Farm. J. Pharm. Sci.*, vol. 43, no. 3, pp. 397–404, 2007, doi: 10.1590/S1516-93322007000300008.

[5] S. Heydari and M. H. Zaryabi, "A rapid spectrophotometric method for simultaneous determination of catechol , hydroquinone , and resorcinol in water samples using mean centering spectra," *J. Biodivers. Environ. Sci.*, vol. 10, no. 4, pp. 217–224, 2017.

[6] Y. Wang, H. Feng, H. Li, X. Yang, H. Jia, and W. Kang, "A Copper (II) Ensemble-Based Fluorescence Chemosensor and Its Application in the 'Naked–Eye' Detection of Biothiols in Human Urine," *sensors Artic.*, vol. 20, no. 1331, pp. 1–13, 2020.

[7] G. Marrubini, E. Calleri, T. Coccini, A. F. Castoldi, and L. Manzo, "Direct analysis of phenol, catechol and hydroquinone in human urine by coupled-column HPLC with fluorimetric detection," *Chromatographia*, vol. 62, no. 1–2, pp. 25–31, 2005, doi: 10.1365/s10337-005-0570-3.

[8] H. Chen, Z. Lin, H. Tang, T. Wu, and C. Tan, "Quantitative analysis of dihydroxybenzenes in complex water samples using excitation-emission matrix fluorescence spectroscopy and second-order calibration," *J. Spectrosc.*, vol. 2014, pp. 1–7, 2014, doi: 10.1155/2014/412039.

[9] E. L. B. Lourenço, A. Ferreira, E. Pinto, M. Yonamine, and S. H. P. Farsky, "On-fiber derivatization of SPME extracts of phenol, hydroquinone and catechol with GC-MS detection," *Chromatographia*, vol. 63, no. 3–4, pp. 175–179, 2006, doi: 10.1365/s10337-006-0719-8.

[10] P. Nagaraja, R. A. Vasantha, and K. R. Sunitha, "A sensitive and selective spectrophotometric estimation of catechol derivatives in pharmaceutical preparations," *Talanta*, vol. 55, no. 6, pp. 1039–1046, 2001, doi: 10.1016/S0039-9140(01)00438-6.

[11] A. K. Kiprop, E. Pourtier, and S. K. Kimutai, "GC-MS and ESI-MS detection of catechol," *Int. J. Educ. Res.*, vol. 1, no. 12, pp. 1–12, 2013.

[12] M. Rezazadeh, Y. Yamini, and S. Seidi, "Microextraction in urine samples for gas chromatography: A review," *Bioanalysis*, vol. 6, no. 19, pp. 2663–2684, 2014, doi: 10.4155/bio.14.215.

[13] M. U. Hossain, M. T. Rahman, and M. Q. Ehsan, "Simultaneous detection and estimation of catechol, hydroquinone, and resorcinol in binary and ternary mixtures using electrochemical techniques," *Int. J. Anal. Chem.*, vol. 2015, pp. 1–8, 2015, doi: 10.1155/2015/862979.