

SPECTROPHOTOMETRIC COLORIMETRIC DETERMINATION FOR RESORCINOL DURING SILVER NANOPARTICLES FORMATION WITH A FOCUSED PLASMON RESONANCE SURFACE USING POLYVINYL PYRROLIDONE AS STABILIZER

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Abstract: In this manuscript, to determine resorcinol (RES) in pure and pharmaceutical forms, we developed a simple colorimetric method based on the formation of environmentally friendly silver nanoparticles (oxidizing agent). The electron cloud formed silver nanoparticles (AgNPs) in an alkaline medium and then reacted (RES) in the presence of Polyvinylpyrrolidone as a stabilizer in nanometer dimensions. It can oscillate on particle surfaces when dispersed in a liquid medium. It showed adequate absorption at a wavelength of 416 nm. Lambert-Beer's law is linear from 1.6 - 12 ppm, and the analysis method was simple, sensitive and highly selective.

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Introduction

Resorcinol (Figure 1) is a chemical compound with many pharmaceutical applications. It is well-known for its effect and its use as a cornea analyzer, and in addition to that, it is used in the manufacture of plastics, resins or dyes. It is also used in the cosmetic industry, in the production of flavoring agents, manufacturing of colors, as well as an antioxidant.¹⁻⁶ *m*-Dihydroxybenzenes released into the environment, are more harmful than phenols. They are phenolic substances commonly present in plants being essential for their biochemical functions, as well as industrial downstream chemicals.

Phenolic compounds occupational and environmental exposures to resorcinol were studied in Finland.⁷ Resorcinol is an antiseptic and anti-infective chemical found in products used to treat minor burns and wounds by eliminating rough and hard skin layers. Resorcinol's concentration has been measured using a variety of analytical spectroscopic techniques. Moreover, eczema, acne, and psoriasis are all treated with topical resorcinol.⁸ Finding novel, straightforward, and precise methods of analysis is essential because of the importance for resorcinol due to its numerous industrial uses. The precision of the analytical procedures utilized, whether for the active substance used in the manufacture of the product or for the product after the production process, generally determines the success of any chemical or pharmaceutical firm. Finding sensitive, precise, and quick analytical techniques is the cornerstone of every research, regardless of whether it's in the area of analytical chemistry or pharmaceuticals analyses. Therefore, the aim of our manuscript was to identify and develop a new, simple, accurate and selective spectrophotometric method for the detection of resorcinol in a variety of materials and to use polyvinyl pyrrolidone

(PVP) as an effective in situ surface resonance anchor for the preparation of silver nanoparticles.

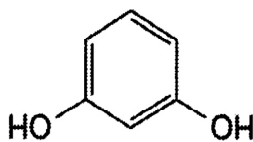


Figure 1. Resorcinol structure.⁹

Experimental

Materials and Methods

All the chemicals used in all the experiments are high purity. All spectroscopic measurements, whether absorbance's and wavelengths, are made using UV-Visible Spectrophotometer (UV-1800 PC, Shimadzu, Japan) connected to the UV-Probe Version 2.21 Software, and using Quartz Cell of 1 cm Path Length (the spectrophotometer found in the Faculty of pharmacy Lab).

Solutions

Deionized water was used to make all of the solutions. In 100 mL of methanol, dissolve 0.01 g of resorcinol to get a solution (100 ppm). By combining 0.02 g of Polyvinyl pyrrolidone with 50 mL of deionized water, a stabilizer solution PVP (0.4 g/L) was created. 200 mL of deionized water were used to dissolve 0.021 g of sodium carbonate. 0.085 g of sodium carbonate needs to be dissolved, and 50 mL of deionized water needs to contain 0.01 M silver nitrate solution in order to create a base with a concentration of 0.001 M. Daily deionized water preparations were made for all solutions required for measurement and calibration curve construction.

Recommended Procedure and Calibration Graph

In a 25 mL volumetric flask, at increasing concentrations of RES mL with 0.01 M AgNO₃, add 2 mL of Na₂CO₃ with 0.4 g/l of 2-stabilizer, dilute to about 10 mL of water, and mix well for 10 minutes. After that, within 15-16 minutes, part of the mixture is poured in a spectrophotometer cell to record the absorbance. The absorbance was measured at 416 nm (λ_{\max}) of the LSPR Ag NPS peak versus the blank solution.

Results and Discussion

Absorption spectra

The solutions of RES, Na₂CO₃, PVP and AgNO₃ were mixed well for a while to interact with each other, until we got a colored product which was scanned in UV-VIS spectrophotometer in the range of 190–800 nm, Figure 2 shows the spectrum of the colored product (RES Ag-NPs) having an absorption maximum at 416 nm that is significantly different from the absorption maxima of both reactants. This red shift of the product that can be used for the assay (RES).¹⁰

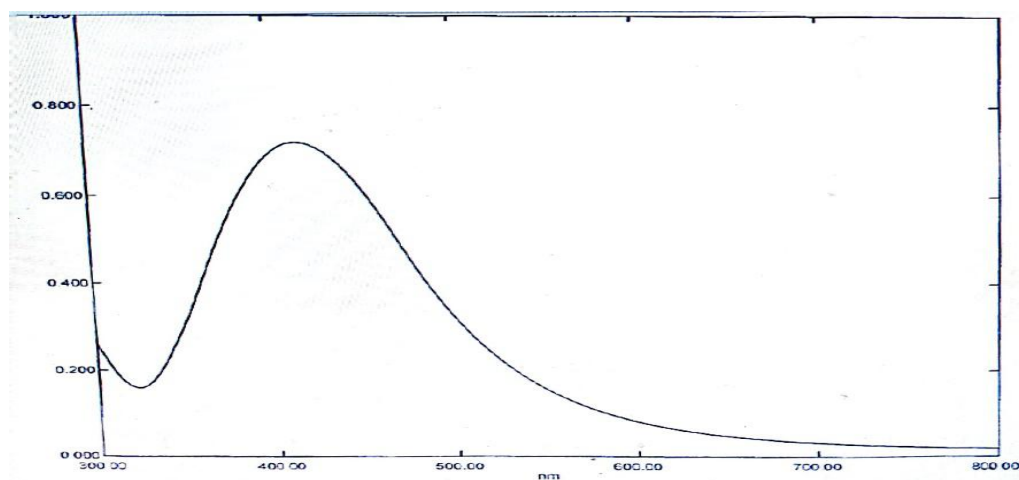


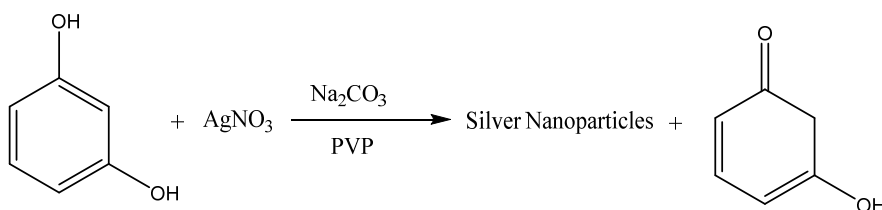
Figure 2. Spectrum of silver nano particles formed.

In order to optimize the method for analysis, visually checking the color changes with time and other parameters on reaction RES Ag-NPs was conducted. Therefore, several conditions were studied to find out the best reaction conditions to conduct the chemical reaction easily, such as the type of base, the type of stabilizer, and the effect of temperature and time required completing the reaction. The stability of the product and the effect of the addition sequence on the occurrence of the reaction were also studied.

Chemistry

Resorcinol can reduce silver ions to Ag-NPs product according to Scheme 1. The colored product has a $\lambda_{\text{max}} = 416 \text{ nm}$ (Figure 2) and this colored form appears due to the broad localized surface Plasmon band of the nanoparticles using Na_2CO_3 as a base and PVP as stabilizer.

Thus, we propose this method as a new solution for the selective colorimetric detection of resorcinol compound in its pure form and in pharmaceutical formulations based on the formation of AgNPs through the interaction of RES with silver ions (oxidizing agent) in the presence of polyvinyl pyrrolidone as a stabilizer, with the formation of silver nanoparticles (AgNPs), when a clear color change occurs. We used UV-Vis spectroscopy to monitor the changes of the plasmon resonance surface of AgNPs at a wavelength of 416 nm and based on previous studies, proving the formation of silver nanoparticles.^{2,11}



Scheme 1. The reaction scheme for obtaining Ag-NPs.

Previous studies indicated that Resorcinol can reduce AgNO_3 with Na_2CO_3 and polyvinyl pyrrolidone (PVP) as the stabilizer to the Ag-NPs (Scheme 1). They reported that nanoparticles formed could be used in the analyses for direct spectrophotometric analysis of RES, the new UV-Vis absorption peak appears due to the localized surface Plasmon resonance peak of Ag-NPs.¹²

To find the best reaction conditions for an optimized analytical method, the reaction conditions were modified to study the impact of various parameters on the Ag-NPs absorption intensity.

Base type effect

Different types of fixed conc. 0.001 M of different base have been examined.¹³ The maximum absorption was obtained when Na_2CO_3 was used as base (figure 3).

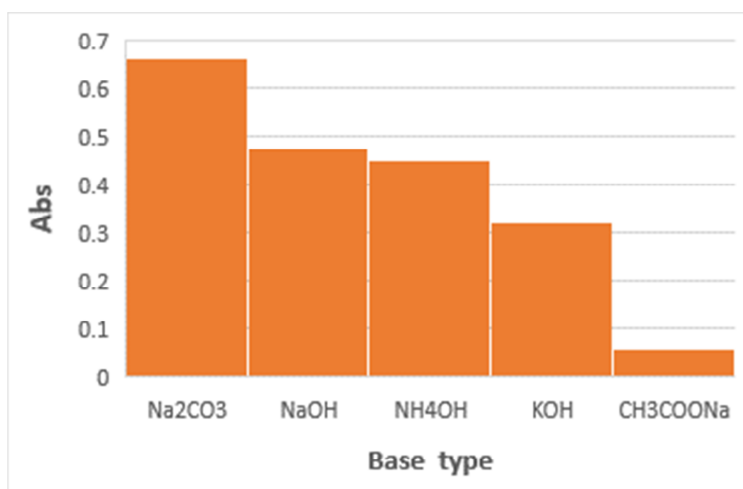


Figure 3. Effect of base type.

Effect of volume of base

Different amounts of Na_2CO_3 in a series of volumes (0.5 - 2.5 mL). Through the study, it became clear that the greatest intensity of absorption was when a volume 2 mL of 0.001 M Na_2CO_3 was used (figure 4)

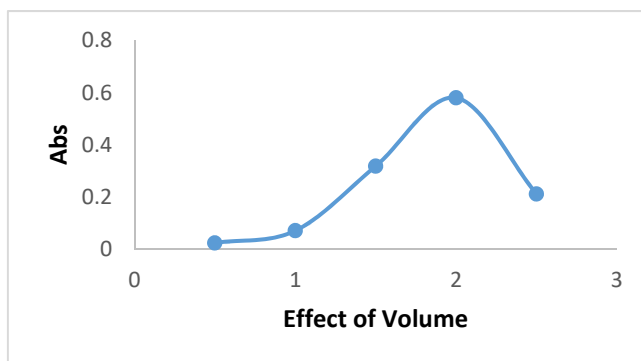


Figure 4. Effect of base volume.

Effect of stabilizer type

Different types of solutions 0.4 g/L of different stabilizer have been examined. It was found that Polyvinyl pyrrolidone (PVP) give the best results (figure 5).

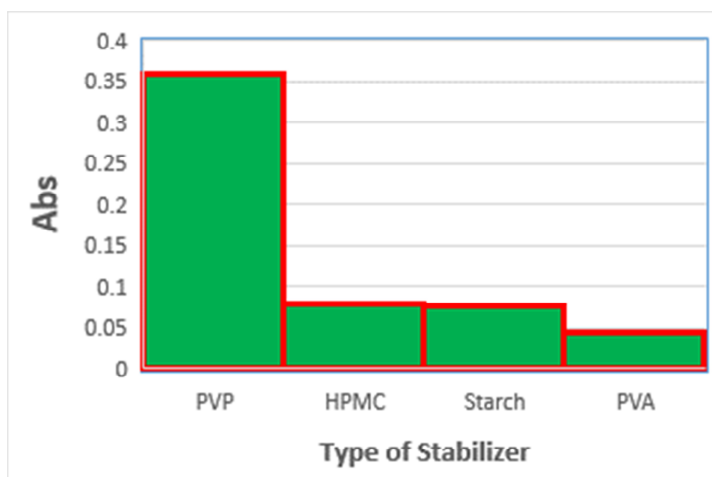


Figure 5. Effect of stabilizer type.

Order of addition

Different orders for the addition have been examined (D = Drug, S = stabilizer, B = Base, A = AgNO₃) (figure 6). It became clear through the experiment that the addition D + S + B + A gives a higher intensity of absorption than the addition D + B + S + A. This is due to the fact that stabilizer prepares the drug for interaction by displacing the proton present in the hydroxyl group by forming a stable intermediate state for the reaction and giving a more stable product in color.¹⁴

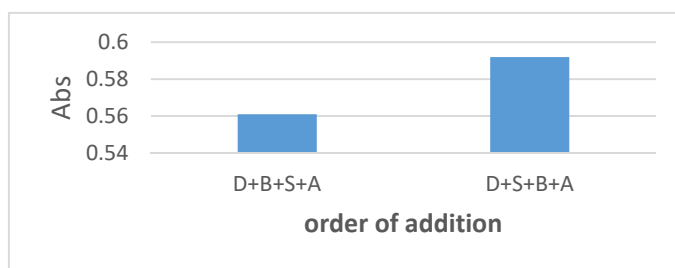


Figure 6. Effect of order of addition.

Time effect and stability

The time required for the formation of the product was 24 minutes, which is sufficient for the formation of silver nanoparticles. It is found that after that the color becomes stable for at least 3 hours. After this time, the absorption intensity decreased (figure 7).¹⁵

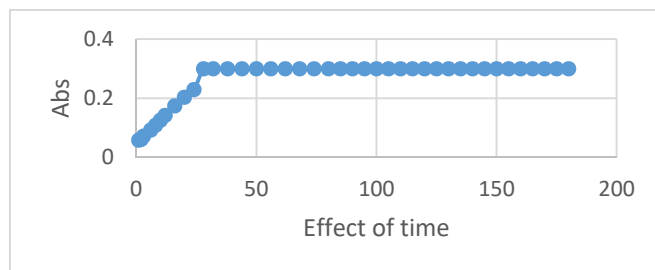


Figure 7. Effect of time on the stability of product.

Temperature Effect

The effect of temperature on the stability of color was investigated with a range of different temperatures of 1–60 °C. It was found that the absorbance is still stable in the range of 5–25 °C with no significant changes occurred.¹⁶ After that, a decrease in the intensity of absorption as a result of the high temperature, when dissociation occurred in the resulting compound (figure 8).

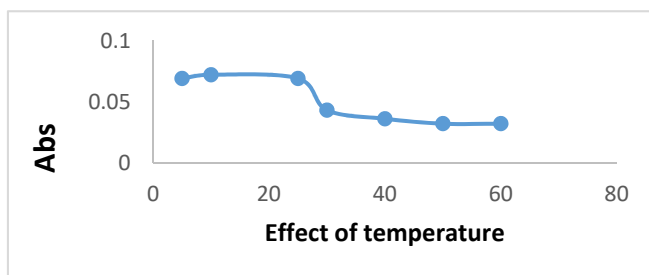


Figure 8. Effect of temperature on the stability of product.

Effect of concentration of AgNO₃

A series of volumes (0.5–1.5 mL) were prepared containing 1M solution of AgNO₃. We found that 1 mL of 1M AgNO₃ gave the highest absorption intensity (figure 9).

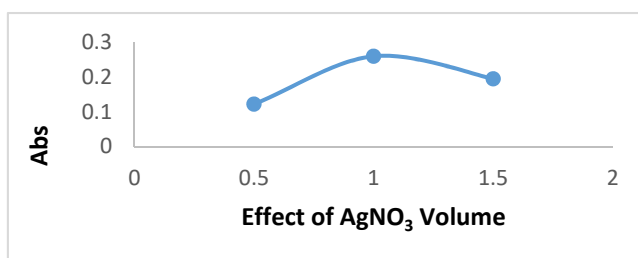


Figure 9. Effect of concentration of AgNO₃.

Calibration curve procedure

Dug stock solution of 100 ppm was prepared and by the law of dilution after applying the conditions that were studied and left for the time required to complete the reaction. A series of concentrations were prepared and after measuring the absorbance at a wavelength of 416 nm, we concluded the calibration curve obeys Lambert's law with a linear in the range of 1.6 – 12 ppm. Then there is a deviation from Lambert's law. Correlation coefficient is 0.9995, Sandal's sensitivity = 0.1515, LOD = 1.2727, LOQ = 4.2424 (table 1).

$$\begin{aligned}\text{LOD} &= 3 \cdot \text{SD} / \text{Slope} \\ &= 3 \cdot 0.0028 / 0.0066 \\ &= 1.2727 \text{ ppm}\end{aligned}$$

$$\begin{aligned}\text{LOQ} &= 10 \cdot \text{SD} / \text{Slope} \\ &= 3 \cdot 0.0028 / 0.0066 \\ &= 4.2424 \text{ ppm}\end{aligned}$$

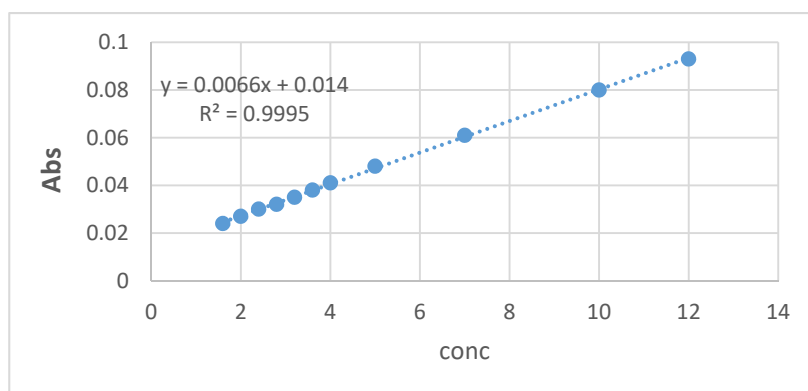


Figure 10. Calibration graph for RES.

Table 1. Analytical parameters of the suggested technique in case of RES.

RES	
Value	Variable
$y = 0.0066x + 0.014$	Regression equation
0.0066	Slope
0.9995	Correlation
0.1515	Sandal's sensitivity
1.6 – 12 ppm	Range
1.2727	LOD
4.2424	LOQ

Conclusions

The proposed spectrophotometric localized surface plasmon-based colorimetric method determining resorcinol is simple, fast and low cost, without danger, quick owing. Also, the method can be implemented in many laboratories, being ecologically friendly and no special reagents or expensive instruments are needed. The detection is fast and can be completed within 24 min. Our method is based on the reaction of resorcinol with silver nitrate using Na_2CO_3 alkaline medium in the presence of a stabilizer, to form the nanocomposite.

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