Colorimetric determination of resorcinol based on localized surface plasmon resonance of silver nanoparticles

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In this paper, we have developed a simple colorimetric method for detection of resorcinol (RE); the method is based on the reaction of RE with silver ions (oxidizing agent) in the presence of starch as a stabilizer and formation of silver nanoparticles (AgNPs). At nanometer dimensions the electron cloud can oscillate on the particle surfaces when dispersed in liquid media so these nanoparticles exhibit a strong UV-Vis extinction band. A UV-Vis spectrophotometer is used to monitor the changes of the localized surface plasmon resonance (LSPR) of AgNPs at a wavelength of 430 nm. There is a linear relationship between absorbance intensity of AgNPs and the concentration of RE over the range of $4 \times 10^{-6}$ to $1.1 \times 10^{-2}$ mol L$^{-1}$ at 430 nm. The detection limit was $1.2 \times 10^{-6}$ mol L$^{-1}$. The proposed method has been successfully applied for the determination of RE in anti-acne solution and spiked shampoo samples.

Introduction

The development of sensitive and selective colorimetric sensors has become widely popular, due in part to their simplicity, rapidity, precision and common availability of the basic equipment in laboratory and field uses. Noble metal nanoparticles (NPs) have fascinated scientists because of their physico-chemical properties and potential applications in different areas such as catalysis, electronics, plasmonics, biotechnology, and so on. Among these nanoparticles, gold and silver nanoparticles have drawn much research attention because of their various promising properties. Various techniques, including chemical and physical means such as chemical reduction, electrochemical reduction, photochemical reduction, and biosynthesis, have been developed to prepare metal nanoparticles. As the dimensions of dispersed particles in liquid media reach to the nanometer region, a strong UV–Vis band appears which is not in the bulk metal spectrum. Since the structure, size and shape of the metal nanoparticles have great effects on their optical, electrical and catalytic properties, it is important to control these parameters. The optical properties of nanoparticles made of gold and silver have been of interest for researchers for many decades. These properties of nanoparticles, which give rise to localized surface plasmon resonance (LSPR) absorption and scattering, can be used in the development of analytical methods such as optical sensing, DNA hybridization and detection. Metal ion detection LSPR excitation results in wavelength-selective absorption with extremely large molar extinction coefficients. Oscillation of electron cloud on the particle surface at nano-scale dimensions is associated with the absorption of particular energy of electromagnetic radiation. LSPR is a photon driven coherent oscillation of the surface conduction electrons, which are excited by electromagnetic radiation. The light interacts with particles much smaller than the incident wavelength and the electrons in the nanoparticles oscillate locally around the nanoparticles. Especially silver nanoparticles exhibit excellent LSPR properties. Solutions of colloidal Ag nanoparticles have distinctive color arising from their tiny dimensions. In comparison with gold nanoparticles, silver nanoparticles have been less employed in research based on optical detection of chemical species. Some previously reported studies are based on the silver nanoparticle surface plasmon peak for the optical detection of chemical species such as phosphates, amylase, cysteine, adenosine and NADH, hydrogen peroxide, dopamine and ascorbic acid, ferulic acid, hydroquinone and cyanide. Silver ion concentration has been determined using this phenomenon by S. Yajima et al. In this study, resorcinol (RE) or benzene-1,3-diol which is a dihydroxybenzene with the formula $C_6H_4(OH)_2$ is determined by LSPR of AgNPs. Resorcinol, catechol, and hydroquinone are dihydroxybenzene isomers which are widely used in cosmetics, tanning, pesticides, flavoring agents, medicines, antioxidants, dyes and photography chemicals. Due to their high toxicity and low degradability in ecological environment, they are considered as environmental pollutants by the US Environmental Protection Agency (EPA) and the European Union (EU). These phenolic compounds are irritants and have severe effects on the central nervous system and especially RE produces a generalized eczema, urticaria and angioneurotic edema. In recent years, many methods have been reported for the determination of RE in different samples, such as electrochemistry, spectrofluorimetry, synchronous fluorescence.
capillary zone electrophoresis, and spectrophotometry. In spite of good sensitivity of these methods, some of them require expensive and sophisticated instrumentation or have complicated sample preparation or time consuming procedures. Thus, the development of a new sensitive, fast and practical method for the detection still remains a great challenge.

In this work a new simple and sensitive method for the determination of RE is proposed. The method is based on the reaction of RE with an oxidizing agent (silver ion) and preparation of silver nanoparticles (AgNPs) in slightly basic medium. The intensity of LSPR of AgNPs was monitored spectrophotometrically at the maximum wavelength of 430 nm vs. time. With the increase of RE concentration, the LSPR spectrum intensity of formed AgNPs was increased, and the enhanced intensity of LSPR was linearly proportional to the RE concentration. The method was applied for the determination of RE in spiked samples of antidandruff shampoo and anti-acne solution samples and satisfactory results were obtained.

**Experimental**

**Materials**

All chemicals were of analytical reagent grade purity. Resorcinol, starch, AgNO3 powder, and NaOH were purchased from Merck (Darmstadt, Germany) and the solutions were prepared with doubly distilled water. Stock solutions of AgNO3 (0.015 M) were prepared by dissolving 0.507 g AgNO3 in deionized water and diluting to 200 ml. Stock solution of resorcinol (0.001 M) was prepared by dissolving 0.011 g of pure RE in water and diluting to 100 ml. Also solutions of 2 g l\(^{-1}\) starch, 0.002 M NaOH and 0.1 M NH3 were used. All experiments were performed at ambient temperature (25 ± 3 °C).

**Instrumental**

The spectrophotometric measurements were carried out with a Cintra 101 spectrophotometer (GBC SCIENTIFIC EQUIPMENT, Australia) using a 1 cm polymeric cell. A pH-meter (model 632 Metrohm, Herisau, Switzerland) and a transmission electron microscope (Zeiss EM 10C (Carl Zeiss Inc., Oberkochen, Germany) 80 kV) were used.

**Procedure**

In a 10 ml volumetric flask were added different concentrations of RE, 1 ml of 0.015 M AgNO3, 1 ml of 0.002 M NaOH, 0.1 ml of 0.1 M NH3 and 0.2 ml of 2 g l\(^{-1}\) starch solution. The mixture was diluted to about 10 ml with water and mixed thoroughly for 10 seconds. Thereafter within 15–16 min a portion of the mixture was transferred into a 1 cm spectrometric cell to record the absorbance. The absorbances were measured at 430 nm (\(\lambda_{\text{max}}\) of AgNPs LSPR peak) against a blank solution. Color changes of the mixture in the presence of various concentrations of RE are shown in Fig. 1.

**Results and discussion**

**Mechanism of formation of AgNPs**

The mechanism of the formation of AgNPs is shown in Fig. 2. It should be noted that the absorption of AgNPs is not observed in the presence of other reagents without RE in the region of 400–700 nm. By the addition of RE as a reducing agent, an absorption peak was appeared at about 430 nm, indicating the formation of AgNPs. Fig. 3 shows the absorption of AgNPs resulting from the reaction between silver cation and RE. Mechanisms of the synthesis of the AgNPs were suggested according to the following equations:

\[
2\text{AgNO}_3 + 2\text{NaOH} \rightarrow \text{Ag}_2\text{O}_3 + 2\text{NaNO}_3 + \text{H}_2\text{O}
\]

\[
\text{Ag}_2\text{O}_3 + 4\text{NH}_3 + 2\text{NaNO}_3 + \text{H}_2\text{O} \rightarrow 2\text{Ag(NH}_3)_2\text{NO}_3(\text{aq}) + 2\text{NaOH}
\]

\[
[\text{Ag(NH}_3)_2]^+_{(\text{aq})} + \text{RE}_{(\text{Red})} + e^- \rightarrow \text{Ag(s)} + 2\text{NH}_3 + \text{RE}_{(\text{Ox})}
\]

where RE\(_{\text{(Red)}}\) is the ionized form of RE in the basic medium and RE\(_{\text{(Ox)}}\) is its oxidized form. Since the redox reaction is between

![Fig. 1](image1.png) **Fig. 1** Color changes of solution due to the LSPR of AgNPs in the presence of various RE concentrations as reducing agent. RE concentrations from left to right in mol l\(^{-1}\): 4 × 10\(^{-6}\), 5 × 10\(^{-6}\), 6 × 10\(^{-6}\), 7 × 10\(^{-6}\), 8 × 10\(^{-6}\), and 9 × 10\(^{-6}\).

![Fig. 2](image2.png) **Fig. 2** Suggested reaction for reduction of Ag\(^+\) in the presence of resorcinol.

![Fig. 3](image3.png) **Fig. 3** UV-Vis absorption spectrum of AgNPs prepared via reduction of silver ions in the presence of RE as reducing agent. Concentrations: RE (8 × 10\(^{-6}\) M), 0.015 M AgNO3; 1.0 ml of 0.002 M NaOH; 0.1 ml of 0.1 M NH3; 0.2 ml of 2 g l\(^{-1}\) starch solution.
resorcinol and \([\text{Ag(NH}_3\text{)}_2]^+\), the order of addition of the reagents as stated in the “Procedure” section is very important to produce \([\text{Ag(NH}_3\text{)}_2]^+\) in the solution. The transmission electron microscopy image (Fig. 4) of the produced AgNPs showed that particles were in the range of 20–40 nm.

Optimization of experimental conditions

In the first few minutes from initiation of the reaction, the absorbance changes slowly to reach a maximum after about 15 minutes and remains nearly constant afterwards. Therefore, all the absorbance measurements were performed within 15 to 16 minutes from addition of NH\(_3\) solution. Fig. 5 shows the changes of the absorbance at 430 nm with time.

The reaction between RE and AgNO\(_3\) is a redox reaction that occurs in a basic medium. Based on the previous works phenolic groups are firstly ionized under this condition and converted to a phenolate anion which is more reducible. So the influence of the pH of the solution is critical. Fig. 6 shows the effect of NaOH concentration on the AgNP LSPR peak intensity.

As it can be seen, the absorbance increases up to a known concentration of NaOH and then decreases which might be due to the Ag\(_2\)O precipitate formation. Thus, a concentration of 2 \(\times\) 10\(^{-4}\) M was selected as the optimum concentration for NaOH.

It is well known that in alkaline solution silver ions can participate in a reaction known as mirror reaction and addition of NaOH can cause the silver ions to precipitate. So we should use ammonia together with NaOH. In the presence of ammonia, silver ions can exist in the complex form and this prevents precipitation. Fig. 7 shows the changes of the absorbance at 430 nm with a change in the concentration of ammonia. As it is obvious, an increase of ammonia concentration yields a decrease in absorbance intensity, because in the presence of higher amounts of ammonia as a ligand, the silver complex reduction is slightly more difficult and RE could not reduce silver ions. Thus the optimum ammonia concentration was chosen to be 1 \(\times\) 10\(^{-3}\) M.

The nanoparticles were ageing in the solution so for the prevention of silver nanoparticles agglomeration the presence of protective agents or stabilizers is important. Starch is a nontoxic agent and has been used as a stabilizer for prevention of silver nanoparticles agglomeration. The results revealed that by the addition of different amounts of 2 g l\(^{-1}\) starch solution the amount of absorbance of AgNPs was nearly constant (Fig. 8). Thus, 0.2 ml of 2 g l\(^{-1}\) was chosen as an optimum value for starch concentration.

![Fig. 4](image)  Transmission electron microscopy image of AgNPs.

![Fig. 5](image)  The changes of the absorbance at 430 nm with time. Concentrations: RE (8 \(\times\) 10\(^{-6}\) M), 0.015 M AgNO\(_3\); 0.1 ml of 0.1 M NH\(_3\); 0.5 ml of 2 g l\(^{-1}\) starch solution.

![Fig. 6](image)  Dependence of the surface plasmon intensity on the concentration of NaOH. Concentrations: RE (8 \(\times\) 10\(^{-6}\) M), 0.015 M AgNO\(_3\); 0.1 ml of 0.1 M NH\(_3\); 0.5 ml of 2 g l\(^{-1}\) starch solution.

![Fig. 7](image)  Effect of ammonia concentration on the surface plasmon intensity of the AgNPs. Concentrations: RE (9 \(\times\) 10\(^{-6}\) M), 0.015 M AgNO\(_3\); 1.0 ml of 0.002 M NaOH; 0.5 ml of 2 g l\(^{-1}\) starch solution.

![Fig. 8](image)  Effect of starch concentration on the surface plasmon intensity of the AgNPs. Concentrations: RE (9 \(\times\) 10\(^{-6}\) M), 0.015 M AgNO\(_3\); 0.1 ml of 0.1 M NH\(_3\); 1.0 ml of 0.002 M NaOH.
Table 1 Effect of interfering ions on determination of RE. [Conditions: RE (8 × 10^{-6} M), 0.015 M AgNO_{3}; 1.0 ml of 0.002 M NaOH; 0.1 ml of 0.1 M NH_3; 0.2 ml of 2 g l^{-1} starch solution.]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (× 10^{-6} mol l^{-1})</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K^+</td>
<td>40</td>
<td>-4.50%</td>
</tr>
<tr>
<td>Na^+</td>
<td>50</td>
<td>-2.40%</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>40</td>
<td>+1.20%</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>50</td>
<td>+0.98%</td>
</tr>
<tr>
<td>Fe^{3+}</td>
<td>50</td>
<td>+2.68%</td>
</tr>
<tr>
<td>Cl^{-}</td>
<td>30</td>
<td>-3.30%</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>8</td>
<td>+20%</td>
</tr>
</tbody>
</table>

* All cations were prepared from nitrate salts and anions were prepared from sodium salt.

Table 2 Figures of merit of the proposed method for determination of the resorcinol

| Limit of detection (mol l^{-1}) | 1.2 × 10^{-6} (mol l^{-1}) |
| RSD\% (n = 6) for two concentrations | 5.0 × 10^{-6} (mol l^{-1}) | 1.78% |
| Linear range | 4 × 10^{-6} to 1.1 × 10^{-5} (mol l^{-1}) | 4.17% |
| Calibration curve equation | Y = 0.0294X - 0.0765 | 0.9978 |

Table 3 Determination of RE in a 5% methanolic anti-acne solution sample by a standard addition method

<table>
<thead>
<tr>
<th>Amount of resorcinol (× 10^{-6} mol l^{-1})</th>
<th>Added</th>
<th>Found</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
<td>7.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>8.32</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>9.17</td>
<td>93.3</td>
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</table>

Table 4 Determination of RE in a spiked shampoo sample by the proposed method

<table>
<thead>
<tr>
<th>Added RE (× 10^{-6} mol l^{-1})</th>
<th>Found (× 10^{-6} mol l^{-1})</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>5.000</td>
<td>4.778</td>
<td>95.60%</td>
</tr>
<tr>
<td>8.000</td>
<td>8.316</td>
<td>103.90%</td>
</tr>
</tbody>
</table>

Table 5 Comparison of the proposed method with some of the methods reported in the literature for determination of RE

<table>
<thead>
<tr>
<th>Analytical technique</th>
<th>Sample matrix</th>
<th>LDR(^a) (μg ml^{-1})</th>
<th>LOD(^b) (μg ml^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPLC</td>
<td>Human plasma, urine</td>
<td>0.00–10.0</td>
<td>0.5</td>
<td>19</td>
</tr>
<tr>
<td>HPLC</td>
<td>Spiked cosmetic samples</td>
<td>Data are not available</td>
<td>0.95</td>
<td>20</td>
</tr>
<tr>
<td>Kinetic spectrophotometry</td>
<td>Cream</td>
<td>0.50–3.00</td>
<td>0.38</td>
<td>21</td>
</tr>
<tr>
<td>Spectrophotometry</td>
<td>Resorcinol lotion, salicylic acid liniment, Pyriamning tincture</td>
<td>0.52–17.9</td>
<td>0.31</td>
<td>22</td>
</tr>
<tr>
<td>Spectrophotometry–chemometrics</td>
<td>Air</td>
<td>0.05–0.6</td>
<td>Data are not available</td>
<td>14</td>
</tr>
<tr>
<td>Kinetic spectrophotometry</td>
<td>Cream</td>
<td>0.50–4.50</td>
<td>0.20</td>
<td>23</td>
</tr>
<tr>
<td>Electrochemical modified GCE(^c)</td>
<td>Spiked local tap water, river water, lake water</td>
<td>0.11–60.5</td>
<td>0.08</td>
<td>13</td>
</tr>
<tr>
<td>Proposed method</td>
<td>Anti-acne solution, spiked shampoo sample</td>
<td>0.22–1.21</td>
<td>0.13</td>
<td>This work</td>
</tr>
</tbody>
</table>

\( ^{a}\) Linear dynamic range (LDR). \(^{b}\) Limit of detection (LOD). \(^{c}\) Glassy carbon electrode (GCE).
variety of methods reported recently in the literature for the
determination of RE (Table 5).

Acknowledgements

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References

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