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Determination of ascorbic acid by modified method based on photoluminescence of silver nanoparticles

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Abstract: In the present research silver nanoparticles colloid were produced by chemical reduction of silver nitrate solution, by trisodium citrate and ascorbic acid as a reductant. The obtained nanoparticles were characterized by the photoluminescence spectra and scanning electron microscopy (SEM). The morphology of silver nanoparticles that obtained consists of a mixture spheres. The photoemission properties of silver nanoparticles are found to be sensitive to ascorbic acid concentration. The photoluminescence intensity is observed by increasing in ascorbic acid concentration. The method has been successfully applied to the determination of ascorbic acid in fruit juice samples with satisfactory results.

Keywords: Ascorbic acid; Silver nanoparticles; Photoluminescence.

1. Introduction

Impact of metal nanoparticles encourages us to produce them with well-controlled sizes and shapes for fine-tuning their applications. It has been established that the optical and magnetic properties of a metal nanoparticles are highly dependent to the size and shape of the structure [1-3]. Silver has been one of the most studied materials for nanoparticles because of its performance in applications. superior Silver nanoparticles was synthesized with a range of different shapes, such as spheres, discs, rods, wires, stars, prisms, right bipyramids, and cubes [4-6], widely has been applied in selective coating for solar energy absorption [8-9], catalysis in chemical reactions [10], surface enhanced raman scattering (SERS) imaging [11], antimicrobial sterilization [12-14] and as

antimicrobial to decrease toxicity toward mammalian cells [15].

UV–Vis absorption spectroscopy is the most widely used method for characterizing the optical properties and electronic structures of nanoparticles, so absorption bands are related to the diameter and aspect ratio of metal and semiconductor nanoparticles [16]. Silver and gold nanoparticles with unique optical properties [17], especially dispersed in liquid media, display very intense colors due to surface plasmon resonance. SPR can be attributed to the collective oscillation of conduction electrons induced by an electromagnetic field [18]. Silver nanoparticles with high efficiency of absorption in UV-Vis, are very sensitive to the particle size and their aggregation state, has strong surface plasmon resonance [19-20]. The SPR depend on the particle size, shape [21], dielectric properties [22], aggregate morphology [23], surface modification and refractive index of the surrounding medium. The SPR has been explored for use in fabricating optical filters [25], photon energy transport devices [26], probes for scanning near-field optical microscopy [27], active surfaces for surface-enhanced raman spectroscopy [28], fluorescence scattering [29], and chemical or biological sensors [30]. The most commonly employed method for the preparation of metal nanoparticles is chemical reduction. In this paper silver nanoparticles were prepared by ascorbic acid as a reductant according to equation. 1 and the interaction were studied by luminescence spectroscopy. The nanoparticles were characterized and identified by SEM and interaction signal was investigated by photoluminescence (PL).

2. Experimental

2.1. Preparation of silver nanoparticles

Silver nitrate AgNO₃ (Merck), trisodium citrate $C_6H_5O_7Na_3$ (Merck) and ascorbic acid $C_6H_8O_6$ (Merck) of analytical grade purity, were used as received without further purification. The silver colloid was prepared by using chemical reduction method based on the reduction of silver salt by trisodium citrate and ascorbic acid according to the described procedure [31]. In 250 mL deionized water, 45mg silver nitrate was dissolved and 10 mL of a 1 % (w/v) trisodium citrate aqueous solution was added drop by drop and solution was mixed vigorously. Then 0.2 mL of 0.005 M ascorbic acid was added into the solution and mixed

vigorously for 10 min till a yellow-green silver nanoparticles colloid was formed according to following equation [31]

$$4Ag^{\dagger} + C_{6}H_{5}Q_{N}q + 2H_{2}O \rightarrow 4Ag^{\theta} + C_{6}H_{5}Q_{H_{3}} + 3Na^{\dagger} + H^{+} + Q^{\uparrow}$$
......(1)

For studying the influence of ascorbic acid on the photoluminescence properties, colloids consisting of different particle size were prepared by adding 0.1, 0.2, 0.3, 0.4 and 0.5 mL of ascorbic acid 5×10^{-2} M to the silver nitrate solution. The resultant Ag sols are found to be highly stable without precipitation or change in color.

2. 2. Instrumentation

Morphology of silver nanostructures was investigated with Jeol-Jem 1011 scanning electron microscope (SEM) operating at an accelerating voltage of 40 kV (Fig. 1). For SEM measurement a drop of the synthesized colloidal sample is deposited and dried on an aluminum grid. The photoemission studies of colloidal solution were evaluated with Perkin Elmer luminescence LS-50 spectrometer in a 1 cm optical path quartz cuvette. In order to obtain high and maximum luminescence signal in aqueous sample the influence of emission and excitation site was examined that the best operation condition was set as 5 nm and 2.5 nm for emission and excitation, respectively.



Fig.1. A SEM image of the spherical silver nanoparticles.



Fig.2. Emission spectra of the silver nanoparticles prepared via reduction of silver nitrate3 in different pH.



Fig.3 Emission spectra of the silver nanoparticles prepared Via reduction of silver nitrate with different volume of trisodium citrate.



Fig.4 Emission spectra of the silver nanoparticles prepared via reduction of silver nitrate

3. Results and discussion

All the prepared colloids are found to be photoluminescent and the influence of citrate concentration photoluminescence on the (PL) properties of Ag nanoparticles was studied. The synthesized colloidal silver nanoparticles of different sizes were found to be photoluminescent. It is observed that the photoemission wavelength is independent of the particle size while the intensity increases sharply with decrease of particle size. This visible luminescence of AgNPs is due to excitation of electrons from occupied bands into states above the Fermi level. Subsequent electron-phonon and holephonon scattering process leads to an energy loss and finally photoluminescent radiative recombination of an electron from an occupied band with the hole [32, 33]. The intensity of photoluminescence peak is increased with increase in ascorbic acid quantity. The emission peak of all the colloids is observed to be at 332 nm, Zhao et al [34].

3.1 Effect of pH value

It is shown in equation 2 that by ascorbic acid oxidation, H^+ was produced. Therefore pH strongly influences on sensitivity in this regard and by increasing pH, the A.A oxidation and sensitivity will increase significantly. pH also is one the most important factors that influence on the oxidation of ascorbic acid and strongly influence on the precipitation of silver nanoparticles. The influence of the pH on the method sensitivity in the range of 3-9 was investigated and results are presented in Fig. 2. At pHs higher than 9 due to silver precipitation as Ag(OH) and formation of a yellow color in solution accuracy was destroyed. Therefore, pH 7.0 was selected for subsequent work.

3.2 Effect of Trisodium Citrate Concentration

Sodium citrate efficiently hindered particles aggregation and make them stable. In the absence of this reagent due to silver precipitation a dark color appears in the reaction. Citrate ion significantly influence on the reduction of silver and ratio of crystal growth. The stable position of absorbance peak indicates that new particles do not aggregate. Since the silver colloidal particles possessed a negative charge due to the adsorbed citrate ions, a repulsive force occurred along particles and prevented aggregation [3]. To understand the role of trisodium citrate concentrations, the reduction reaction was carried out by varying volume of trisodium citrate of 1 % (w/v) in the range of 2-16 mL at 0.09 mM of silver nitrate concentration and ascorbic acid 0.184 mM [10] and results are presented in Fig. 3. As it is shown by

increasing citrate concentration till 10 mL the sensitivity will increase and further addition has not significant influence on the sensitivity, with increasing the trisodium citrate concentrations, the particle size do not changes remarkably (the particle diameter ranges from 60 to 80 nm).

3.3 Effect of Silver nitrate Concentration

In the formation of silver nanoparticles by the chemical reduction method, the order of reactant addition is important to obtain stable silver nanoparticles [16]. There are four different orders [35] for addition of reactants:

- a) A.A_AgNO₃ and sodioum citrate
- b) AgNO₃_sodioum citrate and A.A
- c) sodioum citrate_ $AgNO_3$ and A.A
- d) sodioum citrate_A.A and $AgNO_3$

Fig. 4 shows the emission of colloidal silver nanoparticles prepared with different initial silver nitrate concentrations (0.5-1.2 μ g mL⁻¹). As its shown increasing the silver concentration, increases the absorbance and that's because of creating more nanoparticles. But if we continue this procedure the absorbance decreases because of precipitating excess silver. Thus the suitable silver concentration is 0.9 mM. In other word citrate concentration is not enough for covering all nanoparticles so they grow and eventually precipitate.

3.4 Effect of reaction temperature

The temperature at which the reaction is carried out is an important factor. It was observed that by increasing temperatures above room temperature, the monodispersity and stability of the particles is increased. There are a number of possible reasons explaing this fact. Citrate is known to reduce gold and silver at elevated temperatures [35]. The proposed procedure is superior to other research that nanoparticles are formed at room temperature [2] due to simultaneous presence of citrate and ascorbic acid as reductant and stabilizing agents. Luminescence measurements have shown that size of the nanoparticles in colloid doesn't change, but with time the concentration slowly increases [3].

3.5 .Figure of merit

Variation of photoluminescence intensity with quantity of ascorbic acid is shown in Fig .5. There is a linear relationship between ascorbic acid amount and photoluminescence intensity. It is observed that there is an enhancement in the luminescence intensity with addition of ascorbic acid.

3.6. Linear ranges, detection limits and precision

The linear range of quantitative detection for ascorbic acid was determined to 0.005-0.267 mM with a detection limit of 0.0006 mM (3σ) from the curve y = 2.681x + 0.030 (n=8, R²=0.998). In this paper, there isn't a quenching point in luminescence spectroscopy but in concentration up 0.267 mM of ascorbic acid the intensity of luminescence was constant.

Calibration equation	\mathbf{R}^2	$\mathbf{S}_{\mathbf{bl}}$	RSD (%)
y = 1804.x + 1.907	0/999	0/0006	1.24

3.7 Interference study

assess the validity of the method, То interferences caused by those foreign species that are commonly found with ascorbic acid in the samples analyzed were studied by adding different amounts of other species to a solution containing 1×10^{-5} M ascorbic acid the tolerance limit was fixed, as the maximum amount causing an error in the absorbance < ± 5 % (Table. 1) common ions such as Na⁺, k⁺, Cl⁻, NO₃, $H_2PO_4^-$, HPO_4^{2-} , CO_3^{2-} and SO_4^{2-} did not show interference with AA detection. As for the common interference in biological samples for the

determination of AA, a 50-fold concentration of dopamine, vitamin B_6 , tyrosine, and cysteine had no effective interference with the current response of AA. Many amino acids did not interfered in concentration up to at Least 500-fold excess. Suggesting that this proposed method has good selectivity toward determination of AA.

3.8 Application of the method

The applicability of proposed method was checked by analyzing of fruit juice samples. After suitable dilution to fit the concentration of the analyze within the liner calibration range, the samples were taken for analysis with the luminescence procedure for validation. The results are summarized in table. 2. In all cases, the results obtained by the proposed method were in good agreement with the labeled amount. The accuracy of the proposed method was further checked by adding known amount of AA (0.050 - 0.1 mM) to the previously analyzed samples. The RSD of five parallel detection for each sample is less than 4% for these results, it can be seen that the SPR shows good catalytic activity for pharmaceutical sample analysis and that the obtained results and recoveries were satisfactory.

Table. 1: Tolerance limits for various species in the determination of 1×10⁻⁵ M of AA.

Interferent	Tolerance limit (mg L ⁻¹)	
$Na^{+}, K^{+}, Cl^{-}, No_{3}^{-}, H_{2} PO_{4}^{-}, HPO_{3}^{2^{-}}, CO_{3}^{2^{-}}, SO_{4}^{2^{-}}$	50	
Dopamine, vitamin B_6 , tyrosine, cysteine	100	
Amino acids	881	

Table 2 : Determination of ascorbic acid in some real samples

Samples No.	Added (µM)	Found ^a (µM)	Recovery (%)	RSD (%)
l	0.00	0.15	-	-
	0.05	0.21	107	1.21
	0.10	0.26	107	1.11
2	0.00	0.17		-
	0.05	0.22	100	0.85
	0.10	0.26	94	1.32
3	0.00	0.11	_	-
	0.05	0.16	100	1.10
	0.10	0.20	91	1.70

^aMean standard deviation (n=5)



Fig .5. Variation of luminescence intensity with quantity of a ascorbic acid in wavelength 299nm.

Conclusions

This proposed method is a simple, Sensitive and rapid approach for determining ascorbic acid in real samples such as fruit juices with promising results. Luminscence method suitable for laboratory routine

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control and can be carried out directly without any pretreatment of the samples.

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