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MATERIALS CHEMISTRY | RESEARCH ARTICLE

Sensitive spectrophotometric determination of ascorbic acid in drugs and foods using surface plasmon resonance band of silver nanoparticles

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Abstract: A simple and sensitive procedure was proposed for spectrophotometric determination of ascorbic acid. It was found that the reduction of Ag^+ to silver nanoparticles (Ag-NPs) by ascorbic acid in the presence of polyvinylpyrrolidone (PVP) as a stabilizing agent produce very intense surface plasmon resonance peak of Ag-NPs. The plasmon absorbance of the Ag-NPs at λ = 440 nm allows the quantitative spectrophotometric detection of the ascorbic acid. The calibration curve was linear with concentration of ascorbic acid in the range of 0.5–60 μM. The detection limit was obtained as 0.08 μM. The influence of potential interfering substances on the determination of ascorbic acid was studied. The proposed method was successfully applied for the determination of ascorbic acid in some powdered drink mixtures, commercial orange juice, natural orange juice, vitamin C injection, effervescent tablet, and multivitamin tablet.

Subjects: Environment & Agriculture; Food Science & Technology; Medicine, Dentistry, Nursing & Allied Health

Keywords: ascorbic acid; food and pharmaceutical samples; silver nanoparticle

1. Introduction

Ascorbic acid or vitamin C (Scheme 1) is an essential nutrient for health maintenance. It is used to treat scurvy, and its possible role in cancer prevention is being studied. It is also needed to maintain the health of skin, cartilage, teeth, bone, and blood vessels.

Nearly all species of animals synthesize ascorbic acid and do not require it in their diets, but humans cannot synthesize the vitamin. Fresh fruits, in particular citrus fruit and vegetables (Khan, Rahman, Islam, & Begum, 2006), constitute the principle source of vitamin in most human diets.

It is an antimicrobial and antioxidant in foodstuffs. Therefore, food products are well accepted by the consumer when a high content of vitamin C is indicated. It is also necessary for the synthesis of a number of hormones, neurotransmitters, and other compounds, such as bile acids and DNA

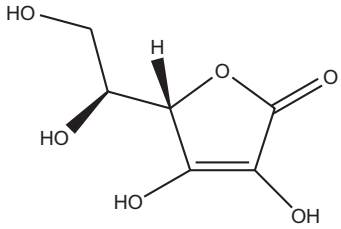
ABOUT THE AUTHOR

My main research activity is analysis of compounds using electrochemical or spectrophotometric methods. In most of my research works, nanoparticles were applied. However, I also use the different chemometrics methods for determination or prediction purposes.

PUBLIC INTEREST STATEMENT

Ascorbic acid or vitamin C is an essential nutrient for health maintenance. It is used to treat scurvy, and its possible role in cancer prevention is being studied. It is an antimicrobial and antioxidant in foodstuffs. Therefore determination of ascorbic acid is very important. In this work, a sensitive, simple and rapid method for determination of ascorbic acid is suggested.

Scheme 1. Molecular structure of ascorbic acid.



(Grahovac, Mitić, Pecev, Pecev, & Pavlović, 2008). The presence of ascorbic acid can cause changes in the chemical and sensory characteristics of the food, such as pH, total acidity, etc. Hence it is important doing an adequate control and quantification of ascorbic acid to verify the authenticity and quality of the fruits used in food manufacturing. Also, such analysis makes it possible to evaluate the degree of maturity and possible microbiological alteration during storage.

Analytical methods such as titrimetry (Sigmann & Wheeler, 2004), spectrophotometry (Abdelmageed, Khashaba, Askal, Saleh, & Refaat, 1995; Ferreira et al., 1997; Güçlü, Sözgen, Tütem, Özyürek, & Apak, 2005; Nejati-Yazdinejad, 2007; Zarei, Atabati, & Karimian, 2007, 2008), chromatography (Iwase & Ono, 1994), electrochemical (Wu, Suls, & Sansen, 2000; Zen, Tsai, & Yang, 2002), and kinetic (Ensafi, Rezaei, & Movahedinia, 2002; Safavi & Fotouhi, 1994) methods have been used in the determination of ascorbic acid. Among these methods, spectrophotometric methods are very simple and low cost, but some of them have low sensitivity. Therefore, a sensitive, simple, and low-cost spectrophotometric method is required in real samples, such as foods and drugs.

Nanoparticles made of silver and gold have been the focus of research for many decades as a result of their intriguing optical properties (El-Sayed, 2001; Sun & Xia, 2003; Templeton, Wuelfing, & Murray, 1999). When these nanoparticles have been dispersed in liquid media, they exhibit a strong UV–vis extinction band. This extinction band is resulted when the incident photon frequency is resonant with the collective excitation of the conduction electrons and is known as the surface plasmon resonance (SPR) (McFarland & Van Duyne, 2003; Tashkhourian, Hormozi-Nezhad, & Khodaveisi, 2011). SPR excitation results in wavelength-selective absorption with extremely large molar extinction coefficients (~3×10^{11} M^{-1} cm^{-1}), which allows higher sensitivity in optical detection methods than conventional reagents. The SPR depend on the particle size, shape (Kelly, Coronado, Zhao, & Schatz, 2002), dielectric properties (Oldenburg, Averitt, Westcott, & Halas, 1998), aggregate morphology (Novak, Nickerson, Franzen, & Feldheim, 2001), surface modification, and refractive index of the surrounding medium.

Recently, the colorimetric nanoprobes have been applied for sensitive and selective detection of some substances such as proteins (Wei, Li, Li, Wang, & Dong, 2007), thiol containing amino acids (Zhang et al., 2002), and neurotransmitters (Baron, Zayats, & Willner, 2005).

In this work, a sensitive, simple, and rapid method for determination of ascorbic acid is suggested. The method is based on the reaction of ascorbic acid with the oxidizing agent (silver nitrate) in the presence of polyvinylpyrrolidone (PVP) and a slightly basic medium. In this condition, silver nanoparticles are formed. The reaction is monitored at maximum wavelength of silver nanoparticles (440 nm).

2. Experimental

2.1. Apparatus

The UV–vis absorbance digitized spectra were recorded on a PerkinElmer (Lambda25) spectrophotometer and a 1.0 cm glass cell was used. Measurement pH was made with a metrohm model 827 pH meter equipped with a Metrohm glass electrode.

2.2. Chemicals and reagents

All solutions were prepared with double distilled water. Chemicals used were of the analytical grade and were purchased from E. Merck. Ascorbic acid, Robinson buffer, silver nitrate, and polyvinylpyrrolidone (PVP) by average mol. wt. 10,000 were used without further purification. A stock solution of $AgNO_3$ (0.01 mol L^{-1}) was prepared by dissolving 0.085 g $AgNO_3$ in deionized water and diluting to 50 mL. For preparation of Polyvinylpyrrolidone (PVP) (0.4 g L^{-1}) solution, daily 0.02 g of PVP was dissolved in water and diluting to 50 mL volumetric flask. Fresh 8×10^{-4} mol L^{-1} ascorbic acid was prepared daily by dissolving appropriate amounts of reagent in deionized water. Robinson buffer solution (0.04 mol L^{-1}) was also prepared (Lurie, 1978).

2.3. General procedure

1 mL PVP, 1 mL Robinson buffer pH 9.5, appropriate volumes of the ascorbic acid and 1 mL $AgNO_3$ were transferred to 10 mL volumetric flask, and diluted with water. Then it was mixed and transferred into 1 cm spectrophotometric cell to record the absorbance at 440 nm, that is λ_{max} of silver nanoparticles SPR band. It should be noted that the order of the addition of the reagents is very important. The blank solution was also prepared as above solution without ascorbic acid addition and the absorbance measurements were made for each sample solution against blank solution.

3. Result and discussion

The system in this study consists of polyvinylpyrrolidone (PVP) as stabilizer and aqueous $AgNO_3$ solution in a slightly alkaline medium. The silver nanoparticles was prepared by using chemical reduction method based on the reduction of silver salt by ascorbic acid (Fang, Zhong, & Mu, 2005). Maximum SPR intensity and wavelength represents an absorption band at 440 nm. Figure 1 shows the absorption spectra of the Ag nanoparticles plasmon that was produced by the analyte against the blank reagent.

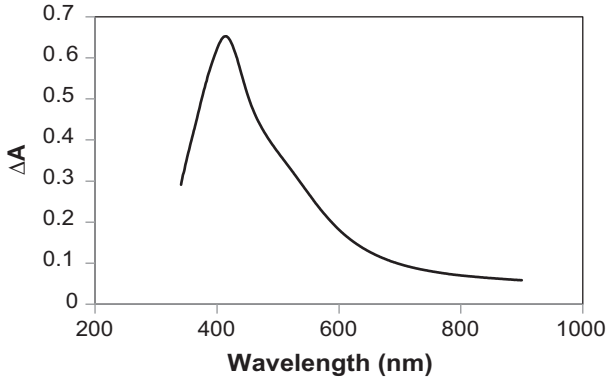


Figure 1. Absorbance spectra of Ag-NPs formed by ascorbic acid against the blank reagent.

Notes: pH 9.5, ascorbic acid 35.0 μM, PVP 0.04 g L^{-1}, 0.001 M $AgNO_3$ and temperature 25°C.

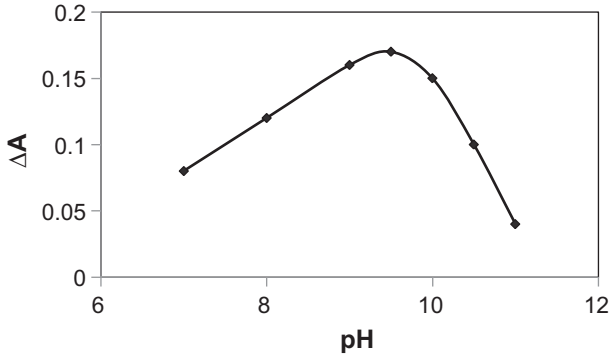


Figure 2. Effect of pH on the absorbance.

Notes: Ascorbic acid 7.0 μM, PVP 0.04 g L^{-1}, 0.001 M $AgNO_3$, reaction time 10 min, temperature 25°C.

3.1. Optimization of experimental variables

In order to find out the maximum sensitivity, the influences of parameters such as pH, PVP, and $AgNO_3$ concentrations, temperature, and reaction time were investigated on the absorbance value.

pH is a very important factor because it influences on oxidation of ascorbic acid and on precipitation of silver nanoparticles. In order to determine optimum pH, the effect of pH on absorbance was examined in the range 7–11. Figure 2 shows the effect of pH on silver nanoparticles SPR peak intensity. Since oxidation of ascorbic acid in basic medium is more comfortable than acidic medium, production of AgNPs increases with increasing pH and also average size of the silver nanoparticles decreased as pH of the reaction system increased and smaller AgNPs are led to higher absorbance and therefore higher sensitivity (Qin et al., 2010). At pH > 9.5, the amount of absorbance decreased, this might be due to Ag_2O formation. At pH > 11, the oxidation of ascorbic acid by O_2 is rapid (Farajzadeh & Nagizadeh, 2003).

As it is shown, the maximum sensitivity in absorbance occurs at pH 9.5, therefore, this amount was selected as optimum.

The PVP concentration effect on the absorbance of silver nanoparticles was studied in the range (0–0.1 g L^{-1}). Maximum intensity was obtained at 0.06 g L^{-1} of PVP.

In order to find optimum concentration of silver nitrate, different concentrations of $AgNO_3$ between 0.1 and 1.5 mM were examined. Maximum sensitivity is obtained at silver nitrate concentration of 1.0 mM as it was shown in Figure 3. Therefore, a concentration of 1.0 mM silver nitrate was selected.

The effect of reaction time was also investigated. For all of the ascorbic acid concentrations in the studied range, the absorbance was constant after 13 min (Figure 4). Therefore, the absorbance was determined 13 min after addition of silver nitrate.

The optimum temperature was also obtained as 25°C.

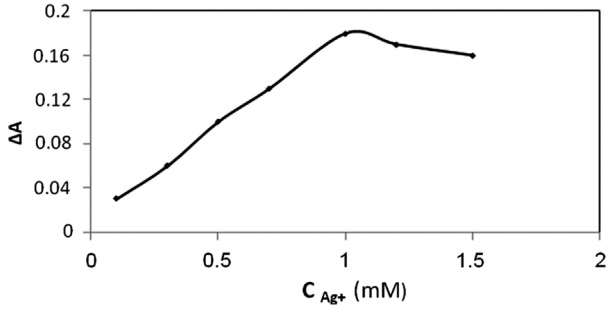


Figure 3. The effect of concentration of $AgNO_3$ on silver nanoparticles absorbtion.

Notes: pH 9.5, PVP (0.06 g L^{-1}), ascorbic acid 8.0 μM, reaction time 10 min, temperature 25°C.

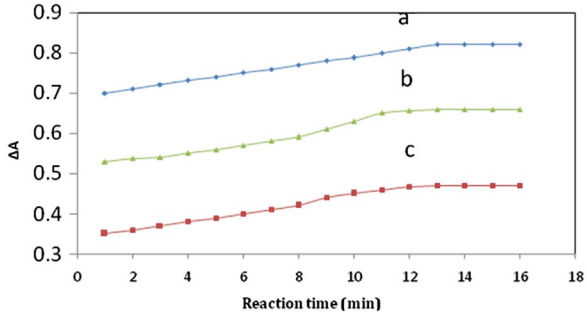


Figure 4. Plot absorbance differences versus time reaction.

Notes: pH 9.5, PVP (0.06 g L^{-1}), $AgNO_3$ (0.001 M), temperature 25°C and ascorbic acid 43.0 μM (a), 35.0 μM (b) and 23.0 μM (c).

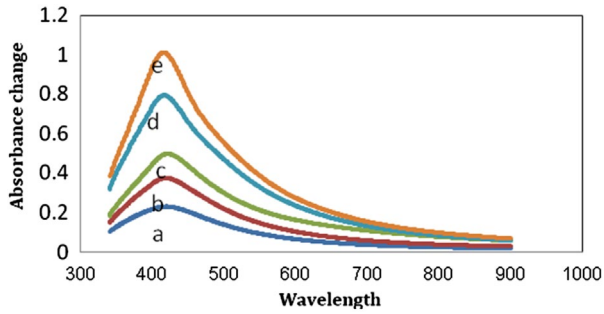


Figure 5. Absorbance spectra of Ag-NPs in different concentration ascorbic acid.

Notes: pH 9.5, PVP 0.06 g L^{-1}, $AgNO_3$ 0.001 M, temperature 25°C, reaction time 13 min, ascorbic acid 11.0 (a), 22.0 (b), 24.0 (c), 38.0 (d) and 47.0 μM (e).

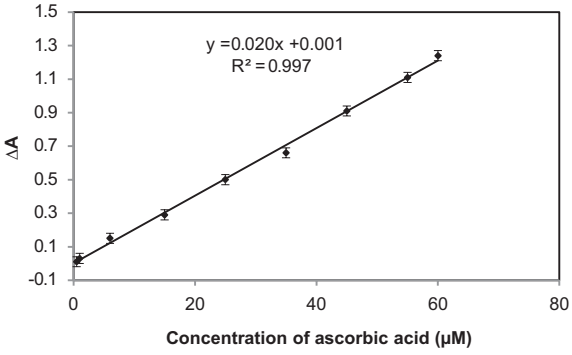


Figure 6. Calibration curve.

Notes: pH 9.5, PVP 0.06 g L^{-1}, $AgNO_3$ 0.001 M, temperature 25°C, reaction time 13 min.

3.2. Linear dynamic range, detection limit, and precision

The absorbance values were increased with increasing ascorbic acid concentration (Figure 5).

Under the optimum conditions, the calibration curve for ascorbic acid was linear in range 0.5–60 μM (Figure 6).

The detection limit of this method was obtained as 0.08 μM ($C_{LOD} = 3S_b/m$, where S_b is the standard deviation for 10 replicates determination of the blank and m is calibration curve slope). Limit of quantification ($C_{LOQ} = 10S_b/m$) was determined as 0.27 μM. Relative standard deviations (RSD) for 25.0 and 35.0 μM ascorbic acid concentration were obtained as 3.6 and 4.2%, respectively.

3.3. Interference study

The effects of some foreign species, such as cations, anions, drugs, and acids, were examined on the determination of 2×10^{-4} M ascorbic acid with the optimized conditions described above and the results are given in Table 1. The tolerance limit is defined as foreign-ion concentration causing an error smaller than 5.0%. The results show high selectivity for this method.

Interference species such as Cl^-, Br^-, I^-, F^- were eliminated by anionic exchange resin at pH value that ascorbic acid was in the non-ionized form.

Table 1. Tolerable concentration of the various substances in determination of AA by the proposed method

Substance	Tolerable concentration (mgL^{-1})
Na^+, K^+,Al^{3+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Ba^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, IO_3^-, $C_2O_4^{2-}$, citric acid, folic acid, piridoxine, glocose, boric acid, biotine, nicotinic acid	100
Cl^-, Br^-, I^-, F^-	
Riboflavine	60
Tartaric acid, maleic acid, oxalic acid	30

Table 2. Determination of ascorbic acid in several real sample solution (n = 3)

Compounds	Added (M)	AA found (M)	Standard method	Recovery (%)
Multivitamin tablet	0	$(1.1 \pm 0.6) \times 10^{-5}$	$(1.0 \pm 0.3) \times 10^{-5}$	–
	1.0×10^{-5}	$(2.1 \pm 0.3) \times 10^{-5}$		100
	2.0×10^{-5}	$(3.2 \pm 0.4) \times 10^{-5}$		105
	3.0×10^{-5}	$(3.9 \pm 0.4) \times 10^{-5}$		93
Effervescent tablet	0	$(1.1 \pm 0.2) \times 10^{-5}$	$(1.0 \pm 0.5) \times 10^{-5}$	–
	1.0×10^{-5}	$(2.2 \pm 0.6) \times 10^{-5}$		110
	2.0×10^{-5}	$(3.1 \pm 0.4) \times 10^{-5}$		100
	3.0×10^{-5}	$(4.0 \pm 0.5) \times 10^{-5}$		96
Vitamin C injection	0	$(1.3 \pm 0.5) \times 10^{-5}$	$(1.2 \pm 0.5) \times 10^{-5}$	–
	1.0×10^{-5}	$(2.2 \pm 0.4) \times 10^{-5}$		90
	2.0×10^{-5}	$(3.3 \pm 0.4) \times 10^{-5}$		100
	3.0×10^{-5}	$(4.5 \pm 0.3) \times 10^{-5}$		106
Natural orange juice	0	$(2.3 \pm 0.8) \times 10^{-6}$	$(2.4 \pm 0.1) \times 10^{-6}$	–
	2.9×10^{-6}	$(5.2 \pm 0.1) \times 10^{-6}$		100
	8.0×10^{-6}	$(10.5 \pm 0.9) \times 10^{-6}$		102
	14.5×10^{-6}	$(16.3 \pm 0.6) \times 10^{-6}$		96
Orange syrup powdered	0	$(1.3 \pm 0.2) \times 10^{-5}$	$(1.2 \pm 0.2) \times 10^{-5}$	–
	1.0×10^{-5}	$(2.3 \pm 0.6) \times 10^{-5}$		100
	2.0×10^{-5}	$(3.4 \pm 0.4) \times 10^{-5}$		105
	3.0×10^{-5}	$(4.1 \pm 0.5) \times 10^{-5}$		93
Commercial orange liquid	0	$(1.4 \pm 0.3) \times 10^{-5}$	$(1.5 \pm 0.5) \times 10^{-5}$	–
	1.0×10^{-5}	$(2.4 \pm 0.2) \times 10^{-5}$		100
	2.0×10^{-5}	$(3.5 \pm 0.3) \times 10^{-5}$		105
	3.0×10^{-5}	$(4.2 \pm 0.3) \times 10^{-5}$		93

3.4. Application of the method

The present method was successfully applied to determination of ascorbic acid in food and pharmaceutical samples. The samples were multivitamin tablet, effervescent tablet, vitamin C injection, natural orange juice, orange syrup powdered and commercial orange liquid. To this purpose, initially, the samples were dissolved in water and then filtered. After suitable dilution to fit the concentration of the analyte within the liner calibration range, the samples were taken for analysis with the SPR procedure using standard addition method. In addition to above procedure, natural orange juice was treated by anionic exchange resin to delete anionic interferences. The results are shown in Table 2. The good agreement between these results and standard method (Sigmann & Wheeler, 2004) results indicates the successful applicability of the proposed models for determination of ascorbic acid in real samples.

4. Conclusion

The proposed method is based on the reaction of $AgNO_3$ by ascorbic acid in present PVP and slightly basic medium to prepare silver nanoparticles. This method is simple, selective, rapid, and sensitive. Using the optimized technique, ascorbic acid was determined in pharmaceutical preparations and foods. The comparison of the results found in the present study and some recent studies using different methods (Habibi, Jahanbakhshi, & Pournaghi-Azar, 2011; Shahrokhian & Asadian, 2010; Wang, Xie, & Hu, 2007; Zenki, Tanishita, & Yokoyama, 2004) is given in Table 3.

Table 3. Comparison of various methods proposed for determination of ascorbic acid

Methods	Liner ranges	Detection limit	RSD (%)	Reference
SWCNT/CCE	5.0–700 μM	3.00 μM	3.5	Habibi et al. (2011)
FIA	0.2–30 mg L^{-1}	0.04 mg L^{-1}	1.2	Zenki et al. (2004)
MWCNT/CPE	1–100 μM	0.80 μM		Shahrokhian and Asadian (2010)
Carbon-coated Ni nanoparticles	140–1300 μM	41.0 μM		Wang et al. (2007)
SPR	0.5–60 μM	0.08 μM		This method

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