International Journal of Scientific Research in Chemistry (IJSRCH)
© 2021 IJSRCH | Volume 6 | Issue 6 | ISSN : 2456-8457

Spectrophotometric Determination of L-Ascorbic Acid Based on its Oxidation by Potassium Peroxymonosulfate in an Acidic Medium

Halid Junuzović*[1], Mirsad Salkić[1], Amra Selimović[1], Mersiha Suljkanović[2]
*[1]Department of Analytical chemistry, University of Tuzla/Faculty of Technology, Tuzla, Bosnia and Herzegovina
[2]Department of Analytical chemistry, University of Tuzla/Faculty of Natural Sciences and Mathematics, Tuzla, Bosnia and Herzegovina
E-Mail of Corresponding Author: halid.j@hotmail.com

Article Info
Volume 6, Issue 6
Page Number : 25-37

Publication Issue :
November-December -2021

Article History
Accepted : 01 Dec 2021
Published : 10 Dec 2021

ABSTRACT

A selective and accurate direct spectrophotometric method was developed for the determination of L-ascorbic acid in pharmaceutical preparations. Background correction was based on the oxidation of L-ascorbic acid by potassium peroxymonosulfate in an acidic medium (pH 4.00). The molar absorptivity of the proposed method was 8.77 ·103 L mol–1 cm–1 at 246 nm. Beer's law was obeyed in the concentration range of 2.37 – 20.00 μg/mL for L-ascorbic acid. The detection limit was 0.71 μg/mL, and the relative standard deviation was 0.97% (n = 7) for 12.00 μg/mL L-ascorbic acid. Other compounds commonly found in pharmaceutical preparations did not interfere with the detectiON of L-ascorbic acid. The proposed method was successfully applied to the determination of L-ascorbic acid in pharmaceuticals, and the results obtained agreed with those obtained by iodine titration.

Keywords : ascorbic acid, oxidation, peroxymonosulfate, spectrophotometry, pharmaceutical preparations

I. INTRODUCTION

L-Ascorbic acid (vitamin C) is an important vitamin having a chemical structure that justifies its classification as a carbohydrate. It is widely distributed in plant and animal tissues, and involves the metabolism of various substances in vivo. The reversible oxidation of L-ascorbic acid to dehydro-L-ascorbic acid is the basis for its physiological activities, stabilities, and technical applications. Often, vitamin C is added during the manufacture of juices or soft drinks to improve their nutritional value or to prevent the autoxidation of commercial products. Owing to the wide use of L-ascorbic acid in canned fruits, vegetables and drugs, numerous analytical techniques have been proposed for the determination of L-ascorbic acid, such as spectrophotometry [1–3], chemiluminescence [4], fluorimetry [5], capillary electrophoresis [6], voltammetry [7] and high-performance liquid chromatography [8]. Of all these techniques, spectrophotometry is, perhaps, the most commonly used.

Direct ultraviolet (UV) spectrophotometry can provide a fast, simple and reliable method for the determination of l-ascorbic acid. However, absorption of UV light by the sample matrix is a major problem with this method. Therefore, several background correction techniques such as UV light decomposition [9], enzymatic [10,11], metal catalytic oxidation [12,13], and oxidation of l-ascorbic acid by peroxodisulfate[14] have been proposed to solve this problem.

The purpose of this work was to develop a direct ultraviolet spectrophotometric method for the determination of ascorbic acid in pharmaceuticals. Background correction was based on the oxidation of L-ascorbic acid by peroxymonosulfate. The effects of some substances commonly encountered in pharmaceutical preparations were studied. The ascorbic acid contents of a number of pharmaceuticals were determined using the developed method.

II. METHODS AND MATERIAL

A. Materials

Chemicals

All reagents used were of analytical reagent grade. A buffer solution of pH 4.00 was a mixture of glacial acetic acid (0.175 mol L^{-1}) and sodium acetate (0.03 mol L^{-1}) in distilled water. An L-ascorbic acid solution ($1.13 \cdot 10^{-3}$ mol L^{-1}) was prepared by dissolving 0.05 g of L-ascorbic acid (Riedel-de Haën) in the buffer solution, and diluting to 250 mL in a volumetric flask with the buffer solution. A potassium peroxymonosulfate solution (0.043 mol L^{-1}) was prepared by dissolving 0.66 g of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (Aldrich) in 50 mL of the buffer solution. Solutions of metal ions, anions, acids, vitamins and sugars were prepared by dissolving calculated amounts of these substances in the buffer solution.

Instrumentations

A Cecil 2021 spectrophotometer (Cecil Instruments, Cambridge, UK) with 1 cm path length was used for the absorbance measurements. A Quatro 220K pH meter was used for pH measurements.

B. Methods

General procedure

An aliquot of the sample solution containing 50 – 500 μg of L-ascorbic acid was diluted to 25 mL in a volumetric flask with the buffer solution. The absorbance (A_1) of the dilute solution was measured at 246 nm using the buffer solution as a blank. Another aliquot of the sample solution was transferred into a 25 mL volumetric flask, potassium peroxymonosulfate solution (2.0 mL) was added, and then the solution was diluted to the mark with the buffer solution. The absorbance (A_2) was measured at 246 nm against a blank solution prepared by dilution of 2.0 mL of the potassium peroxymonosulfate solution to 25 mL with the buffer solution. The value $A_1 - A_2 = A$ was proportional to the ascorbic acid concentration in the sample.

To construct a calibration curve, individual aliquots of the $1.13 \cdot 10^{-3}$ mol L^{-1} ascorbic acid solution were diluted to 25 mL in volumetric flasks with the buffer solution. The absorbance values of these solutions were measured at 246 nm using the buffer solution as a blank.

Analysis of pharmaceutical preparations

Several pharmaceutical preparations in table form were crushed to powders. Accurately weighed quantities of these powders were transferred to 50 mL volumetric flasks. The powder in each flask was dissolved in the buffer solution and diluted to volume with the same solution. If the powder did not dissolve completely, the solution was filtered through a Whatman No. 42 filter paper and an aliquot of the filtrate was diluted to 50 mL in a volumetric flask with the buffer solution. The AA content for each solution was determined using the general procedure.

III.RESULTS AND DISCUSSION

Oxidation of L-ascorbic acid by peroxymonosulfate

Potassium peroxymonosulfate (also known as potassium monopersulfate) is widely used as an oxidizing agent. It is a component of a triple salt with the formula $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. The standard electrode potential of $KHSO_5$ is given by the following half cell reaction:

$$HSO_5^- + 2H^+ + 2e^- \rightarrow HSO_4^- + H_2O$$

$$E^0 = 1.85 \text{ V}$$

L-ascorbic acid (H_2A) undergoes the oxidation reaction with peroxymonosulfate in an acidic medium to yield dehydro-L-ascorbic acid (A), insensitive to ultraviolet at 246 nm. The oxidation of L-ascorbic acid usually takes place in a two-step reaction. The first step yields a relatively stable ascorbate free radical. In the second one, the L-ascorbic acid free radical donates a second electron, yielding dehydro-L-ascorbic acid:

$$H_2A \rightarrow A + 2H^+ + 2e^-$$

The stoichiometry of the reaction between peroxymonosulfate and L-ascorbic acid is represented by the following:

$$H_2A + HSO_5^- \rightarrow A + HSO_4^- + H_2O$$

Optimization of conditions

The absorption properties (λ_{max} and ε) of L-ascorbic acid are dependent on the pH of the aqueous media [15]. Because of this pH dependence, the acetic acid – sodium acetate buffer solutions were used throughout this work. Because L-ascorbic acid was unstable at pH>4.5, the effect of pH on the oxidation of ascorbic acid (20.00 μg mL^{-1}) by peroxymonosulfate was investigated over the range 3.00 – 4.00 in the presence of 2 mL of the peroxymonosulfate solution (0.043 mol L^{-1}). The results showed that ascorbic acid in the solutions at pH 3.00 and 4.00 was completely oxidized. The pH 4.00 solution was selected for subsequent analysis of ascorbic acid because of its higher absorption. The influence of the peroxymonosulfate concentration on the oxidation of L-ascorbic acid was examined by adding different volumes of a 0.043 mol L^{-1} solution of potassium peroxymonosulfate to a solution containing 20.00 μg mL^{-1} ascorbic acid in the acetate buffer (pH 4.00). Ascorbic acid was oxidized completely in the presence of 1.0 – 4.0 mL of the peroxymonosulfate solution. Although a 1 mL volume of the potassium peroxymonosulfate solution was sufficient to oxidize ascorbic acid, 2.0 mL was selected for subsequent analysis in a total volume of 25 mL.

Analytical characteristics

The calibration curve was linear up to an ascorbic acid concentration of 20.00 μg mL^{-1}.

A least-square analysis of Beer's plot gave the following linear regression equation ($n = A_{246} = -0.048 + 0.0497$ C, where A_{246} is the absorbance at 246 nm and C is the concentration of L-ascorbic acid in μg mL^{-1}. The detection limit (three times the standard error of the intercept/slope), quantification limit (ten times the standard error of the intercept/slope), molar absorptivity (ε), and other analytical characteristics are summarized in Table 1. The molar absorptivity was calculated as $8.77 \cdot 10^3$ L mol^{-1} cm^{-1} from the slope of the calibration curve. The present method is more sensitive than other spectrophotometric methods, such as those using Au (III) ions [16] ($\varepsilon = 2.30 \cdot 10^3$), peri-naphthindan-2,3,4-trione [17]

($\varepsilon = 3.18 \cdot 10^3$), the zinc chloride salt of diazotized 1-aminoanthraquinone [18] ($\varepsilon = 4.07 \cdot 10^3$), and 4-chloro-7-nitrobenzofurazane [19] ($\varepsilon = 6.49 \cdot 10^3$). The precision of the proposed method was checked by calculating the relative standard deviation for seven replicate determinations of a standard solution containing 12.00

μg mL^{-1} of L-ascorbic acid (Table 1).

Tabele 1. Analytical characteristics of the proposed method

Parameter	Value
Slope of the calibration graph	0.0497
Intercept	-0.048
Standard error of the slope	0.000893
Standard error of the intercept	0.011846
Correlation coefficient (r)	0.9995
Limit of detection	0.71 μg/mL
Limit of quantification	2.37 μg/mL
Linear dynamic range	2.37 – 20.00 μg/mL
Molar absorptivity (ε)	8.77 x 10^3 L mol^{-1} cm^{-1}
Relative standard deviation	0.97 %

Interference studies

To test the selectivity of the proposed method, other compounds that are commonly found with ascorbic acid in pharmaceutical preparations were added to the 12.00 μg mL^{-1} ascorbic acid solution. If the absorbance was 5% or more outside the expected value, then that species was defined as interfering with the determination. The results are listed in Table 2. The substances tested did not interfere with the determination of ascorbic acid at the levels studied, except nitrite. The negative error caused by nitrite may be ascribed to its oxidation of ascorbic acid in the acidic medium.

Tabele 2. Effect of other species on the determination of L-ascorbic acid.

Foreign substance added	Mass ratio (foreign substance:ascorbic acid)	Error, %
Cl^-	10	-
NO_3^-	0.04	-
SO_4^{2-}	10	-
HCO_3^-	10	-
NO_2^-	1	-30
Benzoate	2	-
Iron(II)	0.02	-
Copper(II)	0.02	-
Calcium(II)	5	-
Magnesium(II)	2	-
Manganese(II)	0.65	-
Molybdenum(VI)	0.2	-
Citric acid	20	-
B_1 (thiamine hydrochloride)	0.5	-
B_6 (pyridoxine hydrochloride)	0.5	-
Nicotinic acid	1	-
Sucrose	200	-
Glucose	200	-
Fructose	200	-

Application of the proposed method to real samples The proposed method was used to determine the L-ascorbic acid contents in commercial pharmaceutical preparations. The results are shown in Table 3. Each sample was analyzed by both the proposed method and iodine titration as a reference method [20]. The results obtained with the proposed method agreed with those obtained by the reference method. Other ingredients commonly found in vitamin C and multivitamin products, such as sodium citrate, acetylsalicylic acid, citric acid, saccharine, sodium carbonate, starch, sugars and B vitamins, did not interfere with the

determination of L-ascorbic acid using the proposed method. The precision and accuracy of the proposed method were evaluated using F- and t-tests, respectively. The t-test values were lower than the tabulated t value (t = 2.31, P = 0.05), which suggests differences between the results obtained by the two methods were statistically not significant at the 95% confidence level. The F-test revealed that there is no difference between the precision of the two methods. In every case, the calculated value of F was lower than the critical value (F = 9.60, P = 0.05). The accuracy of the proposed method was also checked by replicate analysis of the pharmaceutical preparation samples after spiking with 4.00 μg mL-1 L-ascorbic acid. The recoveries of L-ascorbic acid were between 98 and 102%, which indicates that the proposed method is accurate.

IV. CONCLUSION

The proposed method for the determination of L-ascorbic acid does not require an extraction procedure and is simple, rapid, selective and accurate. The method can be used for the determination of L-ascorbic acid in the presence of ingredients commonly found in vitamin C and multivitamin preparations. The results obtained for the determination of L-ascorbic acid in pharmaceuticals using the developed method were compared with those obtained by the reference method, and good agreement was found. Thus, the proposed method can be applied to the determination of vitamin C in commercial pharmaceutical preparations.

Tabele 3. Determination of L-ascorbic acid in pharmaceutical preparations

Commercial name (Supplier)	Ascorbic acid (mg/tablet)				
	Claimed value	Proposed method*	Iodine method*	$F_{calc.}$	$t_{calc.}$
Vitamin C (Biofar)	1000	985.03 ± 13.03	997.53 ± 10.00	1.69	2.11
Aspirin plus C (Bayer)	240	243.65 ± 4.02	240.06 ± 2.53	2.52	2.09
Multivitamin (Krüger)	60	62.43 ± 0.79	61.74 ± 0.73	1.18	1.76
Ca-C 1000 (Calvive)	1000	1011.83 ± 14.56	1001.82 ± 11.44	1.62	1.50

Theoretical value for F is 9.60 (P = 0.05) and for t is 2.31 (P = 0.05).

*The 95% confidence limits of the mean (n = 5).

V. REFERENCES

[1]. Y. Fujita, I. Mori, T. Yamaguchi, M. Hoshino, Y. Shigemura, and M. Shimano, Anal. Sci., 17, 853-857 (2001).

[2]. Y. Bazel, T. Riabukhina, and J. Tirpak, Microchem. J., 143, 160-165 (2018).

[3]. B. Szpikowska-Sroka and J. Poledniok, J. Anal. Chem., 66, 941-945 (2011).

[4]. T. Kato, O. Ohno, T. Nagoshi, Y. Ichinose, and S. Igarashi, Anal. Sci., 21, 579-581 (2005).

[5]. X. Wu, Y. Diao, C. Sun, J. Yang, Y. Wang, and S. Sun, Talanta, 59, 95-99 (2003).

[6]. B. M. C. Costa, A. A. Prado, T. C. Oliveira, L. P. Bressan, R. A. A. Munoz, A. D. Batista, J. A. F. da Silva, and E. M. Richter, Talanta, 204, 353-358 (2019).

[7]. J. B. Raoof, R. Ojani, R. Hosseinzadeh, and V. Ghasemi, Anal. Sci., 19, 1251-1258 (2003).

[8]. M. Stan, M. L. Soran, and C. Marutoiu, J. Anal. Chem., 69, 998-1002 (2014).

[9]. Y. S. Fung and S. F. Luk, Analyst 110 (1985) 201-204.

[10]. N. bin Saari, A. Osman, J. Selamat, and S. Fujita, Food Chem. 66 (1999) 57-61.

[11]. F. Tsumura, Y. Ohsako, Y. Haraguchi, H. Kumagai, H. Sakurai, and K. Ishii, J. Food Sci. 58 (1993) 619-622.

[12]. O. W. Lau, S. F. Luk, and K. S. Wong, Analyst 112 (1987) 1023-1025.

[13]. O. W. Lau, S. F. Luk, and K. S. Wong, Analyst 111 (1986) 665-670.
[14]. M. Salkić, J. Anal. Chem., 71, 153-157 (2016).
[15]. R. R. Eitenmiller and W. O. Landen, Vitamin Analysis for the Health and Food Sciences, CRC Press, USA, 1999.
[16]. T. Pal and P. K. Das, Anal. Lett., 21, 2333-2343 (1988).
[17]. S. S. M. Hassan, M. M. Abd el Fattah, and M. T. M. Zaki, Fresenius Z. Anal. Chem., 277, 369-371 (1975).
[18]. E. Y. Backheet, K. M. Emara, H. F. Askal, and G. A. Saleh, Analyst, 116, 861-865 (1991).
[19]. O. H. Abdelmageed, P. Y. Khashaba, H. F. Askal, G. A. Saleh, and I. H. Refaat, Talanta, 42, 573-579 (1995).
[20]. J. S. Fritz and G. H. Schenk, Quantitative Analytical Chemistry, Prentice Hall, New Jersey, (1987).

Cite this article as :

Halid Junuzovi, Mirsad Salkic, Amra Selimovic Mersiha Suljkanovic, "Spectrophotometric Determination of L-Ascorbic Acid Based on its Oxidation by Potassium Peroxymonosulfate in an Acidic Medium", International Journal of Scientific Research in Chemistry (IJSRCH), ISSN : 2456-8457, Volume 6 Issue 6, pp. 01-06, November-December 2021.
URL : https://ijsrch.com/IJSRCH21656