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Indirect Determination of Ascorbic Acid by Atomic Absorption Spectroscopy

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Abstract

A new and simple method followed by atomic absorption spectrometry has been developed for indirect determination of ascorbic acid (AA). The proposed method was based on the oxidation of AA to dehydroascorbic acid with Cu^{2+}cation(200mgL^{-1})in an ammonium thiocyanatesolution at pH2.4. AA reduces $Cu^{2+}$to Cu^{+}followed by the precipitation of Cu^{+} with SCN^{-}. Then, the excess of Cu^{2+}in the solution was measured by the atomic absorption spectrometry.The results showed that AA can be sensitively measured in the linear range of 2.0 to 40.0 mgL^{-1} with the detection limit of 1.5mgL^{-1}.The relative standard deviation (%RSD) was 0.319 in 7 determination of 2.0 mgL^{-1} AA. Finally, the method was successfully used for the determination of AA in tablets containing various amounts of AA.

Keywords: Ascorbic acid, indirect determination, atomic absorption spectroscopy

1. Introduction

Ascorbic acid (AA) is one of the important vitaminswhich participates in a great variety of biological events concerning electron transport reaction, hydroxylation, and the oxidative catabolism of aromatic aminoacids. Measuring the concentration of some chemical markers commonly assesses food determination and product quality: AA is one such indicator [1].

AA is considered to be essential for the development and regeneration of muscles, bones, teeth and skin. Also it has been identified as a radical scavenger in vivo. AA or vitamin C is present naturally in a wide range of foods particularly fruits and vegetables. But AA has limited stability and may be lost from foods during storage, preparation and cooking. In some foods, it is purposely added to attract consumers and to act as an antioxidant [2] to prolong the shelf-life of the commercial products. Some pharmaceutical preparations add AA to their products as a supplementary source of vitamin C in human diets [3].

The therapeutic importance of AA has prompted many researchers to develop methods for its determination in such samples as well as in pharmaceuticals [4- 6][7].So, it is very important to design a simple, selective

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and sensitive method for the determination of AA in routine analysis.Many analytical techniques are available for direct or indirect determination of AA in different matrices such as titrimetry [8], spectrophotometry [9- 11], HPLC [12,13], enzymatic methods [14], fluorimetry [15,16], various electroanalytical techniques [17,18], chemiluminiscence [19,20], kinetic methods [21], capillary zone electrophoresis and isotachophoresis [22,23].A large number of papers have been published and presented on AA quantification. This shows the importance of this compound. Some valuable articles have also been reviewed the determination of AA [24- 28].

However, indirect determination of AA has also been reported. Among various methods, the special interest is on flame atomic absorption spectrometry (FAAS) [29_ 33]. The main reason is its improved detection limits, low relative standard deviation and selectivity as well as sensitivity.

The present work describes for first time the details of the development of anindirect method for the determination of ascorbic acid with atomic absorption spectroscopy based on the oxidation of ascorbic acid with Cu^{2+} and consequently, the precipitation reaction of resulted Cu^{+} with thiocyanate. The unreacted copper is determined with FAAS without using any separation method.

2. Experimental

2.1. Apparatus

The cation absorbance was measured with a Perkin Elmer atomic absorption spectrometer model AA-800 with an air-acetylene flame and 10 cm burner. The wavelength was set to 324.0nm for $Cu^{2+}$with a spectral slit- width of 0.7 nm and a lamp current of 15 mA.

2.2. Reagents and solutions

All chemicals were of analytical reagent grade. Solutions of ammonium thiocyanate and disodium EDTA were made from purified samples in doubly distilled water.Ascorbic acid stock solution of 1000 mg L^{-1} was prepared by dissolving 0.100 g of ascorbic acid (Merck) in double distilled water in 100-mLflask and diluting to the mark. In order to analyzed real AA samples twenty tablets of vitamin C (Kruger) were weighed and ground into a fine powder. An accuratelyweighed powder equivalent to 100 mg of the active component was transferred into a 100-mLflask and dissolved in doubly distilled water and the mixture was shaken thoroughly for 5 min. Then it was mixed well anddiluted to the mark with distilled water. An aliquot of this solution was diluted appropriately to obtain the working concentrations and analyzedunder proposed procedure.

2.3. Procedure

In this method, the 5.0 mL of copper sulfate solution (200mgL^{-1})was taken in the 100-mL beaker and 5.0 mL of ammonium tiocyanate solution (1%w/v) was added. Then the pH was adjusted to 2.4with sodium hydroxide or hydrochloric acid, and then the exact known volume of ascorbic acid solution (50mgL^{-1}) was added drop wise with constant stirring and heated on a heater stirrer for 15 min (T = 70 °C). The resulted precipitate was filtered through a sinter glass porosity crucible and washedthree times with 0.1% ammonium thiocyanate solution and 20% (v/v) ethanol/water solution and diluted to 25 mL with distilled water. The amount of unreacted Cu^{2+} was determined by atomic absorption spectrophotometer at the wavelength of 324.0 nm. Hydrochloric acid was chosen for acidification of the solutions in the reaction vessel containing Cu^{2+}, SCN^{-} and AA. The various experimental parameters were optimized as well.

3. Results and discussion

Ascorbic acid (AA) is one of the natural

compounds having reducing characteristics. So, AA can be easily oxidized to dehydroascorbic acid (DHAA) by various agents. Cu (II) can oxidize AA during the following reaction:

(1)

$$2Cu(II) + AA + 2H^+ \rightarrow 2Cu(I) + DHAA + H_2O$$

The proposed method was based on the oxidation of AA with the excess amount of Cu (II) cation in hydrochloric acid medium, e.g. pH 2.4, and consequently, the precipitation reaction of resulted Cu^+ with thiocyanate" and then analysis of the unreacted copper by FAAS. It should be noted that the unreacted Cu(II) cannot precipitate with thiocyanate [34].

An increase in AA concentration causes more consumption of Cu^{2+} in the solution, so, the decrease in the measured absorbance of Cu^{2+}.The absorbance is found to be decreased linearly with increase in the concentration of AA.

3.1. Optimization of the experimental variables

A series of experiments were conducted to establish optimal analytical variables. All experimental parameters including pH, thiocyanate concentration, stirring time and temperature were optimized.

3.1.1. The influence of the amount of ammonium thiocyanate

Several aliquotsof the standard solution Cu^{2+}200 mgL^{-1} were transferred into a series of 25 mL standard flasks. Then, a volume of 5.0 mL of 50 mgL^{-1}AA solution was added to each flask followed by acidification by 2.0 mL of 0.1 $molL^{-1}$hydrochloric acid, and then different amounts of 1.0 % thiocyanate was added and the contents were diluted to the mark with distilled water and mixed well. When this solution was heated, precipitat-ion of copper (I) thiocyanate began a few minutes and was complete in 15 min. The amount of unreacted Cu^{2+} was determined by atomic absorption spectrophotometer at the wavelength of 324.0 nm.Blank was prepared similarly omitting the AA and its absorbance was measured against distilled water. The decrease in absorbance corresponding to consumed Cu^{2+} and in turn, to AA concentration, obtained by subtracting the absorbance of AA solution from the corresponding blank. The relationship between thiocyanate amount and the decrease in the measured absorbance of Cu (II) is shown in Fig. 1.

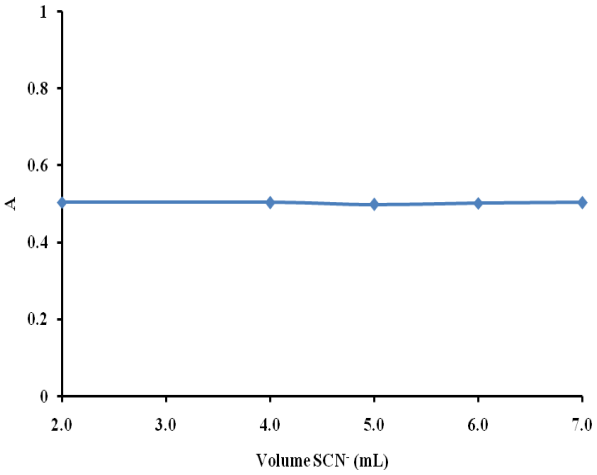

Fig. 1. Influence of the amount of ammonium thiocyanate(1.0%),[Cu (II)] = 16 mgl^{-1}, Ascorbic Acid=4.0 mgl^{-1}, Temp. =70°C, Stirring time=15.0 min, atλ_{max}=324.0 nm.

3.1.2 The effect of pH

As implies from equation (1), the reaction between Cu^{2+} and AA as well as the reduction potential of AA depends on the pH of the solution.At pH values higher than5.0, the rate of copper reduction is much decreased and the precipitation is not completed even after a long time of the reaction [34].

Based on the above reaction an acidic environment is required, care should be taken that the concentration of the acid will give optimum performance. The response of oxidation was studied by using different HCl concentrations. The effect of pH value between 1.0 and 6.47 was evaluated (Fig. 2).The analytical signal decreases as the pH increases. There was increase in absorbance,

when pH value was decreased below 2.38 to 1.0, so the pH 2.38 was chosen as optimum.

Fig. 2 shows the influence of pH on the unreacted Cu^{2+} on condition that 5.0 mL of 50.0 mg/L ascorbic acid is added.

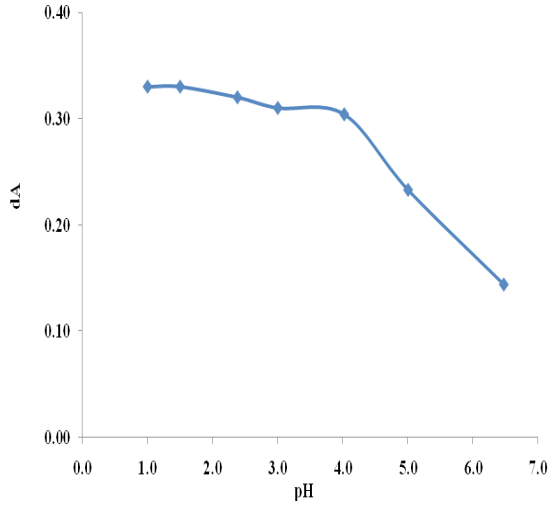

Fig. 2. Optimization of pH, at 5.0cc ammonium thiocyanate (1.0%),[Cu (II)] = 16 mgl^{-1}, Ascorbic Acid=4.0 mgl^{-1}, Temp. =70°C, Stirring time=15.0 min, atλ_{max}=324.0 nm.

3.1.3. Stirring times

Effect of stirring time was also studied. It is from the data shown in Figure 3 that the reaction is completed in 10 min, so as to ensure completion of the reaction between AA andCu^{2+}, time will choose 15 min. (Fig. 3).

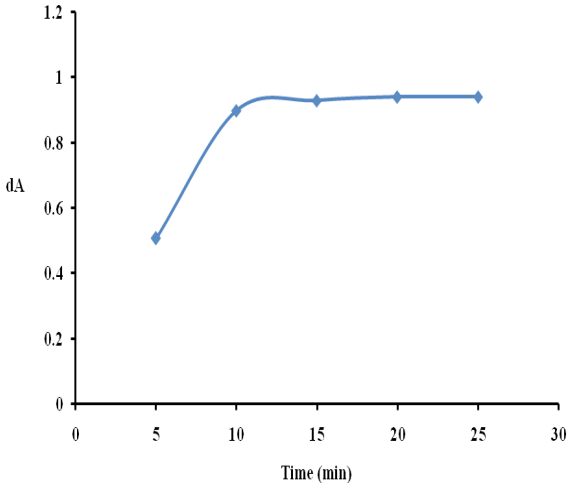

Fig. 3. Influence stirring time, at pH=2.38, 5.0cc ammonium thiocyanate (1.0%), [Cu (II)] = 16 mgl^{-1}, Ascorbic Acid=4.0 mgl^{-1}, Temp. =70°C, at λ_{max}=324.0 nm.

3.1.3. Effect of temperature

The effect of temperature on the consumption of Cu^{2+} is shown in Fig. 4.

The measured absorption of Cu^{2+}decreases with the increase in temperature. As expected, we found that at higher temperatures, the solubility of the precipitate increases, but due to the difficult work at higher temperatures of 70 ºC, this temperature to select the optimum temperature.

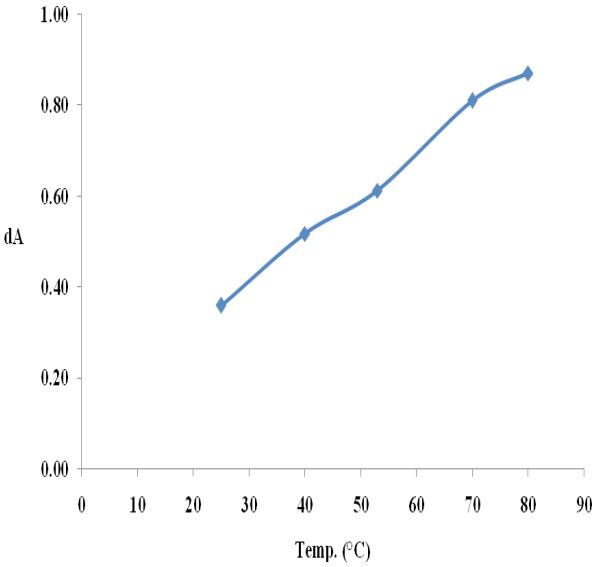

Fig. 4. The effect of temperature, at pH=2.38, 5.0cc ammonium thiocyanate (1.0%), [Cu (II)] = 16 mgl^{-1}, Ascorbic Acid=4.0 mgl^{-1},Stirring time=15.0 min, atλ_{max}=324.0 nm.

3.1.4 Calibration Curve

A calibration curve is constructed by the recommended procedure in optimum condition (Fig. 6). A good linear relationship is observed between the unreacted of Cu(II) and the added of ascorbic acid to the solution. The linear equation for the calibration graph drawn at the wavelength of 324.0 nm as described in the section 2.2 was

$$\Delta A=0.014C + 0.125$$

Where C is the part per million concentration of AA, with correlation coefficient $R^2 = 0.998$.

The calibration curve for the

determination of ascorbic acid was prepared according to the general procedure under the optimum conditions developed above (Fig. 5). The linearity was obtained in the range of 2.0-40.0 mg L^{-1} of ascorbic acid with a correlation coefficient of 0.998. The detection limit of the proposed method (calculated as 3σ) was obtained to be1.5 mgL^{-1}. The relative standard deviation of AA determination (4.0mgL^{-1}) was found to be 0.32% (n=8) (Fig. 5).

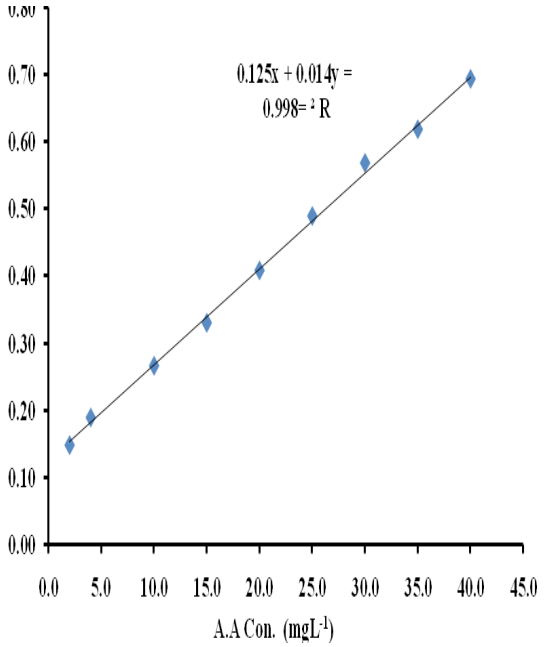

Fig. 5. Calibration curve for AA determination

3.1.5. Sample analysis

Treatments of samples Vitamin C tabletsseveral tablets of vitamin C drug are accurately weighed ground and powered. A given amount of this powder is transferred into a volumetric flask and diluted to the mark. The content of the flask is shaken for about 10 min. Then it is filtered and the first portion of the filtrate is rejected. This solution is further diluted to adjust the concentration to meet the requirement of the experimental conditions adopted.

4. Conclusions

Ascorbic acid can be analyzed at the DL 1.5µg ml^{1-} levelwhen reacting with Cu (II) with the formation of the Cu (I) –thiocyanate precipitate, and concentration and indirect measurement AA. This is a very sensitive, simple and selective one-stepmethod, suitable for laboratory routine controland can be carried out directly without any pre-treatmentof the samples.

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