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Indirect Determination of Ascorbic Acid with Ammonium Sulfate and Isopropyl Alcohol by Extraction-flotation of Copper

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Abstract: A new method of indirect determination of ascorbic acid(Vc) with ammonium sulfate and isopropyl alcohol by extraction-flotation of copper is studied in this paper. It shows that a small amount of Cu(Ⅱ) can be reduced to Cu(Ⅰ) by Vc, then Cu(Ⅰ) reacted with the SCN^-, which precipitated on the interface of isopropyl alcohol and H_2O. A good linear relationship is observed between the flotation yield(E) of Cu(Ⅱ) and the amount of Vc. The detection limit for Vc is 1.76 μg/mL. The method is simple, rapid (5 min), but suffers from little interference of common anions and cations. It has been successfully applied for the determination of Vc in fruits.

Keywords: Ascorbic acid, isopropyl alcohol, extraction and flotation.

Numerous methods have been reported for the determination of Vc taking into account its importance in human physiology, including chromatographic[1], spectrofluorimetric[2] and different electro analytical techniques[3-5], but all these results require sophisticated equipment. Spectrophotometric methods[6-8] is widely used for the determination of Vc. A new method of indirect determination of Vc with $(NH_4)_2SO_4$ and isopropyl alcohol by extraction-flotation of copper is studied in this paper. The detection limit for Vc is 1.76 μg/mL. The advantages of this method are simple, rapid and reliable. In addition, the common ions did not interfere the determination of Vc by this method. The method has been successfully applied for the determination of Vc in fruits.

Experimental

Instrument and reagents: Isopropyl alcohol, $(NH_4)_2SO_4$ and other analytical-reagent were used. A stock of standard solution of 0.1 mol/L NH_4SCN was prepared by dissolving 8 g of NH_4SCN (Tianjin Chemical Plant, Tianjin,China) in distilled water and diluting it to 1 L. Vc solution was prepared freshly by dissolving a given amount of Vc (Shanghai Chemical Plant, Shanghai, China) in newly distilled cool water. A Model 722 grating spectrophotometer (Xiamen Chemical Plant, Xiamen, China) was used.

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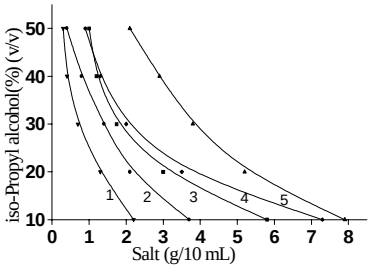
Figure 1 Phase separation conditions



Total volume: 10mL.1.Na_2CO_3; 2.$(NH_4)_2SO_4$; 3.NaCl; 4.NaH_2PO_4; 5.$NaNO_3$

Method: Add 50 μg of Cu(Ⅱ), 1.0 mL of 1×10^{-3}mol/L Vc, a given volume of sample solution of Vc and 3.0 mL of isopropyl alcohol to a 25 mL graduated color comparison tube, then adjust the pH to 3-6 with buffer solution and dilute the mixture to 10 mL. 1.5 g of solid $(NH_4)_2SO_4$ was added and the mixture was shaked for 1min then allowed it to stand for 2 min. Cu(Ⅱ) is reduced to Cu(Ⅰ) by Vc, then the Cu(Ⅰ) with SCN^- formed CuSCN, which was precipitated in the interface of isopropyl alcohol and water. Thereafter phases have separated and 1.0 mL of aqueous salt solution was taken and place it into another 25 mL graduated color comparison tube and determined the absorption of copper with spectrophotometry. Then concentration of Vc in the sample solution can be calculated.

Results and Discussion

Phase separation condition for isopropyl alcohol-water solution

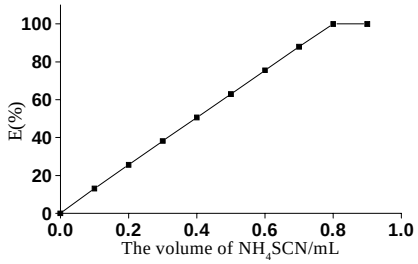
With the concentration of isopropyl alcohol fixed (30%v/v), different amounts of NaCl, $NaNO_3$, NaH_2PO_4, KH_2PO_4, Na_2CO_3 and $(NH_4)_2SO_4$ were added in turn. The results showed that all the salts could make isopropyl alcohol separate from water except KH_2PO_4 (**Figure 1**). The order of salting-out ability is Na_2CO_3＞$(NH_4)_2SO_4$＞NaCl＞NaH_2PO_4＞$NaNO_3$. $(NH_4)_2SO_4$ is preferred as the salting-out reagent because CO_3^{2-} may precipitate with many metal ions.

Influence of amount of ammonium sulfate and thiocyanate

In the system of 3.0 mL of isopropyl alcohol, 1.0 mL of 1×10^{-3}mol/L ammonium thiocyanate, 50 μg of Cu(Ⅱ) and 1.0 mL of 1×10^{-3}mol/L Vc with a total volume 10 mL, the flotation yield(E) keeps 100% when the amount of $(NH_4)_2SO_4$ is increased from 1.5 g to 3.5 g. Hence, 1.5 g of $(NH_4)_2SO_4$ was selected for all further studies.

The influence of amount SCN^- on the E of Cu(Ⅱ) was showed in **Figure 2**. When 0.8 mL of was taken, the E of Cu(Ⅱ) is 100%. To ensure that Cu(Ⅱ) is precipitated with SCN^- completely, 1.5 mL 0.1 mol/L of NH_4SCN solution was selected for all further studies.

Figure 2 Effect of amount of NH_4SCN

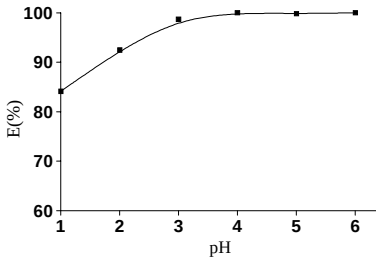


Conc. (Vc): 1×10^{-3}mol/L; Cu(Ⅱ): 50μg; 1×10^{-3}mol/L NH_4SCN: 1.0mL; $(NH_4)_2SO_4$: 1.5g; isopropyl alcohol: 3.0mL; total volume:10mL.

Influence of ph and surfactant

Figure 3 shows the influence of pH on the E of Cu(Ⅱ). It shows that the E of Cu(Ⅱ) increases from 84% to 100% with increase in pH from 1 to 3. At pH>8, the results are erratic. Therefore, the pH range 3-6 was selected. The influence of three different kinds of surfactant was studied. The results showed that 1.0 mL of Triton X-100(0.05%), 1.0 mL of 1×10^{-3}mol/L sodium lauryl sulfonate did not affect the E of Cu(Ⅱ) whereas 1.0 mL of 1×10^{-3}mol/L cetyl-trimethyl ammonium bromide (CTMAB) decreased the E of Cu(Ⅱ) from 100% to 81% with the selected conditions.

Figure 3 Effect of pH



1×10^{-3}mol/L Vc: 1.0 mL, other condition as in **Figure 2**.

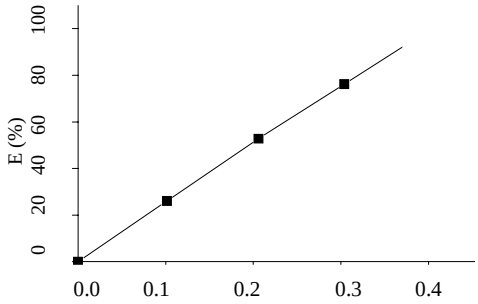
Calibration curve

A calibration curve for Vc was constructed under the selected conditions. A good linear relationship was observed between the E of Cu(Ⅱ) and the amount(x/mL) of Vc(**Figure 4**). The linear equation is found to be E=0.6851+248.13x, with r=0.9998.

Influence of Co-existing Ions

The effects of foreign ions on the determination of 2.00μg/mL Vc were investigated.

Figure 4 Relationship between the amount of Vc and the E of Cu(Ⅱ)



When the permitted relative deviation is less than ±5%, common ions (K^+, Na^+, Ca^{2+}, Fe^{2+}, Al^{3+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, ClO_4^-, NO_3^-, SO_4^{2-}, F^-, Cl^-, Br^-,I^-), citric acid, vitamin B_1, and vitamin B_6 scarcely interfered the determination. 20 fold $NH_2OH \cdot HCl$ and 50 fold vitamin B_{12} did not interfere the determination.

The proposed method is applied to the determinations of Vc in the treated samples and iodimetry as a contrast method (**Table 1**). The results prove that the proposed method is accurate and reliable.

Table 1 Vc concentrations determined by the proposed method and iodimetry

Samples	Proposed method[a]	Iodimetry[b]	t[c]
Orange (mg/10mL)	29.6±0.6	30.1±0.4	2.24
Tomato (mg/10mL)	20.9±0.4	21.2±0.5	2.10
Strawberry (mg/10mL)	35.1±0.6	34.7±0.5	1.86
Tablet (mg/tablet)	97.1±0.2	96.9±0.4	1.95
Injection (mg/mL)	187.1±0.4	186.8±0.5	1.74

a: Average of five determinations; b: Average of three determinations; c: Theoretical value=2.78, n=5 with 95% confidence limits.

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