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Simple photometric determination of free cyanide ion in aqueous solution with 2,6-dichlorophenolindophenol

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Abstract: In this work, a simple photometric method with high accuracy and precision for measuring trace amounts of free cyanide ion in aqueous solution is demonstrated. Under the evaluated conditions, we could determine CN^- concentration in the range of 5-70 ppm easily. The work is based upon the photometric titration of CN^- with Co(II) in the presence of 2,6-dichlorophenolindophenol (DCPIP) at λ_{max}= 602 nm in aqueous solution. The optimal conditions, such as pH, ionic strength, and concentration of chromopher were evaluated. The interference effect of many other cations and anions studied and the results are given here.. The optimized titration was successfully used to determine the concentration of free cyanide ion in aqueous solutions.

Keywords: Cyanide, 2,6-dichlorophenolindophenol, spectrophotometry

1 Introduction

The importance of cyanides in technological and industrial fields is well known, exemplified by their use in the extraction of gold and sliver metals from their mines [1–3]. Their key role as a constitutent of aminoacides in animal and plant structures as has also been studied [2]. The high degree of toxicity that these compounds present to living organisms alone warrants their study [2–4] . Some procedures for measurement of cyanides have been reported, and they generally suffer from high experimental steps, unfavorable preci-

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sion, low accuracy, and demand for fast operations [1–7]. In this paper, we hope to report a fast, simple, and reliable method using a simple photometric titration in which the decrease in DCPIP absorption, due to electrochemical effect of cobalt-cyanide complex on the system, can be related to the concentration of free cyanide ion in the solution.

2 Experimental

2.1 Apparatus and reagents

DCPIP solution were prepared dissolving of 36.6 mg of its sodium salt in 100 mL of 210 mg/L $NaHCO_3$ aqueous solution. Standard solutions of KCN, $Co(NO_3)_2 \cdot 6H_2O$ and trisodium citrate salt ($C_6H_5Na_3O_7 \cdot 2H_2O$) in water were used. All reagents were from Merck and used as received. Electronic spectra were recorded on a Shimadzu UV-256 FW(Japan) UV-Vis spectrophotometer. PH measurements carried out using a Corning 215 pH-meter (±0.1). Photometric absorbance data were collected with a probe-type 662 Metrohm(Swiss) photometer. Ttitration volumes were added using a Metrohm, programmable, 725 Dosimate titratore (with 1 μL step). Deionized and doubly distilled water was used throughout.

2.2 Procedure

150 μL of DCPIP solution (1.4×10^{-5} M), citrate-buffer (pH= 9) 1 mL, trisodium citrate solution (1000 ppm) 1 mL, and an appropriate volume of CN^-solution were transferred into a 10 mL flask and diluting to the mark with distilled water. This final solution was then transferred into the double layer cell vessel of the probe-type photometer, which operates as a thermostatic water circulating bath (15.0 ± 0.1). The titration was carried out with proper amounts of Co(II) solutions.

2.3 Color stability

DCPIP is somewhat unstable in darkness or when exposed to light for a long time [8, 9]. Fig. 1 shows that the color of the DCPIP in the presence of 210 mg/L $NaHCO_3$ is stable and can be used reliably for at least 2 hours.

2.4 Concentration of DCPIP

Amounts of 3 to 30 ppm of DCPIP were tested. As seen from Fig. 2 there is a good linear relationship between the concentration of DCPIP and its absorbance. However, in order to supply good acceptance of and avoiding deviation from Beer's law, 0.2 <absorbance< 0.8 [10], the working concentration of DCPIP 1.4×10^{-5} M ($\sim$ 5 ppm) was selected for subsequent studies.

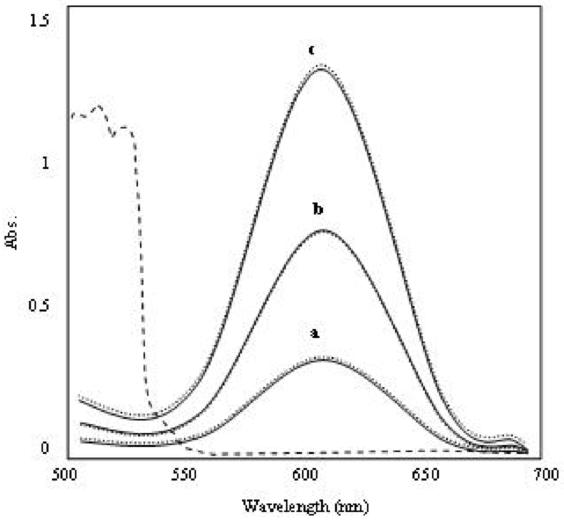


Fig. 1 Color stability of DCPIP: a, b and c were 3, 6 and 9 ppm over the time after the preparation immediately (solid curves), 2 hours later (dot curves) and in presence of CN^- and Co^{2+}(dashed curve), respectively.

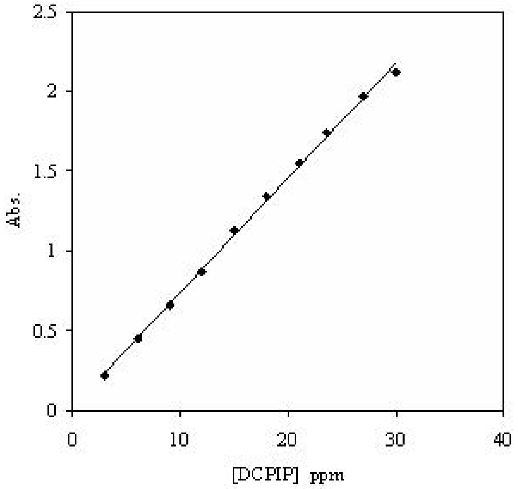


Fig. 2 Variation of absorbance with concentration of DCPIP.

2.5 Effect of pH

DCPIP system potential is depended on pH of the solution vigorously [11]. At pH >5.7 and $\lambda_{\max}$= 600 nm, DCPIP has $\varepsilon_{\max} = 2.2 \times 10^4$ L/mol cm [12, 13]. As seen from Fig. 3, pH = 9 provides the best conditions to do the titration.

The precipitation of cobalt (II) as hydroxide may causes a problem at alkaline pH. This can prevent the reactions from occuring. Addition of the appropriate amount of citrate solution, 0.004 M, could overcome this problem. The resulted curve plots are shown in Fig. 4.

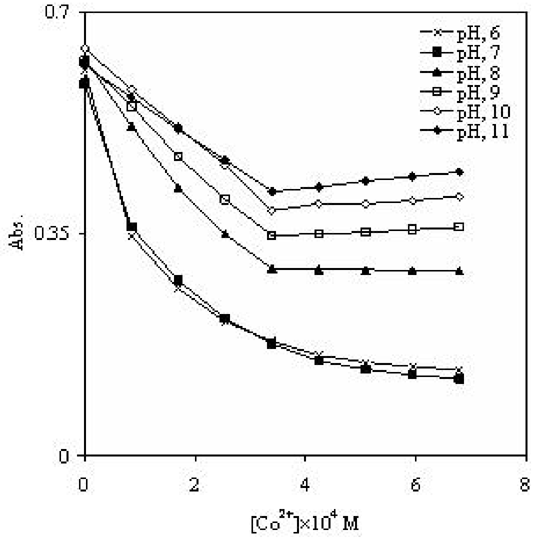


Fig. 3 Effect of pH on determination of free cyanide ion (1.92×10^{-3} M).

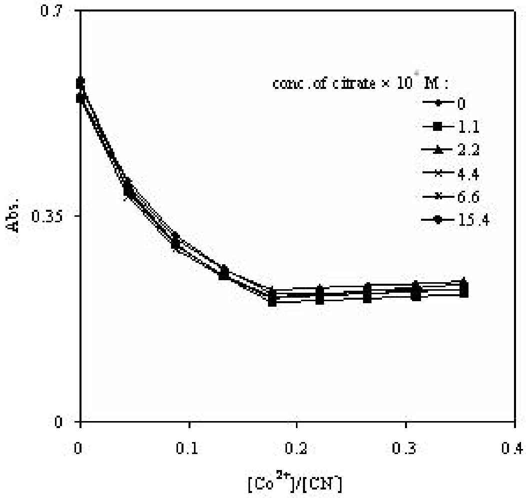


Fig. 4 Effect of concentration of trisodium citrate on titration curves: titration of CN^- (2×10^{-3} M) with Co^{2+} (1.7×10^{-3} M) in the presence of citrate $(0 - 15.4) \times 10^{-4}$ M, pH (9).

Using pH (9) has some other advantages like elimination the interference of some potential interferer ions such as Ce^{3+}, Fe^{2+}, SO_3^{2-} and $S_2O_5^{2-}$. The only disadvantage of mentioned pH is somewhat re-oxidation of DCPIP. This resulted in a slow increase in the slope of the second arm of the titration curve, which happens sufficiently far from the end point of the titration. Thus, it had no considerable influence on the results.

2.6 Temperature and ionic strength

Because of high toxicity and relatively low boiling point of HCN (27 °C) the subsequent works were carried out at 15.0 ± 0.1 °C. The ionic strength of the system was established using trisodium citrate. As shown in Fig. 4, wide range of citrate concentration can be used. Therefore, the ionic strength was set at 0.004 M. The cobalt precipitation problem could also be prevented in the presence of citrate.

2.7 Interferers

Cations with low degrees of oxidation such as Fe(II) and Sn(II) can reduce the absorption of DCPIP in acidic media [11]. Further studies resulted in the following conclusions: a) Some other cations e.g. Al^{3+}, Fe^{3+}, Pb^{2+} and Cu^{2+} can change the pH of system and play a role as Lewis's acid and hence the change in color of DCPIP to red. Cations; Tl^{+}, Cr^{3+}, Hg^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+} and Li^{+} had no effect. Ce^{3+} at $1.5 <$pH< 7.3 affects the DCPIP into reduced form (colorless). b) Some anions were also studied: SCN^{-}, CN^{-}, F^{-}, SO_4^{2-}, BrO_3^{-}, IO_3^{-}, HPO_4^{2-}, $S_2O_3^{2-}$, $Cr_2O_7^{2-}$, $H_2PO_4^{-}$, Cl^{-}, Br^{-}, I^{-}, $S_2O_8^{2-}$, S^{2-}, SO_3^{2-}, $S_2O_5^{2-}$; except three last anions, showing kinetic effects, the rest had no effect on the system. As seen from Fig. 5 and Fig. 6, using citrate buffer (pH= 9) showed that the interference of the above cations and anions can be eliminated easily.

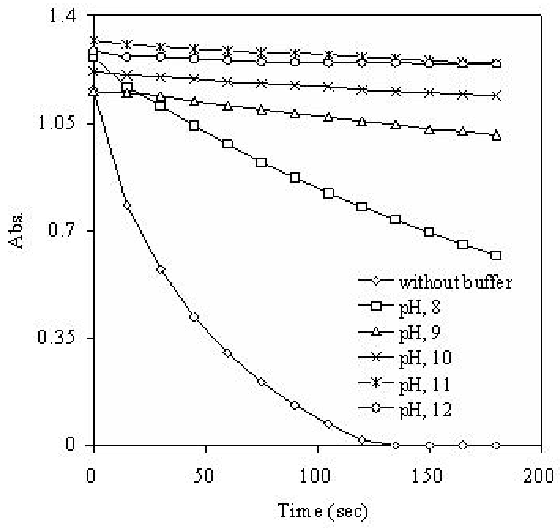


Fig. 5 Effect of pH on kinetic effect of SO_3^{2-} on DCPIP color.

3 Results and discussion

DCPIP as a member of indophenolic indicators family has two distinguishable behavior [11]: a) an acid-base indicator, which is reddish at pH< 5.7. Also, at the pH >5.7 namely

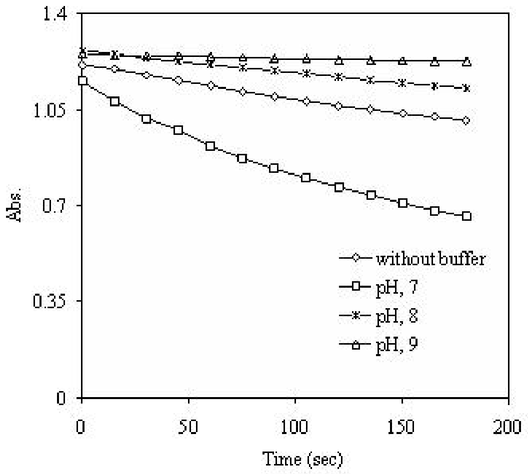
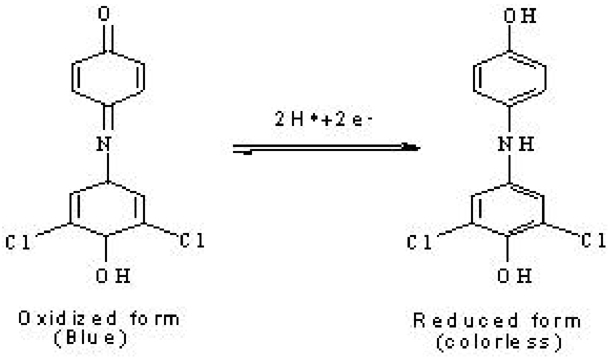


Fig. 6 Effect of pH on kinetic effect of $S_2O_5^{2-}$on reduction of DCPIP.

in alkali and neutral aqueous solutions its color is blue. b) electrochemical response of DCPIP. Under the particular potential, it is able to accept two electrons from its environment, reduced and give up its color. This indicator shows two strong absorption peaks at 520 and 602 nm in acidic and neutral or alkaline media, respectively [14]. Reduction reaction for DCPIP can be shown as the following Scheme 1 [15, 16]:



Scheme 1 Reduction reaction for DCPIP

In this work, based upon the electrochemical characteristics of DCPIP, we provide an electrochemical system by using complexation between Co(II) and CN^-. The proposed system could support the electron demand for the conversion process between the two oxidized and reduced forms of DCPIP (above scheme). The reducing role of Co^{2+} and CN^- is as follow [17]:

$$Co^{3+} + e \rightleftharpoons Co^{2+} \qquad E = 1.8 - 0.06\log([Co^{2+}]/[Co^{3+}]) \qquad (1)$$

$$Co(CN)_6^{3-} \rightleftharpoons Co^{3+} + 6CN^- \qquad K_{ox} = [Co^{3+}][CN^-]^6/[Co(CN)_6^{3-}] \qquad (2)$$

$$Co(CN)_6^{4-} \rightleftharpoons Co^{2+} + 6CN^- \qquad K_{red} = [Co^{2+}][CN^-]^6/[Co(CN)_6^{4-}] \qquad (3)$$

From Eqs. (1)–(3) and $K_{ox}/ K_{red}= 10^{-44}$:

$$E = E'_0 + 0.06 \log([Co(CN)_6^{3-}]/[Co(CN)_6^{4-}]) \tag{4}$$

where $E'_0 = -0.83$ V. $Co(CN)_6^{3-}$ complex is much more stable ($\log K_6= 64$) than $Co(CN)_6^{4-}$ and it is soluble in alkaline solutions [17]. In other word, Co(II) oxidizes to Co(III) and the electron demanding of DCPIP can be provided by this way. This causes the decrease in DCPIP absorption. It was found, at constant concentration of Co(II), this decrease act as a function of concentration of CN^- and can be related to the concentration of free cyanide ion in the solution. However, these two ions showed no effect on the absorption of DCPIP. Reduction of DCPIP in presence of CN^- and Co^{2+} ions was demonstrated in Fig. 1 (dashed curve). From this figure, the absorption peak at 600 nm disappeared in the presence of CN^- and Co(II) ions in the solution. As mentioned above, this could be attributed to the complexation of Co(II) with CN^- ions. Fig. 7 reveals that under the evaluated conditions a distinct end point is resulted for the concentration range of CN^- from 5 to 70 ppm. For the case of concentration less than 5 ppm the system shows not reliable end point. Furthermore, beyond 70 ppm of CN^-, the re-oxidation of DCPIP was significant and we were not able to determine the concentration of free cyanide in the solution accurately.

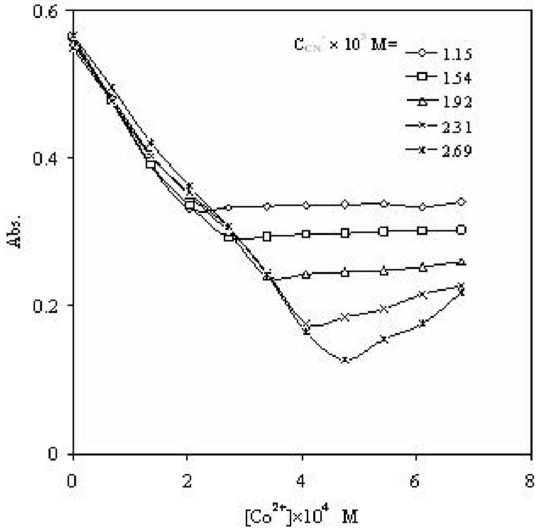


Fig. 7 Titration of CN^- $(1.15 - 2.69) \times 10^{-3}$ M with Co^{2+} solution, citrate 0.004 M, and pH (9).

In order to determine the unknown concentration of free cyanide in aqueous solution, from the end point of the titration, we can write:

A= mmole Co^{2+}= $V_{end} \cdot C_{Co} = V_{end} \times C_{Co} / (59 \times 10^6)$

B= mmole CN^-= $6 \times A$

C_{CN}= $B \times 26 \times (10^6/V_{CN})$= $(V_{end} \times C_{Co}/V_{CN} \times (6 \times 26/59)$

$$\mathbf{C}_{CN} = 2.644 \times (\mathbf{V}_{end} \times \mathbf{C}_{Co})/\mathbf{V}_{CN} \tag{5}$$

where: C_{CN}, V_{end}, C_{Co} and V_{CN} denote concentration of unknown CN^-(ppm), volume of Co(II) solution (μL) at the end point, initial concentration of Co(II) solution (ppm) and volume of unknown CN^-(μL), respectively. Thus, one can calculate the concentration of unknown CN^- from equation 5 easily.

3.1 Analytical application

The proposed method was successfully used to determine the concentration of free cyanide ions in two samples. Wastewater sample was prepared from an electro-coating metal manufacturer factory in Karaj-industrial city (south of Tehran). In the case the interference of S^{2-} may cases difficalt it can be eliminated by precipitation with Zn^{2+} at pH (2.5), using chloroacetic-acid/chloroacetate buffer, and then filtration of the sample [17]. The results of the proposed method compared with those from Cu(II)-phenolphthalein standard method [18] and summarized in Table 1. As seen, the results were in reasonable agreement with those from the standard method.

Table 1 Determination of concentration of free cyanide in aqueous samples (n= 6).

Sample	Standard method (ppm)	Proposed method (ppm)
Electro-coating wastewater	209.2 ± 0.9	208.2 ± 0.2
KCN-added Tap water[a]	15.3 ± 0.2	15.2 ± 0.1

[a] Appropriate and accurately weighed (± 0.00001 g) amounts of dried and pur KCN was used to prepare a 15.2 ppm of CN^- solution in Tap water.

4 Conclusion

From the view point of accuracy and precision, using a simple photometric method to measure the concentration of toxic free cyanide ion in aqueous solutions could be an addventage. We belive that factors such as wide working range of 5 to 70 ppm, ease of use, everywhere executable, reasonable accuracy and precision are the advantages of the method over the other methods. Because of the catalytic effect of Co(II), the proposed method can be used to measure the concentration of Co(II) in aqueous solution inversely.

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