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USE OF FERROCYANIDE FOR POTENTIOMETRIC DETERMINATION OF COPPER (II), AND VANADIUM (IV). ANALYSIS OF BINARY AND TERNARY MIXTURES

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SUMMARY

A rapid and reliable method for estimation of copper and vanadium based on its precipitation by ferrocyanide, and the unreacted ferrocyanide is oxidized with 2% iodine solution dissolved in acetic acid to ferricyanide, and formation of iodide ions. The iodide ions produced are titrated with mercuric nitrate using silver amalgam as the indicator electrode and calomel as the other half cell. This method is applicable to the accurate determination of copper (II) and vanadium (IV) alone or in its mixtures.

INTRODUCTION

Hulanichi [1] decribed a method for the determination of copper in concentrated electrolytes in acidic medium using the chalcocite Cu-selective electrode. Citrate buffer of pH 2 .8 was used for the elemination of interference by Fe (III). Pletencua [2] used atomic absorption method for the estimation of copper. Kiyanshii [3] adopted a potentiometric method for the determination of copper in platine bathe with a copper selective electrode. Gupta [4] used alizarine red S as a new indicator for the direct chelatimetric determination of copper with EDTA. Dimethylglyoxime [5] was used as an indicator in the determination of copper by complexometric titration. The frequently applied methods for the spectrophotometric determination of copper to be mentioned are those making use of the following chromophoric reagents. Diethylthiocarbamate, dithizone, 2,2′-diquinolyl [6–8] and 1–5–diphenyl carbohydrazide [9]. Khalifa [10] introduced fast gray RA as a reagent for copper. Pribil and Vasely [11] suggested a complexometric method for its determination in steel. Patrovsky [12] reported an extractive photometric method for its microdetermination in presence of Al, Ti, Zr and Fe. Iwasaki [13] determined vanadium in some ores with use of phenyl benzolylhdroxamic acid. Korkisch and Steffan [14] determined it in sodium diuranate without interference of Mo and U using Fe(II) as titrant and barium diphenylamine sulfonate as indicator.

EXPERIMENTAL METHODS

Solutions:

All solutions were prepared from high purity chemicals and deionized water and standardized by the recommended methods. The iodine solution 2% was prepared by dissolving previously sublimed solid iodine in acetic acid. 0 .009M Cu(II) solution was prepared by dissolving the calculated amount of $CuSO_4 .5H_2O$. 0 .004M vanadium was prepared from NH_4VO_3. The blue V(IV) solution was prepared by reduction of the yellow Vanadium solution with H_2SO_3 [15]. 0 .015M of $Fe(CN)_6^{4-}$ solution was prepared from A.R. $K_4Fe(CN)_6.3H_2O$.

Equipment:

The titration cell consists of a 150ml Pyrex cell, mechanical stirrer, a 5ml microburatte (1ml division = 0 .02ml), silver amalgam indicator electrode in conjunction with a reference saturated calomel electrode as the other half cell. The two electrodes were fitted to the potentiometer Model E 512 Methorm Herisau.

PROCEDURES

All titrations of unreacted EDTA with $Hg(NO_3)_2$ were performed using 8ml 10% hexamine buffer to control pH.

1. For Cu(II) or V(IV).

   To 0 .5–4ml 0 .009M Cu(II), or 0 .004M V(IV), in a 150ml cell, add a measured excess of ferrocyanide (2–8ml 0 .015M). Cover the cell with a watch glass and leave aside for five minutes to ensure complete precipitation of Cu(II) or V(IV). Add 10ml 2% iodine solution, to oxidize excess ferrocyanide, and titrate liberated iodine with Hg(II). Find out ferrocyanide = Cu or V.

2. Analysis of binary mixtures:

A. For Cu(II) (0 .5ml) + Mn(II) (1ml 0 .005M) or V(IV) (1ml 0 .004M) or Cr(III) (1ml 0 .010M).

i. To the mixture add 3ml ferrocyanide, 30ml water and continue following (1) to obtain Cu or Cu+V or Cu+Cr which equivalence ferrocyanide.

ii. To another identical mixture, adjust pH value to 5 with 10% of H_2SO_4, add 30 ml water, then add 2ml 0 .01M BrO_3^-, boil for 15 minutes to oxidize Mn(II) or V(IV) or Cr(III) to Mn(IV) or V(IV) or Cr(VI). Boil to expel Br_2 gas, then add drops of Na_2SO_3 solution boil for about 10 minutes to expel excess SO_2, and titrate liberated bromide with Hg(I). Find out Br^- = Mn or V or Cr.

B. For Cu(0 .5ml) + Al(1ml 0 .012M).

i. To the mixture add excess ferrocyanide, continue following (1) to obtain Cu=ferrocyanide.

ii. To another identical mixture, add a measured excess of 0.011M EDTA, boil about 15 minutes to ensure complete complexation of Al-EDTA. Cool the mixture and titrate uncreacted EDTA with Hg(II). Find out EDTA=Cu+Al. Find out EDTA=Al by difference.

C. For Cu(0.5ml) + Zn(1ml 0 .007M) or Co(1ml 0 .008M) or Ni(1ml 0 .009M).

i. To the mixture add a measured excess of ferrocyanide, and continue following(1) to obtain ferrocyanide=Cu+Zn or Co or Ni.

ii. To another identical mixture determined Cu iodometrically [16].

3 . Analysis of ternary mixtures.

A. For Cu(0 .5ml) + Zn(1ml) + Al(1ml).

i. To the mixture add a measured excess of ferrocyanide, and continue following(1). Find out ferrocyanide=Cu+Zn.

ii. To another identical mixture add a known excess of ferrocyanide to complete precipitation of Cu and Zn, filter and take the filtrate which containing Al only, add a known excess of EDTA solution, boil about 15 minutes. Cool, add hexamine solution then titrate the excess complexone with Hg(II). Find out EDTA=Al.

iii. To the third identical mixture determined copper iodometrically.

B. For Cu(0.5ml) + Cr(1ml) or Mn(1ml) + Ni(1ml) or Co(1ml).

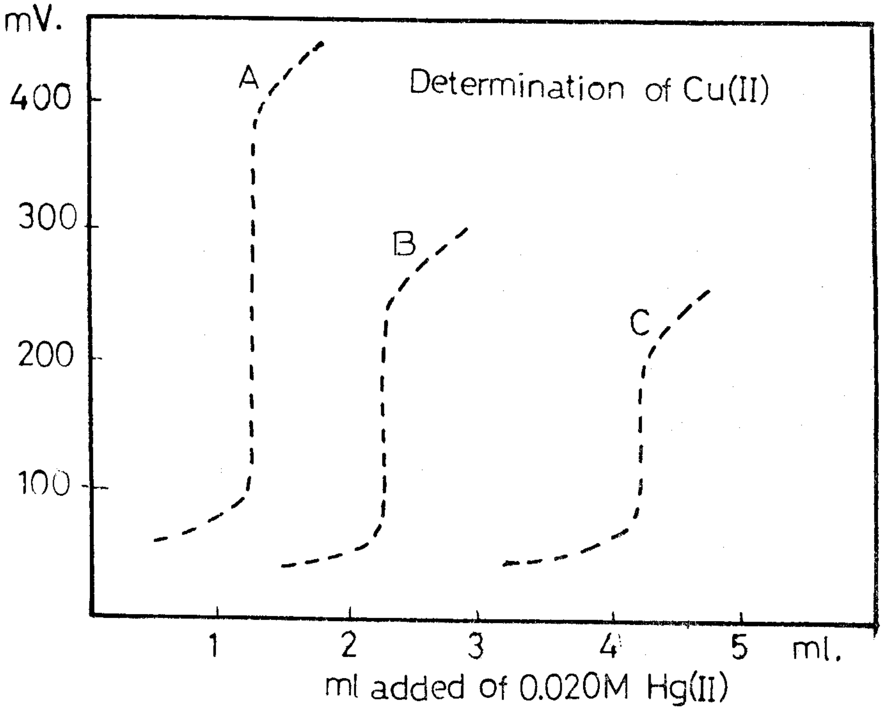
i. To the mixture add a measured excess of ferrocyanide, and continue following(1). Find out ferrocyanide= Cu+Ni+Cr.

ii. To another identical mixture add 3ml 0.01M $KBrO_3$ and continue following (2Aii). Find out Br^-= Cr or Mn.

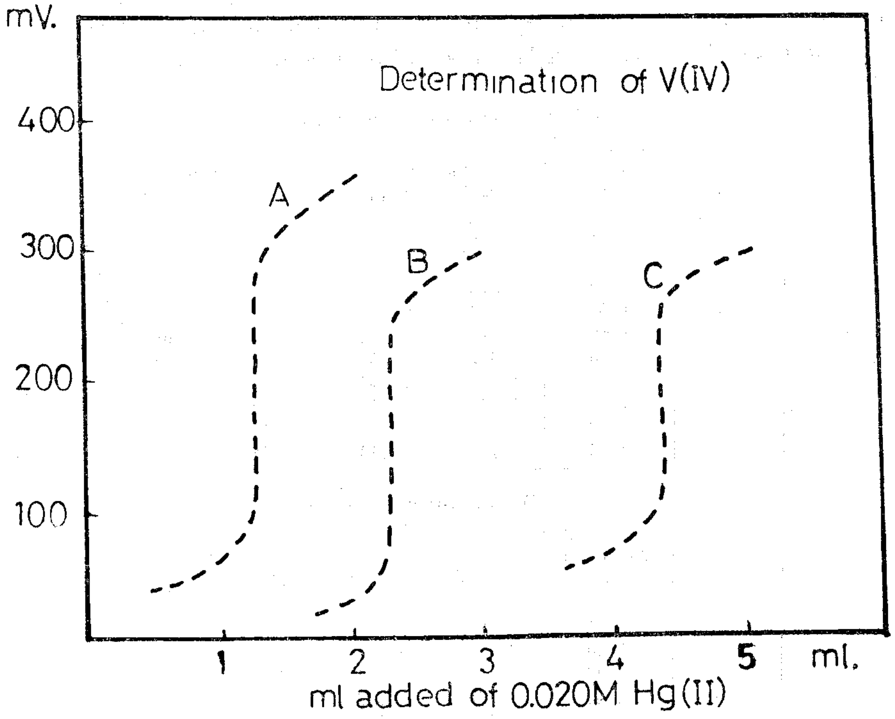
iii. To the third identical mixture determined copper iodometrically.

RESULTS AND DISCUSSION

Tables 1,2,3 and 4 list the results of determination of small ammounts of copper (II) or vanadium (IV) in pure solutions as well as in binary and ternary mixtures. The avarage error was calculated to be ± 0.31 % in case of copper and ± 0.74 % in case of vanadium. The results show good agreement with conventional methods, the equivalence point were accurately determined with potential breaks ranging from 122 to 182 mV/0.1ml Hg(II), which are sharp enough for the accurate determination of the end point.



A) 0.5ml 0.009M Cu(II) + 2ml 0.015M Ferrocyanide.
B) 1.6ml ,, ,, + 4ml ,, ,,
C) 4.0ml ,, ,, + 8ml ,, ,,



A) 0.5ml 0.004M V(IV) + 2 ml 0.015M Ferrocyanide

B) 1.6ml " " +4 ml " "

C) 4.0ml " " +8 ml " "

The quantitativeness of the redox reaction involving iodine as the oxidant and ferrocyanide as the reductant may be predicted by considering the standared potentials of the $I_2/2I^- = +0.535V$ and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-} = +0.720V$.

$$\begin{array}{lll} 2Fe(CN)_6^{4-} - 2e^- = 2Fe(CN)_6^{3-} & E^\circ = -0.360V \\ I_2 + 2e^- = 2I^- & E^\circ = +0.535V \\ 2Fe(CN)_6^{4-} + I_2 = 2Fe(CN)_6^{3-} & E^\circ = +0.175V \end{array}$$

By aid of the relation $E^\circ = (0.0591/n)\log K$, where E° is the standard electrode potential, n is the number of electrons required to oxidized one mole of ferrocyanide to ferricyanide and K is the equilibrium formation constant of the redox reaction, one calculate log K to be 2.96.

Such value indicates that the above reaction should proceed quantitatively to completion and hence the accurate determination of ferrocyanide which precipitate of Cu(II) or V(IV) by the present method.

Table 1. Determination of copper.

No	Vol. of Cu Taken ml 0.009 M.	mg.(Cu)		Error Mv/0.1 ml	
		Taken	Found	+ %	Hg(II)
1	0.50	0.286	0.288	0.70	182
2	0.80	0.458	0.460	0.44	177
3	1.00	0.572	0.568	0.70	175
4	1.40	0.800	0.796	0.50	171
5	1.60	0.916	0.912	0.44	168
6	1.80	1.030	1.022	0.78	165
7	2.00	1.144	1.148	0.35	162
8	2.50	1.430	1.422	0.56	155
9	3.00	1.716	1.706	0.58	150
10	4.00	2.288	2.280	0.35	122

Table 2. Determination of vanadium.

No	Vol. of V Taken ml 0.004 M.	mg. (V)		Error Mv/0.1 ml	
		Taken	Found	+ %	Hg(II)
1	0.50	0.102	0.103	0.98	180
2	0.80	0.163	0.161	1.23	179
3	1.00	0.204	0.202	0.98	177
4	1.40	0.285	0.282	1.05	176
5	1.60	0.326	0.324	0.61	170
6	1.80	0.367	0.364	0.82	168
7	2.00	0.408	0.406	0.49	166
8	2.50	0.509	0.507	0.39	161
9	3.00	0.611	0.618	0.49	160
10	4.00	0.815	0.812	0.37	157

Table 3. Determination of binary mixtures.

mg. (Cu)		mg. Metal		
Taken	Found	Taken		Found
0.286	0.285	0.275	Mn	0.274
0.286	0.284	0.204	V	0.206
0.286	0.283	0.324	Al	0.326
0.286	0.284	0.572	Cr	0.571
0.286	0.283	0.458	Zn	0.459

Table 4. Determination of ternary mixtures.

mg. (Cu)		mg. Metal			mg. Metal		
Taken	Found	Taken		Found	Taken		Found
0.286	0.285	0.458	Zn	0.459	0.324	Al	0.326
0.286	0.284	0.572	Cr	0.574	0.585	Ni	0.583
0.286	0.287	0.275	Mn	0.279	0.471	Co	0.473
0.286	0.283	0.275	Mn	0.278	0.585	Ni	0.582

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