

POLAROGRAPHIC ESTIMATION OF CADMIUM IN PRESENCE OF NICKEL, COBALT AND BISMUTH

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Received June 15, 1959

(Communicated by Prof. S. N. Gundu Rao, F.A.Sc.)

INTRODUCTION

QUANTITATIVE estimation of cadmium has attracted the attention of numerous workers in recent years. Gardiner and Regers¹ made use of stationary mercury plated platinum electrode for determination of sub-micrograms of Cd^{2+} and Zn^{2+} . Dithizone was used for estimation of Cd^{2+} colorimetrically in presence of other interfering metals.² Adams³ titrated Cd^{2+} with ethylenediaminetetraacetic acid (EDTA) using controlled current technique. Cadmium in presence of Zn^{2+} in sodium hydroxide solution was estimated spectrophotometrically with EDTA.⁴ The principle of coullogravimetric analysis was found useful⁵ for the determination of Zn^{2+} and Cd^{2+} . Traces of Ni^{2+} , Co^{2+} , Zn^{2+} and Cd^{2+} in rocks were also determined polarographically by using rubeanic acid and 1-nitroso-2-naphthol.⁶ Nobu-Yuki Tanaka and others⁷ carried out amperometric and potentiometric titrations of Cd^{2+} with EDTA in acetate buffers (pH 4.2) using dropping mercury electrode (d.m.e.). Silve Kallamanu and co-workers⁸ determined Cd^{2+} and Zn^{2+} by separating them from each other and also from other metals by anion-exchange resins. Kohnt⁹ developed a method for separation of Cd^{2+} from a mixture of Cd^{2+} and Bi^{3+} by means of KI, and estimated Cd^{2+} using hydrazone hydroxide. Sandberg¹⁰ used naphthaquinoline in sulphuric acid for titrating Cd^{2+} amperometrically. Author's earlier work¹¹ indicated that Cd^{2+} in pure solutions could be estimated amperometrically using $\text{K}_4\text{Fe}(\text{CN})_6$ as the titrating agent. The present communication describes a simple amperometric method for estimation of Cd^{2+} in mixtures of Cd^{2+} with Ni^{2+} , Co^{2+} , Bi^{3+} , etc.

EXPERIMENTAL

In all experiments reported in the present communication, systems containing pure substances only were examined. The following substances of AnalaR B.D.H. grade were used:

(i) Cadmium sulphate was recrystallised in double distilled water and dried in vacuum. The solutions prepared were standardized by gravimetric method using pyridinethionate.¹²

(ii) Nickel sulphate was recrystallised and dried at 50° C. The exact concentration of Ni²⁺ was estimated gravimetrically using dimethylglyoxime.¹²

(iii) Cobalt sulphate was recrystallised and dried. Gravimetric method using 1-nitroso 2-naphthol was employed for standardisation of cobalt solution.

(iv) Bismuth nitrate was of B.D.H. pure quality and was used without further purification.

(v) Potassium ferrocyanide (B.D.H. AnalaR). Solutions of this substance were standardised against standard solutions of Pb (NO₃)₂ prepared from recrystallised and dried substance.

(vi) Potassium chloride and potassium citrate (B.D.H. AnalaR) were used without further purification, as supporting electrolytes.

The polarograph employed in the present investigation was of manual type and assembled in this laboratory. The following were the characteristics of the capillary used:

Mass of the drop	0.719 mg.
Time	4.1 sec.

RESULTS AND DISCUSSION

In the first series of experiments polarograms of Cd²⁺ in 1 M KCl solution were obtained to examine the accuracy of the assembled polarograph. The half-wave potential of Cd²⁺ corresponded to -0.635 volts vs. S.C.E. in close agreement with the data reported in the literature.¹³ Further, the observed limiting current i_d was in accord with the value calculated from Ilkovic's equation¹³:

$$i_d = 605 n D^{\frac{1}{2}} C m^{\frac{2}{3}} t^{\frac{1}{2}}$$

where i_d is the limiting current in microamperes; n , the number of electrons involved in the reduction process; D , the diffusion coefficient (cm.² sec.⁻¹); and t , the average life of the drop (sec.). Polarograms obtained with Ni²⁺, Co²⁺ and Bi²⁺ solutions also gave data which could be compared well with the results of earlier workers.¹³ Further, the values of i_d attained saturation for all the reducible ions reported here, at and above 1.6 volts vs. S.C.E., at these potentials. i_d values were proportional to the concentration over a

limited range (≤ 15 mM.). All amperometric titrations reported below were carried out at -1.80 volts.

Figure 1 gives results on amperometric titration of cadmium solutions against $K_4Fe(CN)_6$, in presence of potassium citrate as the supporting electrolyte. In accord with earlier data¹¹ obtained with KCl as the supporting electrolyte, Cd^{2+} could be estimated amperometrically using $K_4Fe(CN)_6$ in presence of K.Cit. The end-points as indicated in Fig. 1 were sharp, and the experiment inaccuracy was of the order of ± 0.5 per cent. (see Table I). Unlike at lower concentrations Curves 1-3 (Fig. 1), the decrease in i_d at higher concentrations of Cd^{2+} (Curves 4-6) was not linear with the volume of the titrant; this appears to be due to the limitation in the applicability of Ilkovic's equation to higher concentrations of the reducible ion.

Figures 2-4 give amperometric curves representing the estimation of Cd^{2+} in presence of Ni^{2+} , Co^{2+} and Bi^{3+} respectively, using KCl and K.Cit.

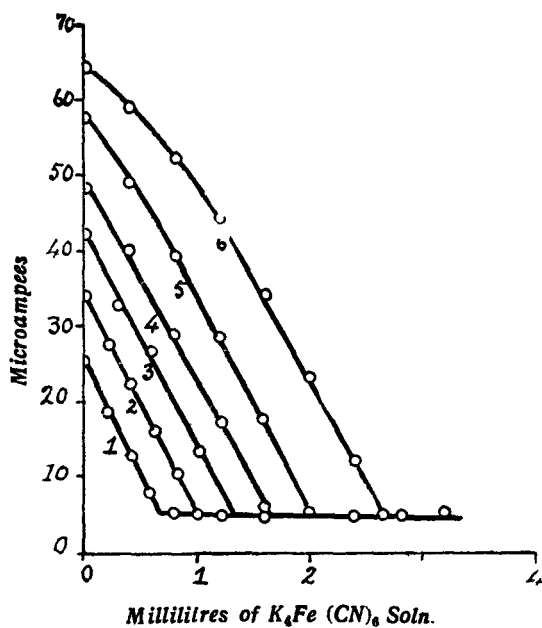


FIG. 1

FIG. 1. Amperometric titration of Cd^{2+} against $K_4Fe(CN)_6$. Curves 1-6 refer to 10, 15, 20, 25, 30 and 40 mM. of Cd^{2+} . Supporting electrolyte—M/2 K.Cit.

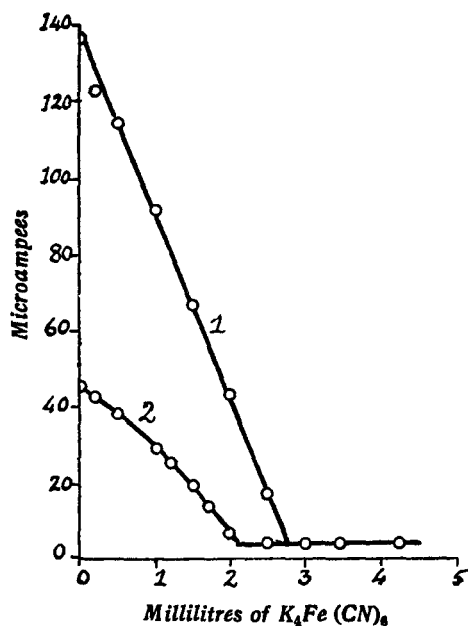


FIG. 2

FIG. 2. Determination of Cd^{2+} in presence of Ni^{2+} . Concentration of $K_4Fe(CN)_6 = 300$ mM.; of $Cd^{2+} = 30$ mM.; of $Ni^{2+} = 10$ mM. Curve 1 refers to KCl and 2, to K.Cit. used as supporting electrolytes.

TABLE I

Amperometric titration of cadmium by potassium ferrocyanide

Strength of $K_4Fe(CN)_6$ = 300 mM.
 Supporting electrolyte = M/2 K.Cit.

Concentration of $CdSO_4$ Soln. in mM.	Volume of $K_4Fe(CN)_6$ in ml.	
	Required	Observed
10	0.675	0.670
15	1.00	1.00
20	1.35	1.33
25	1.65	1.67
30	2.03	2.00
40	2.63	2.66

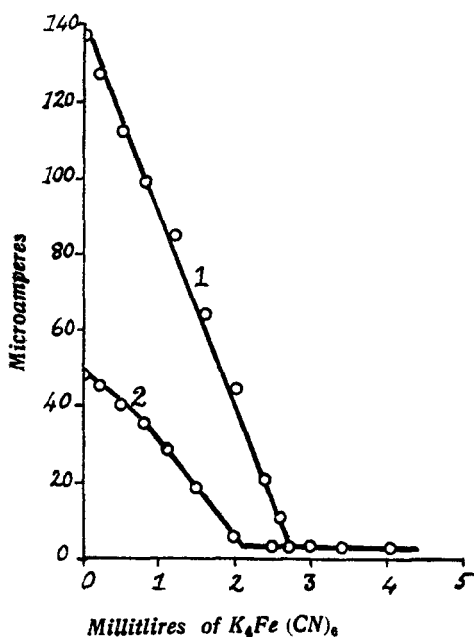


FIG. 3

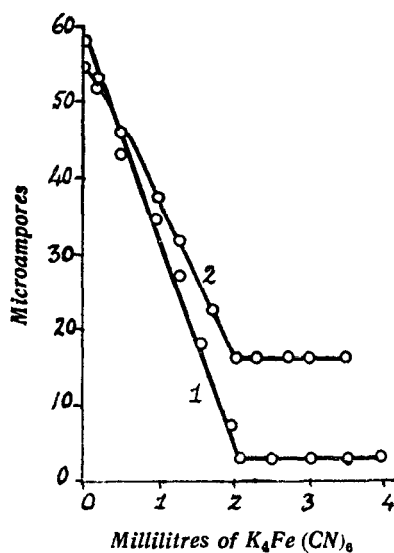


FIG. 4

FIG. 3. Estimation of Cd^{2+} in presence of Co^{2+} . Concentration of $K_4Fe(CN)_6$ = 300 mM; of Cd^{2+} = 30 mM.; of Cd^{2+} = 10 mM. Curve 1 refers to KCl. and 2, to K.Cit. as supporting electrolytes.

FIG. 4. Determination of Cd^{2+} in presence of Bi^{3+} . Concentration of $K_4Fe(CN)_6$ = 300 mM; Supporting electrolyte — M/2 K.Cit. Curve 1 refers to estimation of Cd^{2+} and 2, to a mixture of Cd^{2+} and Bi^{3+} .

as supporting electrolytes. In all the series of experiments, a mixture of $\text{Cd}^{2+} + \text{Ni}^{2+}$, $\text{Cd}^{2+} + \text{Co}^{2+}$ or $\text{Cd}^{2+} + \text{Bi}^{3+}$ was titrated against standard solution of $\text{K}_4\text{Fe}(\text{CN})_6$; Curve 1, Figs. 2-4, refer to KCl, while Curve 2, to K.Cit. as the supporting electrolyte. It is of interest to note that while the amperometric Curve 1, Figs. 2-4 give end-points corresponding to the total amount of $\text{Cd}^{2+} + \text{Ni}^{2+}$, $\text{Cd}^{2+} + \text{Co}^{2+}$ or $\text{Cd}^{2+} + \text{Bi}^{3+}$, Curve 2 indicates only the amount of Cd^{2+} . In other words, the presence of Ni^{2+} , Co^{2+} or Bi^{3+} interferes the amperometric estimation of Cd^{2+} in KCl solutions using $\text{K}_4\text{Fe}(\text{CN})_6$ as the titrating agent; and does not do so in K.Cit. medium. Cadmium could be determined with accuracy in citrate solutions even in the presence of all the three metallic components, *viz.*, Ni^{2+} , Co^{2+} and Bi^{3+} (*see* Fig. 5). This observation is clearly demonstrated by the data in Fig. 6. In this, Curve 1 refers to amperometric titration of 30 mM. of Cd^{2+} alone in

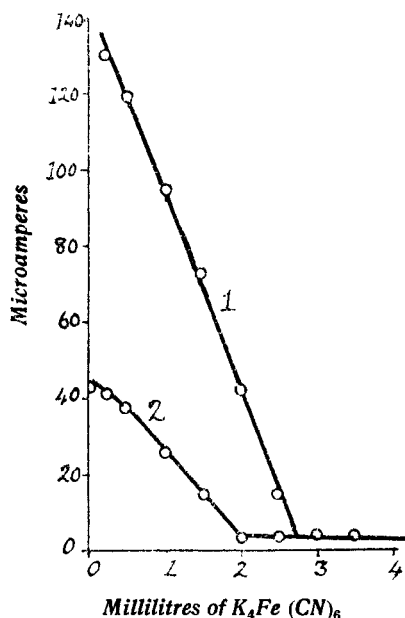


FIG. 5

FIG. 5. Estimation of Cd^{2+} in presence of Ni^{2+} , Co^{2+} , etc. Curve 1 refers to amperometric titration of 30 mM. of $\text{Cd}^{2+} + 5$ mM. of $\text{Ni}^{2+} + 5$ mM. of Co^{2+} in KCl; and 2, to the titration of the same mixture in K.Cit. medium.

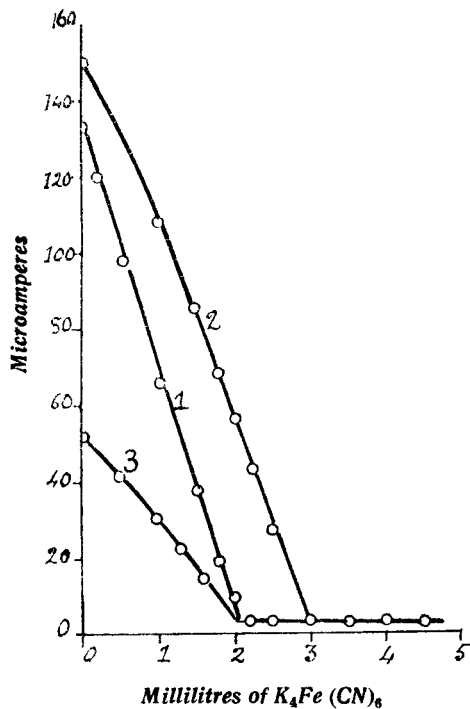


FIG. 6

FIG. 6. Role of K.Cit. in amperometric estimation of Cd^{2+} in presence of Ni^{2+} , Co^{2+} and Bi^{3+} . Curve 1 refers to amperometric estimation of 30 mM. of Cd^{2+} in KCl; 2, of 30 mM. of $\text{Cd}^{2+} + 15$ mM. of Ni^{2+} in KCl; 3, of 30 mM. of $\text{Cd}^{2+} + 15$ mM of Ni^{2+} in K.Cit. medium.

KCl solution; Curve 2 refers to the same of a mixture of 30 mM. of Cd^{2+} and 15 mM. Ni^{2+} in 1 M KCl solution. The shift of the end-point by 1.9 c.c. of the titrant vs. $\text{K}_4\text{Fe}(\text{CN})_6$ corresponding to the amount of Ni^{2+} in the mixture could be noticed. Instructive was the observation that when the same mixture of Cd^{2+} and Ni^{2+} was titrated against $\text{K}_4\text{Fe}(\text{CN})_6$ in potassium citrate solution (Curve 3, Fig. 6) the end-point corresponded to the same as in Curve 1, referring to the amount of Cd^{2+} alone.

The non-interference of the presence of Ni^{2+} , Co^{2+} and Bi^{3+} in the amperometric estimation of Cd^{2+} using $\text{K}_4\text{Fe}(\text{CN})_6$ as the titrating agent and K.Cit. as the supporting electrolyte suggest that the citrate complexes of Co^{2+} , Ni^{2+} and Bi^{3+} are more stable than the corresponding ferrocyanides. Knowledge on the stability constants of the ferrocyanide complexes of the metallic constituents is not available in the literature.

SUMMARY

Cadmium was estimated amperometrically using $\text{K}_4\text{Fe}(\text{CN})_6$ as titrating agent, with an experimental inaccuracy of ± 0.5 per cent. In citrates employed as supporting electrolyte for the reduction at d.m.e. of Cd^{2+} , the presence of Ni^{2+} , Co^{2+} and Bi^{3+} did not interfere with the estimation, due to the formation of more stable citrate complexes of Ni^{2+} , Co^{2+} and Bi^{3+} than the corresponding ferrocyanide complexes.

ACKNOWLEDGEMENT

Author's thanks are due to Dr. N. A. Ramaiah, Head of the Department of Physical Chemistry, National Sugar Institute, Kanpur, for his valuable discussions and encouragement during the work; and to Mr. N. Abraham, Principal, Christ Church College, for his interest in the work.

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