Amperometric Determination of Cobalt as Tungstate

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(Received November 29, 1960)

The use of sodium tungstate as a precipitant for the quantitative determination of cobalt was recently reported by Anand[1]. The method was based on the reaction studied by Smith and Bradbury[2]. A conductometric titration procedure for cobalt[3] based on the precipitation of cobalt as tungstate was also developed. Consequent upon the development of an amperometric titration method for the determination of cobalt as tellurite[4] it was considered worthwhile to examine the validity of the results of gravimetric and conductometric studies on the determination of cobalt as tungstate by the application of the amperometric technique to this precipitation reaction. A further confirmation of the composition of cobalt tungstate was also sought.

Experimental and Results

Solutions.—Sodium tungstate: An approximately 0.1 M solution was prepared from B. D. H. reagent grade sample. It was standardized by precipitating tungsten as the benzidine complex[5] and final weighing as WO_3 after incineration above 1000°C.

Cobalt(II) chloride solution was about 0.1 M and was standardized by the anthranillate procedure[6] and checked by the α-nitroso β-naphtol method[7].

Gelatin solution was prepared according to the details given by Meites[8] and was 0.1%. Fresh solutions of gelatin were prepared every day. B. D. H. Analar salt was used for preparing a stock 1.0 M solution of potassium chloride.

Apparatus. — A Fisher elecdropode (catalog No. 9-317) was used for recording the current potential characteristics during the amperometric determination of cobalt as tungstate. The instrument has a built in galvanometer and works on 115 V. A. C. supply. It is used in conjunction with the dropping mercury electrode. The working of the instrument involves the increment method which makes it necessary merely to obtain current values at a limited number of points both before and after equivalence point in order to carry out an analysis.

Determinations of Cobalt as Tungstate. — In a supporting electrolyte consisting of 0.1 M potassium chloride, having 0.01% gelatin and enough alcohol to give an overall concentration

TABLE I. AMPEROMETRIC DETERMINATION OF COBALT AS TUNGSTATE

No.	Strength of cobalt solution mM	Strength of tungstate solution mM	Amount of cobalt		Error
			Taken mg.	Found mg.	%
1	9.938	98.31	14.64	14.62	−0.14
2	8.944	88.48	13.18	13.18	—
3	7.950	78.65	11.71	11.70	−0.08
4	6.957	68.72	10.25	10.24	−0.09
5	5.963	58.97	8.78	8.79	+0.11
6	4.969	49.16	7.32	7.28	−0.51
7	3.975	39.32	5.86	5.88	+0.34
8	2.981	29.49	4.39	4.39	—
9	1.988	19.66	2.93	2.93	—
10	0.994	9.83	1.46	1.47	+0.69
11	0.497	4.92	0.733	0.74	+0.95
12	0.248	2.46	0.366	0.37	+1.10

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[1] V. D. Anand, *Ann. Chim. (Rome)*, **50**, 432 (1960).

[2] E. F. Smith and R. H. Bradbury, *Ber.*, **24**, 2930 (1891).

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[5] G. von Knore, ibid., **47**, 37 (1908); *Ber.*, **38**, 783 (1905).

[6] P. E. Wenger, C. Cimmerman and A. Corbaz, *Mikrochim. Acta*, **2**, 314 (1938).

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[8] L. Meites, "Polarographic Techniques", Interscience, New York (1955), p. 135.

of 50% was taken an aliquot of the cobalt-(II) solution. The mixture was thoroughly deaerated by a slow stream of purified nitrogen. Necessary connections were made and the drop time adjusted to a drop of mercury every three seconds. A potential of −1.5 V. vs. S. C. E. was applied to the dropping mercury cathode and the mean galvanometer deflection noted.

The process was repeated after every addition of the tungstate solution from a microburette. The mixture was thoroughly mixed and deaerated by a rapid stream of nitrogen and the precipitate allowed to settle for one minute before observing the current reading. The strength of the tungstate solution was maintained at approximately 10 times stronger than that of cobalt to eliminate the dilution effects. Correction factor for volume error $i_{\text{obs}}\{(V+v)/V\}$ was however, applied for greater accuracy. Point of intersection of the graph obtained by plotting the current against the volume of the titrant was read at the volume axis to get the equivalence point. Results of the titrations of cobalt solutions varying in concentration from 0.2∼10 mM are given in Table I.

TABLE II. EFFECT OF ALCOHOL CONCENTRATION ON AMPEROMETRIC TITRATION OF COBALT AS TUNGSTATE

No.	Concn. of alcohol %	Amount of cobalt Taken mg.	Amount of cobalt Found mg.	Error %
I	90	14.64	14.66	+0.14
II	80	14.64	14.65	+0.07
III	70	14.64	14.64	—
IV	60	14.64	14.65	+0.07
V	50	14.64	14.64	—
VI	40	14.64	14.55	−0.38
VII	30	14.64	14.51	−0.89

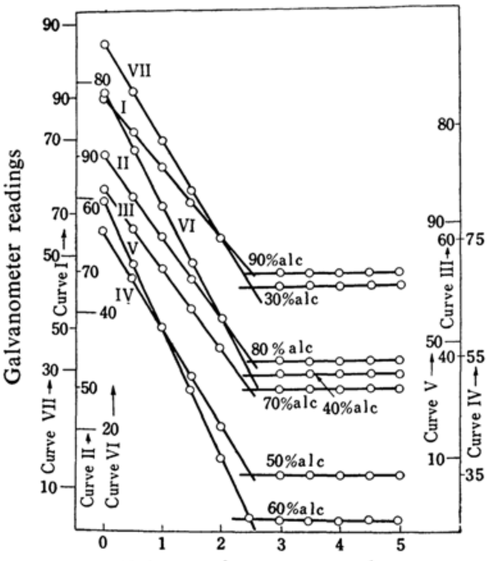

Fig. 1

The effect of addition of alcohol on the equivalence point of the precipitation of cobalt as tungstate was also studied. Alcohol concentrations were varied from 30∼90%. The results are presented in Table II and shown in Fig. 1, which also represents the mode of the titration curves obtained in the amperometric determination of cobalt as tungstate.

Discussion

Von Stackelberg et al.[9] studied the polarography of tungsten (VI) in conentrated hydrochloric acid and reported only a single reduction wave. In neutral or alkaline media tungsten does not produce any reduction wave[10]. Cobalt, however, is not reducible in hydrochloric acid[11]. There were accordingly two possibilities for the choice of a suitable supporting electrolyte in the amperometric titration of cobalt as tungstate. Either concentrated hydrochloric acid could be employed as the supporting medium, in which case the reducible ion would be tungsten (VI); or a supporting electrolyte in which cobalt ion is reduced at the dropping mercury electrode. The WO_4^{2-} ion was, however, reported to exist only alkaline media[12]. As such hydrochloric acid could not be used as the supporting electrolyte, because the precipitation of cobalt tungstate would be inhibited. Potassium chloride was, therefore, chosen as the medium, in view of its earlier use in the amperometric titrations of cobalt as tellurite[4], and also because earlier work on cobalt tungstate had been done in normal aqueous solutions[1,3].

In potassium chloride the $E_{1/2}$ vs. S. C. E. for cobalt was −1.2 V. and though the wave was reportedly irreversible, the magnitude of the current was found to be proportional to cobalt concentration over a considerable range[13] (up to 15 mM). For actual titrations a potential of −1.5 V. was applied during the amperometric titrations of cobalt as tungstate.

The diffusion current due to cobalt fell as more and more of the precipitant was added

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9) V. Stackelberg, M. P. Klinger, W. Koch and E. Krath, *Forschungberichte Tech. Mitt. Krupp., Essen*, **2**, 59 (1939).

10) I. M. Kolthoff and J. J. Lingane, "Polarography", Vol. II, Interscience, New York (1952), p. 461.

11) L. Meites and T. Meites, unpublished experiments in "Polarographic Techniques", Interscience, New York (1955), Appendix B., p. 303.

12) H. J. Emelius and J. S. Anderson, "Modern Aspects in Inorganic Chemistry", Routledge and Kegan Paul, London (1952), p. 212.

13) J. J. Lingane and H. Kerlinger, *Ind. Eng. Chem., Anal. Ed.*, **13**, 77 (1941).

and this continued till the whole of the cobalt in the test solution had been precipitated. Beyond the equivalence point, the current approached the residual current value due to the titration medium.

At low concentrations of cobalt encountered in these studies, the solubility of cobalt tungstate was significant. To overcome this effect, the addition of some non-aqueous medium was necessary. Alcohol up to 50% overall concentration was used in the conductometric studies reported earlier[3]. The effect of varying alcohol concentrations ranging from 30∼90% was studied (cf. Table II, Fig. 1) to determine alcohol concentration required in these studies for getting reproducible results. Best results were obtained with alcohol concentrations above 50%. This concentration of alcohol was, therefore, used in the amperometric titration of cobalt.

The titrations for cobalt as tungstate were performed for different cobalt concentrations. In a series of 12 determination involving 0.2∼10 mM Co, precision was better than 1%; with very dilute samples, however, it was poorer. The concentration limits for cobalt determination by the present technique were found to lie between 0.1∼50 mM. Stronger solutions could be handled after proper dilutions. The method was not applicable in the presence of other cations giving insoluble tungstates.

Amounts of tungstate required during the amperometric titrations agreed with the molar ratio Co : W of unity and agreed with the observations of Smith and Bradbury[2] and Anthon[14], and also of the present author's[1,3] earlier reports. This confirms the composition of the precipitate formed to be $CoWO_4$ i. e. the normal tungstate.

Grateful thanks of the authors are due to Professor S. S. Joshi for keen interest and to Professor G. B. Singh, Head of the Chemistry Department for necessary facilities. The award of a Senior Scholarship to one of us (V. D. A.) from the Ministry of Scientific Research and Cultural Affairs is also acknowledged.

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[14] E. F. Anthon, *J. prakt. Chem.*, (1) **9**, 314 (1836).