was observed in the separation of one from the other at the proper time, intermixtures were formed.

Cadmium cobaltinitrite, $Cd_3[Co(NO_2)_6]_2$, was isolated from the mother liquor by fractional crystallization, and was obtained as a bright canary-yellow compound. It was found to be stable both in solution, and in the solid form. It was slightly hygroscopic, insoluble in cold water, and only slightly soluble in alcohol and ether, but dissolved readily in boiling water.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE ELECTROMETRIC DETERMINATION OF SULFUR IN SOLUBLE SULFIDES

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Introduction

When the bimetallic electrode system previously described[1] is used, the end-point in the electrometric titration of sodium sulfide[2] with an ammoniacal silver solution is unusually sharp. The e.m.f. rises slowly and sometimes irregularly at first, then there is a rise of 200 to 400 millivolts just before the end-point is reached, after which the completion of the reaction is marked by a very abrupt fall in potential. There is often a reversal of polarity during the titration which makes the first part of the rise apparently a fall. The proposed method is based upon the reaction used by Lestelle,[3] the precipitation of silver sulfide in alkaline solution by titration with standard ammoniacal silver solution. It is, however, much more simple and accurate than his visual determination of complete precipitation. The change in e.m.f. at the end-point is so great that it is never necessary to plot the curve.

Experimental Part

The sodium sulfide solution used in this work was prepared by absorbing 9 to 10 g. of hydrogen sulfide in a solution of 96 g. of sodium hydroxide and diluting to 6 liters.

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[1] Willard and Fenwick, THIS JOURNAL, **44**, 2516 (1922).

[2] This is by no means the first attempt to utilize an electrometric indicator for detecting the completion of the precipitation of an insoluble sulfide. A number of workers have studied this end-point in various solutions and with different electrode systems but have met with rather doubtful success. Dutoit and v. Weisse, *J. chim. phys.*, **9**, 578 (1911). Treadwell and Weiss, *Helvetica Chim. Acta*, **2**, 680 (1919). Pinkhof, "Over de toepassing der elektrometrische titraties," *Dissertation*, Amsterdam, **1919**.

[3] Lestelle, *Compt. rend.*, **55**, 739 (1862).

The titrating solution was a 0.05 *N* silver nitrate solution containing an excess of about 30 cc. of 28% ammonium hydroxide per liter and was standardized gravimetrically by precipitation of the chloride.

Samples of the sulfide solution were titrated in the cold, with an initial volume of 75 cc. The addition of more sodium[4] or ammonium hydroxide made no difference either in the quantitative or qualitative character of the end-point.

TABLE I

ELECTROMETRIC TITRATION OF A STANDARD SULFIDE SOLUTION

10.00 cc. of Na_2S taken

0.05 *N* $(NH_3)_2Ag^+$ req. Cc.	S in 10.00 cc. of Na_2S Mg.	0.05 *N* $(NH_3)_2Ag^+$ req. Cc.	S in 10.00 cc. of Na_2S Mg.
18.05	14.47	18.02	14.43
18.04	14.46	36.05[a]	14.45
18.07	14.48	...	Av. 14.46

[a] 20.00 cc. of Na_2S taken.

The weight of sulfur in 10.00 cc. of this solution as determined by the Willard-Cake hypobromite oxidation method[5] was 14.48 mg., a variation of only 0.02 mg. from the average of the results obtained electrometrically. In Table VI a single titration of another solution showed a variation of 0.13 mg. from the value obtained by oxidation. Theoretically, the former method is 4 times as accurate as the latter since the ratio of the equivalents of sulfur in the two reactions is as 1 to 4 but in actual practice at least equal accuracy is claimed for the precipitation method, since it requires fewer operations and standard solutions and, incidentally, less time. The titrating solution is absolutely stable and can be very accurately standardized.

Effect of Sulfite

In taking up the effect of the more common impurities in the alkali sulfides, sulfite was the first to be investigated. Known amounts in the

TABLE II

EFFECT OF SULFITE

10.00 cc. of Na_2S taken

SO_3^{--} added G.	0.05 *N* $(NH_3)_2Ag^+$ req. Cc.	SO_3^{--} added G.	0.05 *N* $(NH_3)_2Ag^+$ req Cc.
none	17.91	0.625[a]	26.75
0.125	17.85	1.25	17.85
0.625	17.84	2.5	17.83
		Av., all titr. in presence of SO_3^{--}	17.84
		(Based on 10.00 cc. of Na_2S)	

[a] 15.00 cc. of Na_2S taken.

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[4] When insufficient sodium hydroxide is present the precipitate does not coagulate nor does the solution clear readily in the vicinity of the end-point.

[5] Willard and Cake, THIS JOURNAL, **43,** 1610 (1921).

form of a solution of sodium sulfite were added to sulfide samples prepared for analysis. The final volume was 100 cc.

The sharpness of the end-point was not in the least impaired by the presence of various concentrations of sulfite. However, the titrations were slightly, but uniformly, lower than in the absence of this substance. It was concluded that this was due to a slight alteration in the nature of the end-point and not to any chemical effect. In any case the difference was only 0.07 cc., equivalent to 0.056 mg. of sulfur, which is negligible for all practical purposes.

Effect of Sulfate

The effect of the presence of sulfate upon the sulfide titration is shown in Table III.

TABLE III

EFFECT OF SULFATE

Sulfate was added to the sulfide samples as a solution of $Na_2SO_4.10H_2O$. The final volume in each case was 100 cc.

SO_4^{--} added G.	0.05 *N* $(NH_3)_2Ag^+$ req. Cc.	SO_4^{--} added G.	0.05 *N* $(NH_3)_2Ag^+$ req. Cc.
10.00 cc. of Na_2S taken	Titrated slowly	15.00 cc. of Na_2S taken	Titrated rapidly
none	17.80	none	26.47
0.12	17.74	0.6	26.42
0.60	17.72	2.4	26.42
1.2	17.63	...	...
2.4	17.61	...	...

The end-point was entirely normal in character. In the presence of sulfate, just as with sulfite, slightly less solution was required. In the first series this varied with the concentration of sulfate to a maximum of 0.19 cc. but in the second series, which was run more rapidly, this deficit was constant and amounted only to 0.05 cc., equivalent to 0.04 mg. of sulfur. It is believed that part, if not all of the apparent concentration effect was due to oxidation of the sulfide solution.

Effect of Chloride

Chloride did not interfere with the sharpness of the end-point even when present in large quantities but caused a more marked decrease than either sulfite or sulfate in the amount of silver required. This error in-

TABLE IV

EFFECT OF CHLORIDE

Conc. NH_4OH added Cc.	Cl^- added G.	$(NH_3)_2Ag^+$ req. Cc.	Error due to end-point effect
	First series.	10.00 cc. of Na_2S taken	
none	none	17.55	
none	0.1	17.46	
none	0.5	17.48	0.08 cc. = 0.06 mg. S.

TABLE IV (*Continued*)

Conc. NH_4OH added Cc.	Cl^- added G.	$(NH_3)_2Ag^+$ req. Cc.	Error due to end-point effect
	Second series. 10.00 cc. of Na_2S taken		
none	none	17.46	
10	1.0	17.24	0.22 cc. = 0.18 mg. S.
10	2.0	17.13	0.33 cc. = 0.26 mg. S.
	Third series. 15.00 cc. of Na_2S taken		
none	none	26.08	
10	2.0	25.77	0.31 cc. = 0.25 mg. S.

creased with the concentration of chloride but was somewhat decreased by the addition of ammonia to the sulfide solution probably because this increased the solubility of silver chloride.

Effect of Thiosulfate

The presence of thiosulfate rendered the potential drop with excess of the titrating solution less distinct but did not seriously affect the preceding rise nor the clarity of the end-point in general.

TABLE V

EFFECT OF THIOSULFATE

Thiosulfate was added as a solution of $Na_2S_2O_3.5H_2O$. The final volume was 100 cc.

$S_2O_3^{--}$ added G.	Vol. 0.05 *N* $(NH_3)_2Ag^+$ req. Cc.	$S_2O_3^{--}$ added G.	Vol. 0.05 *N* $(NH_3)_2Ag^+$ req. Cc.
10.00 cc. of Na_2S taken		15.00 cc. of Na_2S taken	
none	16.89	none	25.23
0.12	16.82	0.58	25.16
0.58	16.82	..	...
1.17	16.82	..	...
2.34	16.82	..	...

The deficit due to the presence of thiosulfate was 0.07 cc., the equivalent of 0.056 mg. of sulfur.

Effect of Polysulfide

A fresh solution of sodium sulfide was prepared and one portion of it shaken vigorously with pure, freshly precipitated sulfur from sodium thiosulfate in order to form polysulfide. Both solutions were titrated electrometrically and the total sulfur content was determined by hypobromite oxidation.[5]

TABLE VI

EFFECT OF POLYSULFIDE

Sample Cc.	0.05 *N* $(NH_3)_2Ag^+$ req. Cc.	S in 10.00 cc. (elec.) Mg.	Total S in 10.00 cc. (by oxidation) Mg.	Difference Mg. S
10.00 Na_2S	23.53	18.86	18.73	+0.13
12.50 Na_2S	29.42	18.86		
10.00 Na_2S_x	23.52	18.85	19.44	−0.58
12.50 Na_2S_x	29.43	18.87		

Using the electrometric method no difference between the two solutions could be detected although the total sulfur content varied considerably, showing that only the sulfur present as normal sulfide is titrated.

Determination of Sulfur in Steel

To apply this titration to the determination of sulfur in steel, 2 samples from the Bureau of Standards were analyzed.

A 10g. sample of steel was placed in a 250cc. flask connected through a condenser to a hydrogen generator, a dropping funnel for admitting acid and a "10-bulb tube" containing 100 cc. of a 10% sodium hydroxide solution. The apparatus was flushed out with hydrogen, 100 cc. of hydrochloric acid (sp. gr. 1.1) added and when the rapid evolution of hydrogen began to abate the solution was boiled. The stream of hydrogen was continued for 5 minutes after the steel had dissolved. The sodium hydroxide solution was washed into a beaker and titrated with standard ammoniacal silver solution. After the absorption process, the completion of the determination was a matter of only 2 or 3 minutes.

TABLE VII

DETERMINATION OF SULFUR IN STEEL

			Certificate Value % S	
B. of S. Steel	Sample G.	S Found %	Oxidation method	Evolution method
1.0% C	10.0000	0.026	0.027	0.028
B.O.H.	10.0034	0.026	...	...
0.1% C	10.0006	0.032	0.035	0.036
B.O.H.	10.0042	0.032	...	...

Summary

The electrometric end-point in the precipitation of sulfide by an ammoniacal silver solution is extremely sharp and gives a rapid and very accurate method for determining sulfide sulfur in the presence of sulfite, sulfate, chloride, thiosulfate and polysulfide.

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