[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE GRAVIMETRIC AND VOLUMETRIC DETERMINATION OF ZINC[1] PRECIPITATED AS ZINC MERCURY THIOCYANATE.

BY GEORGE S. JAMIESON.

Received April 19, 1918.

The determination of zinc in alloys as zinc mercury thiocyanate has been described by G. E. F. Lundell and Mai K. Bee.[2] The zinc was precipitated after the removal of the copper by electrolysis from the solution of the alloy, by a reagent which contained 39 g. of potassium thiocyanate and 27 g. of mercuric chloride per liter of solution. The usual practice was to add 25 cc. of this reagent for each 100 cc. of the solution containing the zinc. In order to get a quantitative precipitation of the zinc they found it necessary to take precautions so that the amount of free acid in the zinc solution did not exceed 5 %. After the addition of the thiocyanate reagent, the solution was thoroughly stirred and allowed to stand for about a half hour before filtration. The precipitate was collected on a Gooch crucible and washed with a solution containing 10 cc. of the thiocyanate reagent and 490 cc. of water, on account of the solubility of the zinc mercury thiocyanate in pure water. The crucible containing the precipitate was dried for an hour between 102 and 108° and weighed. Lundell and Bee calculated the weight of the zinc by multiplying the weight of the precipitate by 0.1266, which was based upon the assumption that the double thiocyanate after drying has the composition $ZnHg(SCN)_4.H_2O$. However, the factor 0.13115, calculated from the anhydrous zinc mercury thiocyanate should be used, because no water is obtained when the double salt, previously dried at 102°, is heated in a closed tube. Furthermore, excellent results are obtained by employing a precipitating reagent prepared with ammonium thiocyanate in place of the potassium salt which was especially recommended by Lundell and Bee. In applying this method to the determination of zinc, it should be observed that cadmium, cobalt, copper, bismuth, manganese, and mercurous compounds give insoluble double thiocyanates. Nickel in small amounts does not interfere appreciably with the method. The former investigators stated that arsenious compounds interfered. However, it will be shown below that zinc can be satisfactorily determined in zinc arsenite without removing the arsenic. When appreciable quantities of ferric compounds are present, it is best to reduce them with sulfur dioxide; otherwise some of the ferric thiocyanate is carried down with the zinc precipitate.

The volumetric determination of zinc is based upon the precipitation of zinc mercury thiocyanate which is then titrated with a standard solu-

---

[1] Published by permission of the Secretary of Agriculture.

[2] *Trans. Am. Inst. Met.*, 1914, pp. 146–147; *C. A.*, 8, 3404 (1914).

tion of potassium iodate in the presence of strong hydrochloric acid and an immiscible solvent such as chloroform in a manner similar to the titration of cuprous thiocyanate which has been previously described.[1] The volumetric method was found more rapid than the gravimetric and the results given below show that it was very satisfactory.

In order to test the gravimetric method two solutions of zinc sulfate were prepared from Kahlbaum's purest zinc sulfate. These solutions were standardized by the well-known phosphate method. Measured volumes of these solutions were taken in perfectly cleaned small beakers. Each solution was treated with 20 to 25 cc. of the thiocyanate reagent and 20 cc. of water. The solutions were vibrated by striking the sides of the beakers with a stirring rod to facilitate the separation of the crystals. After the solution had stood for about 5 minutes, they were briskly stirred with a glass rod previously moistened with water, for about a minute. This treatment permitted the rod to be easily rinsed free from the precipitate so that it could be removed from the beaker. In all cases, the solutions were allowed to stand at least an hour before filtration. The precipitates were collected on Gooch crucibles and washed 4 or 5 times with the washing solution described above. The crucibles containing the precipitates were dried for an hour at 102° to 108° and weighed. The following results were obtained, using the factor 0.13115:

TABLE I.—GRAVIMETRIC ANALYSES.

No.	Zinc taken.[2] G.	$ZnHg(SCN)_4$. G.	Zinc calc. G.	Error. G.
1	0.0321	0.2454	0.0321	0.0000
2	0.0321	0.2455	0.0321	0.0000
3	0.0321	0.2453	0.0321	0.0000
4	0.1028	0.7857	0.1030	+0.0002
5	0.0308	0.2352	0.0308	0.0000
6	0.0016	0.0132	0.0017	+0.0001
7	0.0321	0.2458	0.0322	+0.0001
8	0.0308	0.2348	0.0308	0.0000
9	0.0925	0.7061	0.0926	+0.0001
10	0.0843	0.6422	0.0842	—0.0001
11	0.0617	0.4689	0.0615	—0.0002

The zinc in Expts. 8 to 11 was precipitated with a reagent prepared with ammonium thiocyanate instead of the potassium salt. Also this reagent was used in the washing solution. It will be observed from the table of analyses that satisfactory results were obtained with both precipitating reagents.

In order to test the volumetric method for the determination of zinc when precipitated as the double thiocyanate, a solution containing 19.644 g.

---

[1] THIS JOURNAL, **30,** 760 (1908).

[2] Calculated from results obtained by standardization of the zinc sulfate solution.

of normal potassium iodate in 1000 cc. was prepared. According to the equation of the reaction

$$ZnHg(SCN)_4 + 6KIO_3 + 12HCl = ZnSO_4 + HgSO_4 + 2H_2SO_4 + 4HCN + 6ICl + 6KCl + 2H_2O$$

1 cc. of this solution would be equivalent to 0.00100 g. of zinc. When this potassium iodate solution was exhausted another twice as strong was prepared. For convenience, measured volumes of the two standard zinc solutions, mentioned above, were precipitated and allowed to stand for an hour or longer as previously described. The solutions were filtered on 7 cm. washed filters using a gentle suction. Then the filters were washed 4 or 5 times with small quantities of the washing solution. When the filters had drained, the suction was stopped. The filters were removed from the funnels and were folded so that they could be put into 8-ounce glass-stoppered titration bottles. A thoroughly cooled mixture of 35 cc. of concd. hydrochloric acid and 10 cc. of water along with 7 to 8 cc. of chloroform was added to one of the titration bottles containing the zinc mercury thiocyanate, because it is best to titrate immediately after adding the acid to the precipitate. During the first part of the titration, the potassium iodate solution is added rapidly while rotating the bottle in order to keep the contents mixed. When the iodine which is liberated during the first stage of the reaction has disappeared from the solution, the stopper is inserted and the contents of the bottle are thoroughly mixed by shaking for about half a minute. From this point the titration is

TABLE II.—VOLUMETRIC ANALYSES.

No.	Zinc taken.[1] G.	Cc. of KIO_3 required.	Zinc calc. G.	Error. G.
1	0.0321	32.20	0.0322	+0.0001
2	0.0401	39.90	0.0399	—0.0002
3	0.0401	40.30	0.0403	+0.0002
4	0.0160	16.20	0.0162	+0.0002
5	0.0160	15.90	0.0159	—0.0001
6	0.0411	41.10	0.0411	0.0000
7	0.0616	61.30	0.0613	—0.0003
8	0.0493	49.40	0.0494	+0.0001
9	0.0493	49.30	0.0493	0.0000
10	0.0720	72.30	0.0723	+0.0003
11	0.0411	41.10	0.0411	0.0000
12	0.0925	46.15	0.0923	—0.0002
13	0.1007	50.35	0.1007	0.0000
14	0.0822	41.00	0.0820	—0.0002
15	0.1028	51.20	0.1024	—0.0004
16	0.0411	20.55	0.0411	0.0000
17	0.0966	48.15	0.0963	—0.0003
18	0.0616	30.75	0.0615	—0.0001
19	0.0493	24.60	0.0492	—0.0001

[1] Calculated from results obtained by standardization of the zinc sulfate solution.

continued slowly, shaking the closed bottle thoroughly after each addition of potassium iodate until the iodine color has disappeared from the chloroform indicator which marks the end-point. If more than 50 cc. of the potassium iodate solution is required for the titration, 10 to 15 cc. more of conc. hydrochloric acid is added in order to prevent the hydrolysis of the iodine monochloride which is formed during the reaction. The results are shown in Table II.

Analyses 12 to 19 were made with a solution which contained 39.2882 g. of potassium iodate in 1000 cc. and 1 cc. was equivalent to 0.002000 g. of zinc. Analyses 16 to 19 were made by precipitating the zinc with a reagent prepared from ammonium thiocyanate. The very satisfactory results obtained with the test analyses show that the reaction of the titration may be represented by the equation given above.

The method was applied to the analysis of two samples of commercial zinc arsenite. Weighed portions were dissolved in 3 cc. of conc. hydrochloric acid. About 10 cc. of strong sulfur dioxide water was added and the solutions were heated upon the steam bath until the odor of sulfur dioxide had largely disappeared. This treatment was made to reduce the ferric chloride because it was previously found that there was enough iron in these samples to give the precipitated zinc mercury thiocyanate a strong purple color which could not be removed by washing. When the heated solutions had cooled to room temperature 25 cc. of the reagent prepared from ammonium thiocyanate and mercuric chloride was added and the analyses were finished as described above. The precipitates were titrated with a solution which contained 39.288 g. of potassium iodate in 1000 cc. and had the value 1 cc. = 0.002498 g. of ZnO. The following results were obtained:

TABLE III.—ANALYSES OF COMMERCIAL ZINC ARSENITE.

No.	Zinc arsenite. G.	Cc. KIO_3 required.	Zinc found. %.	Zinc determined by phosphate method. %.
1	0.2117	47.30	55.62	55.66
1	0.2167	48.50	55.59	...
1	0.2146	48.00	55.68	...
1	0.2518	56.30	55.66	...
2	0.1217	27.20	55.64	55.59
2	0.1607	35.90	55.61	...
2	0.2110	47.15	55.63	...
2	0.2178	48.65	55.61	...

These analyses show that arsenious compounds do not interfere with the accuracy of the method. The results of this investigation show that zinc can be readily determined by the gravimetric method of Lundell and Bee or by the volumetric procedure described above, providing the directions are closely followed.

WASHINGTON, D. C.