

peated several times, except that the solutions were saturated for 5-10 minutes with  $H_2S$  at  $20^\circ$ : a precipitate formed when the volume became 60-70 cc.

*Delicacy of Confirmatory Test for Tin.*—0.5 Sn as  $SnCl_4$  was treated in several experiments according to P. 47: in all cases a precipitate of  $SnS_2$ , and in most cases one of  $Hg_2Cl_2$ , was obtained.

## A STUDY OF THE FERROCYANIDE METHOD FOR THE DETERMINATION OF ZINC

BY W. H. SEAMAN.

Received October 15, 1906.

The Committee on Uniformity of Analysis for the Society of Western Chemists and Metallurgists in their provisional method recommended the employment of granulated lead to remove copper, previous to titration. Low in his "Technical Methods," says—"The use of granulated lead as a precipitant of copper is not recommended."

This disagreement of opinion between authorities of their weight persuaded me to settle the question for myself and led to a fuller study of the conditions influencing the determination, the results of which follow. In all instances the burette was kept covered until end point was determined in order to avoid any possible tendency to reach checks by knowing the burette reading.

*Effect of Acid.*—Bulk at starting 150 cc.; weight of zinc used 0.18546 gram. Ammonium chloride 5 grams.

Excess of acid in CC.	CC. of Ferrocyanide consumed	
	$85^\circ - 40^\circ$	$95^\circ - 70^\circ$
0	38.2	38.2
1	37.1	37.1
3	37.0	37.0
5	37.0	37.0
7.5	37.0	37.1
10	37.15	37.4
15	37.3	38.1
20	38.0	38.6

A certain amount of free hydrochloric acid is necessary to sharpen the end reaction. An excess of from one to ten cc. does not affect the results sensibly. Beyond these limits increase of acid increases consumption of ferrocyanide, particularly when the titration is conducted at a high temperature.

*Effect of Potassium Chlorate.*—Conditions as before with constant use of an excess of 5 cc. of concentrated hydrochloric acid.

Weight of potassium chlorate	Consumption of Ferrocyanide	
	85° — 40°	95° — 70°
0	37.1	37.1
1	37.1	37.3
2	37.3	37.5
3	37.5	37.7
4	37.6	37.9
5	37.6	38.1

The effect of the chlorate is to evolve chlorine, which decomposes the ferrocyanide. A high temperature increases this decomposition and increasing the amount of free acid also increases it. Low, in his directions is particular to emphasize the necessity for decomposing the chlorates after evaporation to dryness and the above results will no doubt add emphasis to his warning. The bad effect of undecomposed chlorate is most clearly demonstrated by titrating to end reaction and then testing after standing one minute, when it will be found necessary to add from one-tenth to three-tenths of a cc. additional. This fading out continues until room temperature is reached, beyond which I have not followed it. In some instances I have, after reaching the end point, waiting a minute at a time, continued adding ferrocyanide until I have added as much as 5 cc. additional. Sometimes it is necessary to employ chlorate to ensure decomposition of the ore. If more than one gram is employed, the operator should be sure to follow Low's instruction to decompose it, before titrating; otherwise he is apt to become uncertain as to his end point, which will lead him to report too high a result.

*Effect of Increase of Acid with Constant Amounts of Chlorate.*—Conditions as before, except as stated.

CC. of acid	With one gram chlorate		With five grams chlorate	
	85° — 40°	95° — 70°	85° — 40°	95° — 70°
0	38.0	38.1	38.0	37.9
3	37.0	37.1	37.3	37.5
5	37.0	37.1	37.6	37.8
7.5	37.0	37.5	38.0	38.2
10	37.5	37.8	38.4	38.8
15	38.0	38.1	39.0	39.3
20	38.1	38.3	41.0	42.2

The evil effects of large amounts of free acid, accompanied with chlorate are here shown; consumption of ferrocyanide being largely increased with titrating at high temperature.

*Effect of Ammonium Chloride.*—The effects of this salt with varying amounts of acid were studied. Conditions as before, except as noted.

CC. of acid	Ferrocyanide consumed			
	With five grams chloride		With ten grams chloride	
	85°—40°	95°—70°	85°—40°	95°—70°
0	37.1	37.1	37.1	37.0
3	37.0	37.1	37.1	37.1
5	37.0	36.9	36.9	37.0
10	37.0	37.0	37.1	37.2
15	37.2	37.3	37.3	37.4
20	37.8	38.0	38.4	38.7

The effect of ammonium chloride is to help settle the precipitate and contributes to sharpening the end reaction. There is no apparent evil effect, the increase of acid accounting for the high consumption in the last two experiments.

*Effect of Metallic Salts.*—In the following experiments 0.185 gram of zinc was employed with 5 cc. excess hydrochloric acid and five grams of ammonium chloride. Volume at beginning of titration 150 cc.; temperature at beginning titration never above 85° and at end never below 40°. Metallic salts were added in quantity to equal the weight of metal stated, approximately.

Weight of metal added	Iron	Aluminum	Copper	CC. of Ferrocyanide consumed				Lime
				Lead	Cadmium	Tin	Manganese	
0	37.0	....	....	....	....	....	....	....
0.05	47.4	37.0	46.6	39.3	42.3	41.5	47.5	37.0
0.10	57.5	37.0	56.0	41.7	47.7	46.0	57.7	37.0
0.15	67.4	37.0	65.2	44.0	52.9	....	67.6	37.0
0.20	....	37.1	74.2	46.4	58.4	....	....	37.0
0.25	....	37.0	83.8	48.7	64.1	....	....	37.0

The influence of iron, cadmium and copper has long been known, as well as that of manganese. The bad influence of lead has been generally overlooked, owing no doubt to the fact that one per cent. of lead increases the apparent amount of zinc by only about thirty-two hundredths of one per cent., owing to its higher atonic weight and one cc. of ferrocyanide will precipitate about three times as much lead as zinc. As lead is frequently a constituent of zinc ores, those assayers who have not been removing it in determining zinc have been getting high results; varying also, since frequently more or less of the lead would be rendered insoluble, and all of it would not follow into the liquid to be titrated. Low is the only one, to my knowledge who has sounded a warning concerning lead and he has not been as emphatic as now seems necessary. It should be noted that aluminum, in the form of chloride, does not affect the results and it naturally suggested that aluminum might be used to remove copper. A set of experiments was made using 0.25 grams of zinc oxide, corresponding to 0.200875 of metallic zinc, five grams ammonium chloride, five cc. excess hydrochloric acid and varying amounts of copper, removing the copper with metallic lead.

Weight of copper added	CC. of Ferrocyanide consumed
0.	40.8
0.02046 gram	42.4
0.05850 "	43.5
0.10326 "	45.7

The disappearance of color indicated the complete precipitation of copper, lead going into solution corresponding atomically to the weight of copper removed, increasing the percentage of zinc but not to the same extent that an equal weight of copper would have done had it been allowed to remain. Experiments were then made to determine the influence of aluminum when used to remove copper and those results are found in the last table, at the end of this article.

*Influence of varying amounts of zinc.* In these experiments the bulk at the beginning of the titration was 150 cc. ; excess of hydrochloric acid five cc. ; ammonium chloride five grams, together with the amount formed in neutralizing the first excess of hydrochloric acid in effecting solution of the zinc. Temperature of titration  $85^{\circ}$ - $40^{\circ}$ . A blank assay was run to determine the amount of ferrocyanide required to give the end reaction, a strongly marked coloration being selected. In this connection I desire to say that I find that more of the ferrocyanide is required to color the uranium solution when a blank assay is run, than when the ferrocyanide is run into an equal bulk of acidulated water.

Weight of Zinc	Ferrocyanide consumed		Factor calculated	
	Used	Corrected	Used	Corrected
0.07418	15.0	14.5	0.00494	0.00505
0.18546	37.0	36.5	0.00501	0.00508
0.37092	73.0	72.5	0.00503	0.00510
	Average factor		0.00501	0.00507

Another series was run using zinc oxide, ignited previous to weighing, treating each portion with 10 cc. strong nitric acid, then with 5 cc. strong hydrochloric, adding 5 grams of ammonium chloride and evaporating to dryness ; then adding 5 cc. of strong ammonia water making alkaline, followed with 25 cc. of hot water, neutralizing with dilute hydrochloric acid, then adding 5 cc. of strong hydrochloric acid, diluting to 150 cc., heating and commencing titrating at  $85^{\circ}$ , completing the same before the temperature fell to  $40^{\circ}$ . The ferrocyanide used was made equal to about 1 cc., equal to 0.004 grams of zinc.

Weight of Zn	Equivalent w't of Zinc	CC. of Ferrocyanide Consumed		Strength of solution	
		Consumed	Corrected	Consumed	Corrected
0.05	0.0401	10.7	10.2	0.00375	0.00393
0.10	0.0803	20.9	20.4	0.00384	0.00394
0.15	0.1205	30.5	30.0	0.00395	0.00402
0.20	0.1607	40.0	39.5	0.00402	0.00407
0.25	0.2009	49.9	49.4	0.004025	0.00407
0.30	0.2410	60.0	59.5	0.004026	0.00405
0.35	0.2812	70.2	69.7	0.00400	0.00403
		Average factor		0.003944	0.00402

A cursory glance at the above results shows that a slightly different factor is obtained as the amount of zinc varies but the necessity in technical work for standardizing with an amount of zinc approximating the varying percentages of ores is not evident until calculations are made as in the following table :

Per cent. of zinc in ore	Per cent. found using factor nearest corresponding		Per cent. found using average factor		Per cent. found using extreme factors	
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
8.02	8.02	8.02	8.34	8.22	8.56	8.22
16.06	16.05	16.06	16.56	16.32	16.72	16.44
24.10	24.09	24.10	24.03	24.00	24.40	24.18
32.14	32.16	32.14	31.92	31.60	30.00	30.35
40.16	40.16	40.16	39.32	39.52	37.42	38.82
48.20	48.32	48.19	47.38	47.60	45.00	46.76
56.24	56.16	56.18	55.32	55.76	52.65	54.82

Differences of from two-tenths to as much as four per cent. demonstrate that in control and umpire work the operator *must* use the factor nearest corresponding to the percentage of the ore. All determinations depending upon an end color reaction are also much improved in their accuracy, if the operator will run a standard with his daily runs, not so much for a correction in a varying standard solution as to enable him better to judge the end point.

*Effect of Bromine.* But one experiment was made, which showed that the addition of 2 cc. of strong bromine water increased the consumption of ferrocyanide by 1.5 cc.

These experiments led naturally to a modification of the method developed by Low and as it is much shorter, equally as accurate and not at all laborious, I outline it briefly.

*Decomposition of the ore.* Cover 0.5 gram of the ore, in a No. 3 casserole, with 7 cc. concentrated nitric acid, after which add an equal amount of hydrochloric; allow these acids to act for 15 minutes at a temperature not exceeding 60°, after which add 7 grams of ammonium chloride and evaporate to dryness on a hot plate. Remove from this hot plate, make alkaline with ammonia water, 5 cc. is enough, add 15 cc. of bromine water and boil for three minutes and filter while hot, through a 11 cm. filter paper, into a 400 cc. beaker. Wash carefully three times with a hot solution of ammonium chloride and dilute ammonia. Make the filtrate weakly acid with dilute hydrochloric, place a piece of aluminum foil in the beaker, cover with a watch glass and boil for about three minutes, when all copper, lead and cadmium present will be precipitated.

Remove the foil, wash it off and heat to boiling for titration. It is unnecessary to remove the precipitated metals, as their presence does not affect the results.

*Titration.* The operator should use a constant bulk, which may be

150 cc. or 200 cc., as he elects. Add five cc. strong hydrochloric acid and titrate according to the method given by Low, starting the titration at a temperature of about 85° and completing it before temperature falls to 40°.

*Standardization.* A solution of about 22 grams of ferrocyanide to the liter is satisfactory and the acetate, or nitrate, of uranium is used as indicator. If accurate work is to be done, the conditions for standardization should be close to those employed in treating an ore. Zinc oxide, freshly ignited, or metallic zinc may be employed as convenient. Weigh out into casseroles 0.05, 0.1, 0.15 and 0.2 gram of the oxide and treat precisely as if it were an ore, omitting only the bromine treatment, the aluminum foil and the filtration. Run one blank assay to determine the amount of ferrocyanide required to produce the coloration of the indicator to the depth selected by the operator and deduct this from all burette readings. Use the factor nearest corresponding to the percentage of zinc in the ore.

*Remarks.* The ore must be decomposed. The method outlined has decomposed all the varieties of ores that have come under my observation. The operator will observe that on the addition of ammonium chloride there is an evolution of chlorine which assists decomposition. The ammonium chloride also makes the iron precipitate, formed when the ammonium is added, somewhat granular, making the filtration more rapid and eliminating the tendency of the gelatinous iron hydroxide to hold up zinc salts. As much as one gram of a potassium chlorate may be employed to decompose sulphides without disturbing the results; but if more is used, Low's direction to decompose the excess must be followed.

Hydrogen peroxide may be advantageously substituted for the bromine water to remove manganese. If manganese is known to be absent, the treatment may be omitted, just as the aluminum treatment may be omitted in the absence of copper, lead and cadmium.

The following table of results gives a fair idea of the accuracy of the method, the runs being made on different days, to test the accuracy of the method.

Number	Character of sample	CC. of Ferrocyanide consumed				Average
		I	II	III	IV	
1.	0.115 g. of Zn	23.0	23.0	23.0	23.0	23.0
2.	" " and 0.05Cu	23.1	23.0	23.0	23.0	23.025
3.	" " " 0.1 Cu	23.0	23.0	23.0	23.1	23.025
4.	" " " 0.2 Cu	22.9	23.0	23.0	23.0	22.975
5.	" " " 0.05Pb	22.9	23.1	23.1	22.9	23.000
6.	" " " 0.25Pb	22.8	23.0	23.0	23.0	22.950
7.	" " " 0.10Cd	23.0	23.0	23.0	23.0	23.00
8.	" " " 0.10Cd					
	" " " 0.15Pb					
	" " " 0.15Cu	22.9	23.0	23.0	23.0	22.975

	Per cent. of Zinc by Gravimetric method		Per cent. of Zinc by Ferrocyanide method				Average
	I	II	I	II	III	IV	
9. Silicate	39.25	39.24	40.00	40.00	40.00	40.00	40.00
10. Carbonate	53.45	53.49	54.15	54.18	54.33	54.35	54.25
11. Sulphides with Fe, Mn, Pb and Cu	43.12	43.01	43.50	43.62	43.35	43.52	43.49
12. " "	29.78	29.65	30.00	30.08	29.92	29.72	29.93
13. " "	22.10	21.67	22.56	22.56	22.56	22.65	22.58
14. " "	37.84	37.53	38.24	38.36	38.48	38.86	38.48
15. " "	41.62	41.75	42.60	42.80	42.40	42.20	42.50
16. " "	42.28	42.00	43.20	43.40	43.28	43.20	43.27
17. " "	38.76	38.91	39.20	39.25	39.32	39.20	39.40
18. " " and Bi, As, Sb and Ag	14.49	15.34	15.48	15.52	15.43	15.45	15.47
19. " "	6.35	6.43	6.32	6.59	6.50	6.48	6.47
20. " "	13.95	14.21	14.20	14.22	14.22	14.27	14.23

As is generally known, the gravimetric method for the determination of zinc gives low results. I give them to call attention to the differences in results likely to occur by different assayers using the two methods. In technical work the conditions under which the chemist works will generally cause loss of zinc in considerable quantity. It is my opinion that the results for zinc by the ferrocyanide method obtained by technical chemists more nearly approach the absolute amount of zinc in an ore sample than the results of chemists, working slowly, with the gravimetric method.

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## THE DETERMINATION OF ZINC PRESENT AS CARBONATE AND SILICATE IN ORES

BY PERCY H. WALKER AND HERMAN SCHREIBER.

Zinc carbonate ores are more easily reduced than zinc silicate ores, and the former should be more valuable for the same zinc content. It is of some interest, therefore, to determine the relative proportion of zinc carbonate and zinc silicate present in a given ore. This problem presents a number of difficulties. It will not do to determine the carbon dioxide and from it calculate the zinc as carbonate, for the presence of other carbonates even in small amounts would cause absolutely false results. Equally as objectionable would be to determine the silica and calculate to zinc silicate.

Minor<sup>1</sup> suggests determining total zinc in one portion and extracting the zinc carbonate from another portion by boiling 15 minutes with

<sup>1</sup> Chem. Ztg. 13, 1670—Classen's Ausgewählte Methoden der Analytischen Chemie—Vol. 1, page 352.