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A STUDY OF CONDITIONS AFFECTING THE PRECISE DETERMINATION OF ZINC AS THE SULFIDE.

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The necessity of a precise method for the determination of zinc is evident after reading the report of the Sub-Committee on Zinc Ore Analysis,[1] which shows the wide discrepancies encountered in the determination of zinc by the methods in ordinary use. The difficulties to be met by any method are twofold; the quantitative precipitation of zinc sulfide in a form suitable for rapid filtration and washing, and the subsequent conversion of this precipitate to a definite compound.

Concentration of Hydrogen Ion.

Early investigators have shown that the completeness of precipitation of zinc as the sulfide is a function of the concentration of the hydrogen ion, but the complete range of concentration of hydrogen ion, within

Table I.

Change in concentration of hydrogen ion due to sulfuric acid liberated during precipitation of zinc as the sulfide, according to the reaction $ZnSO_4 + H_2S \longrightarrow ZnS + H_2SO_4$. The solution for precipitation contained one g. of zinc ammonium sulfate[2] in a volume of 200 cc.

No.	Initial conc. H^+.[3]	Final conc. H^+.
1	$10^{-3.90}$	$10^{-1.86}$
2	$10^{-3.93}$	$10^{-1.86}$

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[1] This Journal, **26**, 1648 (1904); **29**, 262 (1907).

[2] The pure salt used for all experimental work was prepared by recrystallization of the product obtained from theoretical amounts of zinc sulfate (Kahlbaum's), and ammonium sulfate (Baker and Adamson's analyzed). Its purity was tested by heating a one g. sample in an air bath, and finally over an open Bunsen flame until free from water and from all ammonium salts, then moistening with conc. sulfuric acid and evaporating in the air bath to constant weight. The conc. sulfuric acid was tested for residue on evaporation.

No.	Sample $Zn(NH_4)_2(SO_4)_2.6H_2O$. G.	$ZnSO_4$. Calc. G.	Found. G.	Diff. G.
1	0.9791	0.3935	0.3934	—0.0001
2	0.7741	0.3111	0.3112	+0.0001
3	1.0069	0.4047	0.4046	—0.0001

The air bath consists of a quartz beaker, 8 cm. by 7 cm., supported by means of a nichrome triangle on an iron ring stand. A crucible may be placed on a quartz triangle inside of the beaker, and the contents rapidly evaporated. Using a Bunsen burner the temperature of the crucible is approximately 385°.

[3] The electromotive force method was used for the measurement of the hydrogen ion concentration with the following combination:

$$Hg \mid HgCl, \text{sat. } KCl \mid \text{sat. } KCl \mid H^+ \mid Pt, H_2$$

in which all measurements were made at the temperature of 25°. The value of the pole potential difference Hg | HgCl, sat. KCl for this temperature has been taken as 0.5272 volt.

which the precipitation of zinc sulfide is quantitative has never been definitely established, nor has the increase in concentration of hydrogen ion during precipitation been quantitatively measured so that intelligent provision might be made to keep it within the required range.

That such provision is necessary is shown by the measurements given in the preceding experiment.

Having thus shown the increase in concentration of hydrogen ion during the precipitation of zinc sulfide from a sulfate solution. further experiments were conducted to determine the limits of concentration of hydrogen ion for the quantitative precipitation of zinc, with the results given in the following table and graph (Table II, Fig. 1). The acids chosen for this purpose were sulfuric acid and formic acid, because these are the acids used respectively in the two most accurate methods for the determination of zinc as the sulfide, namely, the Weiss[1] method of precipitation from 0.01 *N* solutions of sulfuric acid, and the Waring[2] method of precipitation from solutions slightly acid with formic acid.[3]

TABLE II.

Incompleteness of precipitation of zinc sulfide as a function of the concentration of hydrogen ion.

a. Sulfuric acid. Volume of solution in each case = 200 cc.

No.	Molarity. H_2SO_4.	Initial[4] conc. H^+.	Sample $Zn(NH_4)_2(SO_4)_2.6H_2O$. G.	Zinc sulfate. Added. G.	Zinc sulfate. Found. G.	Average error.[5] Pts. per 1000. G.
1	0.050	$10^{-1.22}$	1.0004	0.4021	0.3642	121
	0.050	$10^{-1.29}$	0.9999	0.4019	0.3431	
2	0.037	$10^{-1.36}$	1.0010	0.4023	0.3721	79
	0.037	$10^{-1.31}$	1.0005	0.4021	0.3688	
3	0.025	$10^{-1.45}$	1.0009	0.4023	0.3975	10
	0.025	$10^{-1.46}$	1.0009	0.4023	0.3989	
4	0.005	$10^{-1.81}$	1.0008	0.4022	0.4012	4
	0.005	$10^{-1.90}$	1.0002	0.4020	0.3999	

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[1] G. Weiss, *Ueber die quantitative Bestimmung und Trennung von Zink und Nickel*, München, 1906.

[2] THIS JOURNAL, **26**, 1648 (1904); **29**, 265 (1907).

[3] For other methods using formic acid, see: Berg, *Z. anal. Chem.*, **25**, 512 (1886); Bragard, *Ibid.*, **27**, 209 (1888); Dohler, *Chem. Ztg.*, **23**, 399 (1899); Neumann, *Z. anal. Chem.*, **28**, 57 (1889); Funk, *Ibid.*, **46**, 93 (1907).

[4] The initial concentration of hydrogen ion before precipitation is given, owing to the difficulty of running a number of measurements on the final concentration after saturation with hydrogen sulfide.

[5] The scheme of expressing error used in this paper is to take the differences between the theoretical value and the found value and express this difference as a ratio to the theoretical value, as shown in the following example:

Zinc sulfate. Theoretical. G.	Zinc sulfate. Found. G.	Zinc sulfate. Difference. G.	Average difference. G.	Average error. Pts. per 1000.
0.4022	0.4021	—0.0001	—0.00035	0.9
0.4018	0.4012	—0.0006		

b. Formic Acid + formic mixture.[1] Volume of solution = 200 cc.

No.	Formic acid. Cc.	Formic mixture. Cc.	Initial conc. H+.	Sample $Zn(NH_4)_2(SO_4)_2.6H_2O$.	$ZnSO_4$. Added. G.	$ZnSO_4$. Found. G.	Av. error. Pts. per 1000.
5.....	45	25	$10^{-1.61}$	1.0012	0.4024	0.4017	2
6.....	35	25	$10^{-1.84}$	0.9997	0.4018	0.4009	2
7.....	20	25	$10^{-2.16}$	1.0008	0.4022	0.4022	1
	20	25	$10^{-2.08}$	1.0007	0.4022	0.4013	
8.....	10	25	$10^{-2.45}$	1.0008	0.4022	0.4015	1
	10	25	$10^{-2.45}$	1.0009	0.4023	0.4021	
9.....	..	25	$10^{-2.97}$	1.0008	0.4022	0.4021	1
	..	25	$10^{-3.02}$	0.9997	0.4018	0.4012	

c. Formic acid + ammonium formate + ammonium sulfate.[2]

No.	Formic acid. Cc.	Ammonium formate. G.	Ammonium sulfate. G.	Initial conc. H+.	Sample $Zn(NH_4)_2(SO_4)_2.6H_2O$. G.	$ZnSO_4$. Added. G.	$ZnSO_4$. Found. G.	Av. error. Pts. per 1000.
10.....	10	0.70	6.25	$10^{-3.19}$	1.0000	0.4019	0.4014	1
	10	0.70	6.25	$10^{-3.10}$	1.0006	0.4021	0.4023	
11.....	1	0.70	6.25	$10^{-3.98}$	1.0000	0.4019	0.4013	2

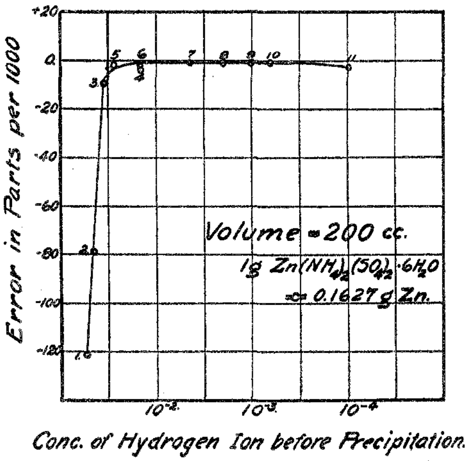

Fig. 1.

From the graph (Fig. 1) it is easily seen that the best range of hydrogen ion for the quantitative precipitation of zinc sulfide is between 10^{-2} and 10^{-3}. With concentrations of hydrogen ion greater than 10^{-2}, the completeness of precipitation falls off rapidly, while with concentrations less than 10^{-3}, although zinc is still quantitatively precipitated, it tends to come down in a slimy form which is difficult to filter.[3]

Now it is also evident from the preceding graph that the method

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[1] Formic acid used was 23.6 molar (d_{20} = 1.205). The molarity column is omitted in this table because of the presence of the formic mixture (see author's method) added for the double purpose of controlling the sulfuric acid liberated during precipitation, and of forming a granular precipitate of zinc sulfide.

[2] Added for same purpose as formic mixture in (*b*).

[3] Regions beyond 10^{-4} were not investigated because of the formation of slimy zinc sulfide. Experiments conducted by Glixelli (*Z. anorg. Chem.*, **55**, 306 (1907)) show that the precipitate from neutral solutions is 4.6 times as soluble as that from acid solutions, the difference in solubility being attributed to the difference in size of the grains. There is also some evidence that zinc sulfide, first precipitated from solutions alkaline with ammonium hydroxide, dissolves in the presence of excess of hydrogen sulfide, a result similar to that reported by McCay in solutions alkaline with sodium or potassium hydroxide. This Journal, **30**, 376 (1908).

of precipitation of zinc sulfide from 0.01 *N* sulfuric acid (point 4 in Fig. 1) lies very close to the danger line with respect to the concentration of hydrogen ion. Moreover no provision is made to control the increase of hydrogen ion during precipitation which is usually carried out in a sulfate solution The following table (Table III) shows the results of 12 determinations of zinc from the pure salt, zinc ammonium sulfate. Fol-

TABLE III.

Determination of zinc by precipitation as the sulfide from 0.01 normal (0.005 molar) sulfuric acid,[1] and conversion of the sulfide to the sulfate.

No.	Sample $Zn(NH_4)_2(SO_4)_2.6H_2O$. G.	$ZnSO_4$. Calc. G.	Found.[2] G.	Difference. G.
1	1.0073	0.4048	0.4038	—0.0010
2	1.0152	0.4080	0.4048	—0.0032
3	1.0103	0.4060	0.4052	—0.0008
4	1.0224	0.4109	0.4093	—0.0016
5	1.0227	0.4110	0.4079	—0.0031
6	1.0083	0.4052	0.4037	—0.0015
7	1.0815	0.4347	0.4342	—0.0005
8	1.0668	0.4288	0.4272	—0.0016
9	1.0003	0.4020	0.4003	—0.0017
10	0.9992	0.4016	0.4013	—0.0003
11	1.0008	0.4022	0.4012	—0.0010
12	1.0002	0.4020	0.3999	—0.0021
			Average,	—0.0015

The Average error is 4 parts per 1000.

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[1] Weiss (*loc. cit.*) gives the following results for the precipitation of zinc as the sulfide from 0.01 *N* sulfuric acid, with conversion of the sulfide to the oxide at a temperature of 850°.

No.	Sample $ZnSO_4$. G.	$ZnSO_4$. Added. G.	Found. G.	Difference. G.
1	0.8046	0.4048	0.4048	0.0000
2	0.8046	0.4048	0.4052	+0.0004

Now the experiments of Borneman (*Z. anorg. Chem.*, 82, 216 (1913)) show that zinc sulfide on roasting is partially converted to the compound $3ZnO.2SO_3$ at a temperature of 840°, and converted to zinc oxide only at 935°.

That Weiss was aware of the incomplete transformation to the oxide at the temperature of 850°, is shown by his results on the conversion of zinc sulfate to zinc oxide.

No.	Sample $ZnSO_4$. G.	ZnO. Added. G.	Found + impurity. G.	SO_2 determined by pptn. with $BaCl_2$. G.	ZnO. Corrected. G.	Difference. G.
1	0.8046	0.4048	0.4064	0.0003	0.4061	+0.0013
2	0.8046	0.4048	0.4060	0.0002	0.4058	+0.0010
3	0.8046	0.4048	0.4059	0.0003	0.4056	+0.0008
4	0.8046	0.4048	0.4060	0.0006	0.4054	+0.0006

The results from 0.01 *N* sulfuric acid were not corrected for SO_3, nor for impurities in the reagents.

[2] A determination of the blank with the same reagents gave a residue of 0.0003 g. for which correction has been made in the above results.

lowing the directions given in the Bureau of Standard Certificate of Analysis of Sheet Brass, Sample No. 37, the ammonium salts in the original sample were first removed by a double evaporation with conc. nitric and hydrochloric acids, and the residue evaporated to fumes with conc. sulfuric acid. The solution was diluted, neutralized with sodium hydroxide, made up to 250 cc. and enough sulfuric acid added to make the solution 0.01 normal. The zinc sulfide was precipitated at room temperature, filtered and washed with a cold aqueous solution, 0.01 normal with sulfuric acid saturated with hydrogen sulfide. The zinc was determined by conversion of the sulfide to the sulfate.

The Weiss method, therefore, is seen to be in the danger zone with regard to concentration of hydrogen ion, in that it gives an initial concentration of hydrogen ion sensibly equal to $10^{-1.85}$ and makes no provision for increase in concentration of hydrogen ion; also it leaves room for doubt as to the nature of the compound formed on ignition of zinc sulfide.

The Waring method, on the other hand, meets the difficulties in precipitation by working with a very low concentration of hydrogen ion, and by the presence of sodium formate in variable amount, taking care of the acid which is formed as a result of the precipitation.

The method developed in this paper provides not only for a much wider range of concentration of hydrogen ion than the Waring method, but also for the definite control of hydrogen ion within this range.

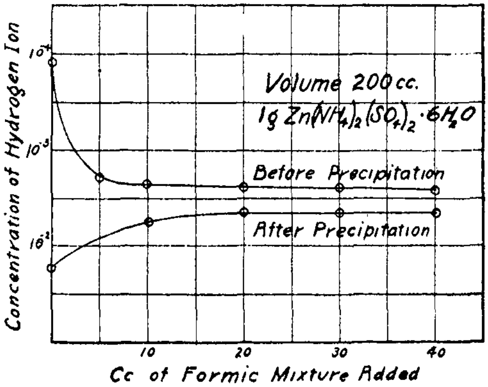

Fig. 2.

The following table and graphs (Table IV, Figs. 2 and 3) show that such a control may be established by means of ammonium formate[1] alone, or by ammonium formate and citrate[2] together, whereby the concentration of hydrogen ion can be kept within the range desirable for the quantitative precipitation of zinc, namely 10^{-2} and 10^{-3}. In order to maintain uniform conditions in all experimental work, a

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[1] Ammonium formate is used because of its volatility in the subsequent treatment of the zinc sulfide.

[2] Ammonium citrate is used for the purpose of forming complexes with interfering metals. Spiller (*J. Chem. Soc.*, **10**, 113 (1857)) has shown that the alkali citrates and citric acid will entirely prevent the precipitation of manganese sulfide, and will cause incomplete precipitation of the sulfides of iron, unless the solution is boiled or allowed to stand for a long time. The sulfides of cobalt, nickel and zinc are precipitated as usual.

stock solution, or "formic mixture," is made up, containing in one liter, 30 cc. ammonium hydroxide (15 molar), 200 cc. formic acid (23.6 molar), and 250 g. ammonium sulfate.[1]

Varying amounts of this formic mixture were used in a series of experiments where a uniform amount, one g. of zinc ammonium sulfate (0.1627 g. zinc) was used, and the total volume of the solution from which the precipitation of zinc sulfide was to be made, was kept definitely at 200 cc. each time. The measurement of the hydrogen ion concentrations in these solutions, gave the values of this factor before precipitation.

TABLE IV.

Change of hydrogen ion concentration as a function of sulfuric acid liberated.

a. Formic mixture.

No.	Formic mixture. Cc.	Initial conc. H^+.	Final conc.[2] H^+.
1	0	$10^{-3.90}$	$10^{-1.77}$
2	10	$10^{-2.71}$	$10^{-2.25}$
3	20	$10^{-2.60}$	$10^{-2.35}$
4	30	$10^{-2.62}$	$10^{-2.35}$
5	40	$10^{-2.58}$	$10^{-2.35}$

b. Formic mixture + ammonium citrate.[3] Using 5 g. citric acid and 2.4 cc. 15 *M* ammonium hydroxide.

1	0	$10^{-3.71}$	$10^{-3.39}$
2	10	$10^{-3.19}$	$10^{-2.99}$
3	20	$10^{-2.99}$	$10^{-2.85}$
4	30	...	$10^{-2.78}$
5	40	$10^{-2.86}$	$10^{-2.72}$

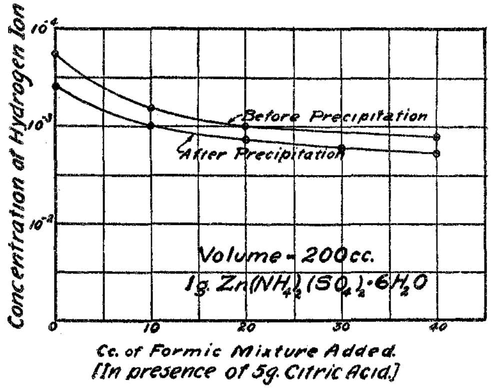

Fig. 3.

While the concentration of hydrogen ion is undoubtedly the most important factor in the precipitation of zinc sulfide, there are certain other conditions favorable to quantitative precipitation which should be mentioned at this point.

Presence of Ammonium Salts.—The "salting-out" of zinc sulfide by Treadwell's[4] method using a high concentration of an ammonium salt of a

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[1] For the purpose of forming a granular precipitate of zinc sulfide.

[2] Since the presence of hydrogen sulfide makes it difficult to measure the concentration of hydrogen ion after actual precipitation, the final concentration of hydrogen ion in each case was obtained by measurement of blank solutions containing the correct amount of formic mixture and 0.244 g. sulfuric acid, the theoretical amount freed from one g. of zinc ammonium sulfate during precipitation of zinc sulfide.

[3] A stock solution of citric acid, 200 g. per liter, was used in the experimental work, and neutralized with 15 molar ammonium hydroxide.

[4] *Analytical Chemistry*, 3rd Ed., 2, 160 (1914), John Wiley & Sons, New York.

strong acid, is well known; and it has been shown by the experiments of G. H. Kramers[1] that ammonium sulfate, chloride, and sulfocyanate are equally good for this purpose. Since zinc is usually precipitated from a sulfate solution in the analysis of an alloy or an ore, ammonium sulfate has been chosen by the present authors for the purpose of "salting-out" zinc sulfide.

Volume for Precipitation.—It has been found advisable in the authors' method to fix the volume at 200 cc. If the amount of zinc present exceeds 200 mg., the value advised by Waring,[2] the volume should be proportionately increased, aliquot portions being taken for precipitation when necessary.

Temperature.—An initial temperature of 95–100° is most favorable for the precipitation of zinc sulfide in a coarsely granular form suitable for rapid filtration and washing.

Method of Saturating with Hydrogen Sulfide.—An Erlenmeyer flask is used for precipitation. After heating to the required temperature, the air over the hot solution is replaced by an atmosphere of hydrogen sulfide,[3] and the solution, as it cools to room temperature, is saturated with hydrogen sulfide under increased pressure. Under these conditions a large reservoir of hydrogen sulfide is available, and quantitative precipitation in solutions where the concentration of hydrogen ion ranges 10^{-2} to 10^{-3} is possible in 25 to 40 minutes.[4]

Time of Standing before Filtration.—The precipitate may usually be filtered off when the supernatant liquid is clear; but the time of settling varies somewhat with different conditions, such as concentration of hydrogen ion, volume, temperature, etc. For this reason standing for 3 to 4 hours is recommended, or even overnight, if interfering metals are not present in large concentration. When this is the case, long standing is to be avoided, since it favors the precipitation of the interfering metal with the zinc.

Conversion of Zinc Sulfide to the Sulfate.—In addition to a knowledge of the conditions favorable for quantitative precipitation, it is necessary to have an accurate method for the estimation of zinc in the precipitate.

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[1] *Analytical Chemistry,* 3rd Ed., 2, 160 (1914), John Wiley & Sons, New York.

[2] THIS JOURNAL, 29, 265 (1907).

[3] A Kipp generator provided with a pressure bulb is used for the supply of hydrogen sulfide. The generator is connected in series with a wash bottle which contains a manometer bulb with a stem of such length that when the liquid level reaches the bottom of this bulb the pressure in the precipitation flask is approximately one-third of an atmosphere.

[4] As we increase the concentration of hydrogen ion, however, to values equal to or greater than 10^{-2}, the rapidity of precipitation of zinc sulfide decreases. Thus it is sometimes 10 minutes before any precipitate appears, and as much as one mg. of zinc per cc. of solution may be overlooked in an analysis. When the solution once becomes cloudy, further precipitation proceeds rapidly.

A modification of the method of Sullivan and Taylor for the conversion of zinc sulfide to the sulfate has been chosen for this purpose.[1,2,3]

The modification,[4] which is chiefly a time-saving device, consists in the direct treatment of the sulfide with conc. sulfuric acid, after ignition of the filter paper, thus avoiding the resolution of the sulfide in dilute hydrochloric acid and the evaporation before treatment with sulfuric acid.

Method as Finally Selected.—An outline of the method as finally selected will show how the modified method of Sullivan and Taylor[5] has been used to determine the zinc precipitated under the conditions recommended.

The zinc solution, which has been freed from interfering elements such as copper and cadmium, is evaporated to a volume of about 125 cc., and ammonium hydroxide is added until the precipitate at first formed just fails to redissolve. 25 cc. of the stock citric acid solution is then added and made neutral to methyl orange with ammonium hydroxide. After addition of 25 cc. of the stock solution of "formic mixture," the total volume is made up to 200 cc.[6] The solution is heated to about 60°, and then connected with the hydrogen sulfide generator so that the air in the flask is slowly displaced by hydrogen sulfide as the heating continues. At 90° to 100°, when steam issues from the flask, the exit is closed, and the solution, as it cools, saturated with hydrogen sulfide under increasing pressure. The flask should be shaken frequently to ensure saturation, which is usually complete when the precipitate settles rapidly, in about 20 to 40 minutes. The precipitate is filtered and washed with a cold aqueous solution about 0.1 molar with formic acid (4 cc. of 23.6 molar formic acid per liter), saturated with hydrogen sulfide. The precipitate is transferred to a weighed porcelain crucible, and the filter paper charred,

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[1] *J. Ind. Eng. Chem.*, **1**, 476 (1909). In the method of Sullivan and Taylor the precipitate of zinc sulfide is first dissolved in dil. hydrochloric acid, and boiled to expel excess of hydrogen sulfide, then transferred to a weighed porcelain crucible, and evaporated on a water bath with a little more than the theoretical weight of sulfuric acid required to form zinc sulfate. The crucible is then heated in an air bath (U. S. Geol. Survey, *Bull.* **305**, 29), and finally ignited over a Bunsen burner. The authors state that the method is accurate to 0.1 or 0.2%.

[2] The experiments of Euler (*Z. anorg. Chem.*, **25**, 146–154 (1900)) show that determination of zinc as the sulfate is comparable with Volhard's sulfate method for manganese.

[3] Breyer states that the sulfate method is just as accurate as the oxide method. *Report of 8th Internat. Congress*, **25**, 10 (1912).

[4] The details of the modification are given under "The Method as Finally Selected."

[5] *Loc. cit.*

[6] An excess of formic acid, 5–30 cc. (23.6 molar), depending on the amount of interfering metal present, should be added before dilution in case certain interfering metals, particularly iron and nickel, are present in quantity. Compare Hampe, *Chem. Ztg.*, **9**, 543 (1885).

preferably by standing the crucible upon a quartz plate, which is heated strongly by means of a Méker burner.[1] The ignition of the filter paper is very slowly and carefully completed in an oxidizing atmosphere over a Bunsen burner. The reaction should proceed only to the formation of $ZnSO_4$ and not to ZnO.[2] After cooling, the precipitate is carefully moistened with conc. sulfuric acid (18 *M*) and the crucible heated in an air bath, until the excess acid is driven off, then heated over the Bunsen burner to remove any charred material. The precipitate is again moistened with conc. sulfuric acid, and the crucible heated in the air bath, until the excess of acid is driven off; it is then allowed to cool and weighed; this moistening with sulfuric acid and subsequent evaporation is continued to constant weight, two such treatments usually being sufficient. A blank is run to correct for any impurities in the reagents, and the residue (usually 0.2 mg.) subtracted from the final weight of zinc sulfate.[3]

It often happens, in the process of precipitation, that a layer of zinc sulfide sticks so firmly to the sides of the flask that it cannot be removed. The precipitate adhering to the flask is then dissolved in hot dil. sulfuric acid (2 to 3 cc. of 18 *M* sulfuric acid in 25 cc. of water), just neutralized with ammonium hydroxide, or better, neutralized and then made slightly acid with formic acid, saturated with hydrogen sulfide under pressure, heated to boiling to coagulate the precipitate, and filtered through the

TABLE V.

Determination of zinc by precipitation as the sulfide by the modified formic acid method. Volume = 200 cc.

No.	Sample. $Zn(NH_4)_2(SO_4)_2.6H_2O$. G.	$ZnSO_4$. Added. G.	$ZnSO_4$. Found. G.	Difference. G.
1	1.0484	0.4214	0.4211	—0.0003
2	1.0041	0.4036	0.4036	0.0000
3	1.0645	0.4278	0.4279	+0.0001
4	1.0225	0.4109	0.4106	—0.0003
5	1.0008	0.4022	0.4021	—0.0001
6	0.9997	0.4018	0.4012	—0.0006
				Av., —0.0002

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[1] This is a convenient method, in general, for charring filter paper previous to ignition.

[2] If the reaction proceeds to ZnO, the subsequent moistening of the residue with conc. sulfuric acid often generates heat enough so that the water which is formed according to the reaction $ZnO + H_2SO_4 \longrightarrow H_2O + ZnSO_4$ is converted into steam, and particles of the precipitate are thrown out of the crucible.

[3] Determination of the blank with reagents used in the method as finally selected.

No.	Formic acid (23.6 *M*). Excess cc.	Residue. G.
1	0	0.0002
2	10	0.0002
3	20	0.0002
4	30	0.0001

filter containing the already washed precipitate of zinc sulfide. Further washing is unnecessary, as any salt or acid present is volatile.[1] The results given in the preceding table show that the method is accurate to within 0.5 to 1 part per 1000.

Separation of Zinc from Iron, Manganese, Nickel and Cobalt.

The method just outlined holds for the precipitation of zinc under ordinary conditions, where the separation from only small amounts of the usual interfering metals is required. Since the value of the solubility product of zinc sulfide is nearer to that of iron than to that of any of the other sulfides, conditions that will separate zinc from iron should also hold for separation from the other interfering elements.

The chance of exceeding the solubility product of iron sulfide, before the zinc has been quantitatively precipitated, is lessened by two means: first, by increasing the concentration of the hydrogen ion from 10^{-3} to 10^{-2}, thus decreasing the concentration of the sulfide ion; and second, by the formation of a complex with the ammonium citrate present in the solution.[2]

TABLE VI.

Separation of zinc from varying amounts of iron.[3,4]

				$ZnSO_4$.			
No.	Sample $Zn(NH_4)_2$-$(SO_4)_2.H_2O$. G.	Fe added. G.	Fe found with $ZnSO_4$. Calc. to $Fe_2(SO_4)_3$. G.	Added. G.	Found + impurity G.	Found. Corrected. G.	Diff. G.
1.....	1.0009	0.032	0.0006	0.4023	0.4025	0.4019	—0.0004
2.....	1.0005	0.064	0.0008	0.4021	0.4028	0.4020	—0.0001
3.....	1.0002	0.128	0.0009	0.4020	0.4037	0.4028	+0.0008
4.....	1.0007	0.160	0.0010	0.4022	0.4027	0.4017	+0.0007
5.....	1.0008	0.320	0.0026	0.4022	0.4050	0.4024	+0.0004

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[1] The whole process of re-solution, reprecipitation and filtration takes less than 15 minutes, as the amount of precipitate is so small. Compare Hampe, *Loc. cit.*

[2] Spiller, *Ibid.*

[3] The solution was prepared by the modified formic acid method. A ferric sulfate solution standardized against potassium permanganate, was used for the added iron. The iron precipitated with the zinc was determined by the colorimetric method ("Standard Methods of Water Analysis, *A. P. H. A.*, 1915, p. 45).

[4] The addition of ammonium thiocyanate (2 g.) was tried with the following results, which show that, in the present method, this salt does not lower the amount of iron precipitated to any appreciable degree, up to concentrations of iron 20 times the concentration of the zinc, a condition seldom met with.

				$ZnSO_4$.			
No.	Sample $Zn(NH_4)_2$-$(SO_4)_2.6H_2O$. G.	Fe added. G.	Fe found with $ZnSO_4$. Calc. to $Fe_3(SO_4)_3$. G.	Added. G.	Found + impurity. G.	Found. Corrected. G.	Diff. G.
1.....	1.0009	0.016	0.0002	0.4023	0.4013	0.4011	—0.0012
2.....	1.0011	0.032	0.0002	0.4023	0.4012	0.4010	—0.0013
3.....	1.0008	0.080	0.0005	0.4022	0.4020	0.4015	—0.0007
4.....	1.0002	0.160	0.0010	0.4020	0.4021	0.4011	—0.0009
5.....	1.0003	0.320	0.0009	0.4020	0.4039	0.4030	+0.0010

From a series of experiments with iron as an added impurity it has been found that it is necessary to add at least 20 cc. excess formic acid (23.6 *M*) to prevent the precipitation of iron when present in a concentration equal to 1/10 the concentration of the zinc.

Experiments on the separation of zinc in the presence of manganese show that, although a trace of manganese is always carried down by zinc sulfide, the actual amount is not more than 0.2 mg. even with concentrations of manganese equal to the concentration of the zinc.

TABLE VII.

Separation of zinc from varying amounts of manganese.[1]

No.	Sample $Zn(NH_4)_2$-$(SO_4)_2.6H_2O$. G.	Mn added. G.	Mn found with $ZnSO_4$ calc. to $MnSO_4$. G.	$ZnSO_4$.			
				Added. G.	Found + impurity. G.	Found, Corrected. G.	Diff. G.
1.....	1.0042	0.016	0.00003	0.4036	0.4034	0.4034	—0.0002
2.....	1.0003	0.032	0.00006	0.4020	0.4018	0.4017	—0.0003
3.....	1.0003	0.082	0.00006	0.4020	0.4026	0.4025	+0.0005
4.....	1.0001	0.160	0.00016	0.4019	0.4023	0.4021	+0.0002

In the case of cobalt and nickel only a few experiments were tried, because the conditions favorable for iron should hold for these metals. It was found that 20 cc. of formic acid (23.6 *M*) is needed for the separation of equal concentrations of zinc and nickel, just as in the case of iron. With cobalt, however, we find that cobalt is carried down with zinc and cannot be separated by one precipitation.[2]

TABLE VIII.

No.	Sample $Zn(NH_4)_2$-$(SO_4)_2.6H_2O$. G.	Formic acid excess, cc.	$ZnSO_4$.		
			Added. G.	Found + impurity. G.	Diff. G.
a. Separation of Zinc from Nickel. 0.160 nickel added.					
1...............	1.0000	..	0.4019	0.4008	—0.0011
2[3].............	1.0001	20	0.4019	0.4004	—0.0015
b. Separation of Zinc from Cobalt. 0.16 g. cobalt added.					
1...............	1.0011	..	0.4023	0.6943	+0.2920
2...............	1.0014	20	0.4025	0.4251	+0.0226

In order to make a practical application of the method finally selected, the percentage of zinc was determined in a standard brass and a zinc ore.

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[1] The solution was prepared by the modified formic acid method. A manganous sulfate solution standardized by the sodium bismuthate method (Blum, THIS JOURNAL, 34, 1379 (1912)) was used for the added manganese. The manganese precipitated with the zinc was determined colorimetrically (Bur. of Standards, *Circ.* 26, 15).

[2] Attention should, at this point be called to the fact that zinc sulfide is always carried down with the sulfides of copper and cadmium, even when precipitation takes place from a 0.4 molar solution of hydrochloric acid. Cf. Classen, *Ausgewählte Methoden d. Anal. Chem.*, B 1, 346 (1901).

[3] Precipitate from 2 was perfectly white.

Analysis of Standard Brass.

The sample taken for analysis was the Bureau of Standards Sheet Brass No. 37. The percentage of zinc determined by 12 different chemists varies from 26.80 to 27.03, with the grand average of 26.89.

The sample of brass was dissolved in 40 cc. of 8 *M* nitric acid, and the copper removed by electrolysis. The solution was then evaporated below 200 cc., neutralized with ammonium hydroxide, made 0.4 *M* with hydrochloric acid, and the lead and tin precipitated by hydrogen sulfide. The filtrate was again evaporated to about 125 cc., neutralized with ammonium hydroxide, and the zinc precipitated by the recommended method, with the following results:

Determination.	1.	2.
Per cent. zinc	26.93	26.91

Analysis of Zinc Ore.

For the purpose of applying the method to the determination of zinc in an ore the Bureau of Standard Zinc Ore, Sample D, was selected, with the average percentage of zinc on the air-dried sample given as 31.43.

The ore was dissolved by the usual acid treatment with removal and fusion of the silica, the copper separated by electrolysis, and the remaining heavy metals precipitated by boiling with aluminum[1] in sulfuric acid solution, with the exception of cadmium which was removed by double[2] precipitation with hydrogen sulfide from 0.4 *M* hydrochloric acid. The zinc was determined by the recommended method, with the addition of 20 cc. formic acid in excess, with the following results:

Determination.	1.	2.
Per cent. zinc[3]	31.45	31.40

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[1] Modified Waring method. THIS JOURNAL, **29**, 265 (1907).

Three samples of the zinc ore treated by the aluminum method of Waring gave the following results:

Determination.	1.	2.	3.
Apparent % zinc	32.02	31.77	31.58
True % zinc	31.43	31.43	31.43
Difference probably due to cadmium	+0.59	+0.34	+0.15

The cadmium content being about 0.6%, the results show that either none of the cadmium is removed by aluminum or precipitation is incomplete. Compare Breyer, *Report of 8th Internat. Congress*, **25**, 25–26 (1912).

[2] In another sample of the ore, the cadmium was removed by double precipitation with hydrogen sulfide, and the zinc determined separately in the two filtrates.

Determination.	From filtrate 1.	From filtrate 1.	Total.
Per cent. zinc	27.49	3.56	31.05

Double precipitation with hydrogen sulfide is therefore necessary for the separation of cadmium from zinc. Compare Classen (*Loc. cit.*).

[3] The per cent. of zinc given is based on the zinc ore dried at 110°. The per cent. of moisture was found to be 0.203.

Summary.

The precipitation of zinc from solutions of formic acid by means of hydrogen sulfide has been studied with special reference to the conditions affecting the accuracy of the determination. It has been shown that:

(1) The range of hydrogen ion concentration between 10^{-2} and 10^{-3} is the most favorable for quantitative precipitation of zinc sulfide in a form suitable for rapid filtration and washing.

(2) The concentration of hydrogen ion may be kept within this range during precipitation by the use of buffers, as described, namely ammonium citrate and "formic mixture," this latter being a solution containing ammonium sulfate, ammonium formate and formic acid.

(3) The precipitation of granular zinc sulfide is favored not only by a concentration of hydrogen ion within the limits 10^{-2} to 10^{-3}, but also by a high concentration of an ammonium salt of a strong acid, by a volume of 100 cc. for every 0.1 g. of zinc present, and by a temperature of 95° to 100°.

(4) The passing of hydrogen sulfide under pressure is desirable both for rapid saturation, and for avoidance of loss of formic acid by evaporation.

(5) The conversion of zinc sulfide to the sulfate, a modification of the method of Sullivan and Taylor,[1] is accurate and satisfactory where precise determinations are desired.

(6) The method recommended is applicable to the separation of zinc from iron, manganese and nickel, and to the analysis of zinc alloys and ores.

(7) For the conditions discussed in this paper the method is accurate to within one part per thousand.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE DETERMINATION OF SURFACE TENSION (FREE SURFACE ENERGY), AND THE WEIGHT OF FALLING DROPS: THE SURFACE TENSION OF WATER AND BENZENE BY THE CAPILLARY HEIGHT METHOD.

BY WILLIAM D. HARKINS AND F. E. BROWN.

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The accurate determination of surface tension is of importance in investigations on theories of surface structure, the structure of liquids, molecular cohesion, in the study of colloids, especially in physiological work, and in various lines of technical chemistry. It is, therefore, unfortunate that almost all of the surface-tension data in the literature are

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[1] *Loc. cit.*