Silicon	Si	28.4	28.2
Silver	Ag	107.93	107.12
Sodium	Na	23.05	22.88
Strontium	Sr	87.6	86.94
Sulphur	S	32.06	31.83
Tantalum	Ta	183.	181.6
Tellurium	Te	127.6	126.6
Terbium	Tb	160.	158.8
Thallium	Tl	204.1	202.6
Thorium	Th	232.5	230.8
Thulium	Tm	171.	169.7
Tin	Sn	119.0	118.1
Titanium	Ti	48.1	47.7
Tungsten	W	184.	182.6
Uranium	U	238.5	236.7
Vanadium	V	51.2	50.8
Xenon	Xe	128.	127.
Ytterbium	Yb	173.0	171.7
Yttrium	Yt	89.0	88.3
Zinc	Zn	65.4	64.9
Zirconium	Zr	90.6	89.9

THE VOLUMETRIC DETERMINATION OF ZINC.

BY W. GEORGE WARING.

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THE delicacy and precision of the ferrocyanide titration of zinc in properly conditioned solution is almost wholly negatived by inexact methods used for the separation of zinc from interfering elements and by misleading, contradictory and useless directions given in text-books.

An inquiry into the causes of extraordinary discrepancies in zinc determinations made by a number of public analysts, zinc works chemists, and college instructors upon identical samples has led the writer to prepare this paper, in which he endeavors first to discuss the sources of error peculiar to zinc determinations by the ferrocyanide volumetric methods, adding in the sequel, a description of the methods followed in his laboratory at Webb City, Mo., for the determination of zinc in various combinations.

SOURCES OF ERROR.

Losses may result from:

(1) Volatilization of zinc as chloride.

(2) Recombination of zinc with silica.

(3) Imperfect decomposition by acids.

(4) Occlusion by ferric hydroxide, etc.

(5) The use of hydrogen sulphide for separating copper, cadmium, etc.

(6) Failure to make the final titration under the same conditions as in standardization.

(7) Insufficient dilution of the solution.

(8) Too great haste in titrating, especially with cold solutions.

On the other hand, results may be too high, owing to:

(9) The presence, in the solution, of cadmium, copper, antimony, manganese, aluminum, or some organic acid as tartaric acid, oxalic acid, etc.

(10) The decomposition of the ferrocyanide solution by chlorine, bromine, nitrous oxides, hydrogen peroxide, etc.

(11) The addition of an inordinate excess of acid to the solution.

(12) The use of an incorrectly standardized solution of ferrocyanide.

(1) *Volatilization of Zinc Chloride.*—Although zinc chloride alone is volatile only at a red heat, it volatilizes freely at 145° C. and over when heated with ferric chloride and ammonium chloride, or with ammonium chloride alone, in an acid mixture such as often occurs in the course of the analysis of zinc ores. Experiments made to decide this point showed that when a solution of zinc and ammonium chloride in hydrochloric acid was evaporated to dryness, the mixture became pasty at 119° C., solidified at 120.5°, with a sudden decrease of the temperature to 117°, from which point the temperature rose rapidly, with evolution of aqueous vapors, to 145°, when the chloride began to sublime. A neutral solution of the same chlorides showed no volatilization of the chlorides up to 210°. When zinc blende, containing a little iron, was heated with aqua regia and evaporated with ammonium chloride, the mixture became pasty at 122.5°, solidified at 135°, with momentary recession of temperature to 132°, and volatilization of the chlorides began immediately after the temperature increased again, being very copious at 145°.

The evaporation of acid solutions containing zinc, iron and

ammonium chlorides should therefore not be finished at a temperature much exceeding 100°.

(2) *Recombination of Zinc with Silica.*—This invariably occurs when ammonia is added to a solution of zinc containing silica. The importance of removing silica by filtration before adding ammonia to separate iron, etc., has been demonstrated by Prost and Hassreidter,[1] as well as by other chemists; but this precaution seems to be disregarded in some American schemes, *e. g.*, the method of Von Schulz and Low. The following experimental results obtained in the analysis of ores containing silicate of zinc will illustrate this point:

(*a*) The first filtrate, without evaporating to separate silica, gave zinc 45.65 per cent. After dissolving out the ferric hydroxide from the silica on the filter by hydrochloric acid, precipitating iron, etc., by ammonia, and filtering through a clean filter, there was found 1.75 per cent. additional zinc in the filtrate. A repetition of the procedure gave 2.17 per cent. more zinc in the third filtrate. Total, 49.57 per cent.

(*b*) The same ore, decomposed as usual with hydrochloric acid, evaporation stopped very much short of dryness, water and ammonium chloride added, the gelatinous silica filtered off and washed, the iron precipitated by ammonia, dissolved and reprecipitated and the two filtrates titrated separately, gave, in first filtration, 49.15; in second, 0.50; total, 49.65 per cent.

(*c*) The same ore treated as in (*b*), except that the acid solution was evaporated to complete dryness at 180°, then taken up with water, filtered, and ammonium chloride and ammonia added. The first filtrate gave, as before, 49.15 zinc, and second, 0.50; total, 49.65 per cent.

The silica obtained in (*b*) amounted, after ignition, to 29.15 per cent. That from (*c*) to 29.50. Both (*b*) and (*c*) gave identical results for iron, namely, 1.43 per cent.

In the following cases, operating upon different ores, the silica was not removed until after the first precipitation by ammonia. Three precipitations were made in each case; the first and second filtrates titrated together and the third separately.

(*d*) Zinc in first and second filtrates, 36.35; in third, 6.60; total 42.95.

[1] *Ztschr. angew. Chem.* (1892), p. 168.

(*e*) Zinc in first and second filtrates, 35.80; in third, 7.00; total, 42.80.

(*f*) Zinc in first and second filtrates, 48.32; in third, 5.70; total, 54.02.

(3) *Imperfect Decomposition by Acids.*—Attention should be called to the insolubility of the zinc aluminates (the zinc spinels, Gahnite or Automolite and Dysluite found in the New Jersey ores, and the compounds formed in the zinc retorts). These are only perfectly decomposed by fusion with sodium or potassium bisulphate (see also page 25). Rhodonite and some garnets are said to contain zinc occasionally. We have never found any zinc in rhodonite, even in that from Broken Hill, Australia. Both garnet and rhodonite require fusion with alkaline carbonates.

(4) *Occlusion by Ferric Hydroxide, etc.*—It is stated by Sutton[1] that the iron precipitated by ammonia "tenaciously holds about one-fifth of its weight in zinc."

The following tables show the results of an examination as to the retention of zinc by ferric and aluminous hydroxides made in our laboratory some years ago. The method of analysis followed was the first one described in the sequel.[2] Variations are noted in or appended to the tables.

Table I.—Using pure materials containing known proportions of zinc and iron with no other substances which might affect the results.

No.	Zinc taken. Per cent.	Iron taken. Per cent.	Ammonium chloride added. Grams.	Water. cc.	Ammonium hydroxide. cc.	Zinc found in first filtrate.	Zinc found in second filtrate.	Total zinc found. Per cent.	Zinc retained by each part iron in first precipitate.
1	60	2	2	33	5	59.10	0.94	60.04	0.47
2	60	2	2	66	5	59.18	0.82	60.00	0.42
3*a*	60	2	2	132	5	59.02	1.03	60.05	0.51
3*b*	60	2	2	132	5	30.30	29.35	59.65	4.67
4	60	2	4	66	5	59.25	0.65	59.90	0.32
5	60	2	8	66	5	59.28	0.70	59.98	0.35
5*c*	60	2	8	66	8	59.48	0.42	59.90	0.21
6	60	10	4	66	5	58.80	1.50	60.30	0.15
7	60	10	4	66	10	58.87	1.23	60.10	0.12
8	60	10	6	66	10	58.90	1.00	59.90	0.10

[1] "Volumetric Analysis," 8th ed., p. 378.

[2] See page 20.

No 3*b* was evaporated to complete dryness and maintained at a temperature of about 120° for half an hour or more. The results in this case are instructive.

Table II.—Showing the proportion of the zinc retained by aluminum hydroxide, metallic aluminum being added to the assay instead of iron.

No.	Zinc taken. Per cent.	Aluminum taken. Per cent.	Equivalent to aluminum oxide.	Zinc found in first filtrate.	Zinc found in second filtrate.	Total zinc found. Per cent.	Parts zinc held by 1 part aluminum.	Ditto by 1 part aluminum oxide.
1	60	7.00	14.30	57.80	1.85	59.65	0.31	0.15
2	60	1.40	2.86	59.32	0.50	59.82	0.50	0.24

Table III.—Giving a few typical results selected from a large number of experiments made upon zinc blende concentrates, etc.

No.	Material.	Iron found. Per cent.	Zinc found in first filtrate.	Zinc found in second filtrate.	Total zinc found. Per cent.	Zinc retained by 1 part iron in first precipitate.
1	Pure yellow blende	0.33	65.30	0.26	65.56	0.79
2	"Sludge".....	1.12	57.37	0.60	57.97	0.54
16	Blende ore.....	3.54	49.92	0.55	50.47	0.31
19	Blende ore.....	4.95	53.77	1.11	54.88	0.22
20	Blende ore.....	5.86	48.90	1.00	49.90	0.17
21	Mexican blende...	13.54	42.90	1.50	44.40	0.11

In the four following, three precipitations of iron were made each filtrate being titrated by itself.

TABLE IV.

No.	Material.	Iron found. Per cent.	Zinc found in first filtrate.	Zinc found in second filtrate.	Zinc found in third filtrate.	Total zinc found. Per cent.	Zinc to iron in second filtrate.	Zinc to iron in third filtrate.
1	Marmatite..	9.70	44.30	2.50	0.45	47.25	0.25	0.05
2	Blende.....	8.62	47.20	3.00	0.58	50.78	0.35	0.07
3	Blende.....	8.75	46.05	4.75	0.40	51.20	0.55	0.05
4	Blende.....	14.32	16.50	2.05	0.55	19.05	0.14	0.04

The following note, communicated by Geo. C. Stone, of the New Jersey Zinc Co., is of interest in connection with the separa-

tion of ferric iron by ammonia: "In the case of our ores we find that if a thoroughly oxidized solution is evaporated and heated to render the silica insoluble, treated with hydrochloric acid and washed, the resulting filtrate frequently contains some ferrous salt, making it necessary to oxidize before precipitating iron. I believe that the tendency of manganese salts to exert a reducing effect upon ferric iron in solution is probably the cause of this phenomenon. It certainly deserves investigation."

Manganese, when precipitated by oxidizing agents from solutions containing zinc, often carries down very considerable quantities of the latter, more especially when the precipitate contains lower oxides of manganese than manganese dioxide. In the presence, however, of considerable ferric iron, the manganese goes down as the black flocculent manganese hydroxide and little, if any, more zinc is carried down than would be the case if iron alone were present.

In the following experiments (Table V) the sample used contained a considerable proportion of willemite, together with franklinite and other minerals peculiar to the New Jersey ores. The silicious residue resulting from the treatment of the sample by hydrochloric acid, etc., was therefore separated by filtration before addition of ammonia. In No. 1 no ammonium chloride was added before the first precipitation by ammonia, but sufficient ammonium persulphate was added with the ammonia in each case to separate all the manganese as manganese hydroxide. In No. 2, four precipitations were made and the insoluble residue from the preliminary treatment was fused with potassium bisulphate to recover about 0.24 per cent. of zinc found to be insoluble, probably as dysluite. In No. 3 the sample was first treated according to Dr. Low's method,[1] and the first precipitate, including

[1] By Low's method is here meant the attack of the ore by a saturated solution of potassium chlorate in nitric acid, without previous decomposition by other means. An analysis of the same sample made by first decomposing the ore with strong hydrochloric acid, (franklinite is insoluble in the chlorate mixture) evaporating to dryness in a platinum dish, expelling silica by means of hydrofluoric acid, then treating the residue with the chlorate mixture, etc., gave a correct result with a single filtration. The separation of iron and manganese from zinc is absolutely perfect when the silica is first removed either by hydrofluoric acid or by Furman's more tedious but equally effective method, provided a diluent such as Dr. Low recommends is employed. Caution is required regarding the proper use of the chlorate mixture. If less chlorate is used than will precipitate all of the manganese, the results of the titration will be too high by 1.6 per cent. of zinc for every per cent. of manganese in the filtrate. If an excess of chlorate be used, and remain undecomposed, the titration will also give too high results, even when a large excess of sodium sulphite is added. This is due to a peculiar decomposition of the ferrocyanide that occurs when a chlorate is present in an acid solution.

the insoluble material, was redissolved and precipitated twice by persulphate and ammonia as in Nos. 1 and 2, giving two additional filtrates. An analysis of this sample made by the special hydrogen sulphide method described in the sequel gave:

Zinc	17.90	Aluminum oxide.....	2.00
Iron	20.35	Calcium oxide.....	10.93
Manganese.....	9.37	Insoluble.....	12.80

TABLE V.

No.	Manganese found. Per cent.	Iron found. Per cent.	Zinc found in first filtrate.	Zinc found in second filtrate.	Zinc found in third filtrate.	Zinc found in fourth filtrate.	Total zinc found. Per cent.
1	9.37	20.35	13.95	2.42	1.43	...	17.80
2	9.37	20.35	15.05	2.25	0.55	0.10	17.95
3	9.37	20.35	12.73	1.33	2.77	...	16.83

The sample used in the above tests is one of a set of three recently sent to a number of chemists as a preliminary to an inquiry into the causes of discrepancies in zinc analyses, instituted under the auspices of the Committee on Uniformity in Technical Analyses, New York Section of the Society of Chemical Industry.

To prevent manganic oxide from carrying down zinc when precipitated by bromine, peroxide of hydrogen, persulphate, etc., it appears to be absolutely necessary that the manganese shall be separated as hydrated binoxide, as before stated, and, if the separation is to be effected from an ammoniacal solution, it should be concentrated and contain a large amount of ammonium chloride. The recent researches of Dittrick and Hassel[2] on the separation of manganese by ammonium persulphate, in which it is found that manganese can be separated completely from zinc by having the solution highly diluted, refers to sulphuric acid solutions.[3] When no ferric compound exists in the solution, the persulphates give a brownish yellow slimy precipitate rich in zinc, but the addition of bromine water produces the black flocculent precipitate nearly free from zinc under the conditions prescribed. One part of ammonium persulphate precipitates about 0.6 part of manganese from an ammoniacal solution.

[1] *Ber. d. chem. Ges.*, **35**, 15, 3266-3271.

[2] See also papers on the subject by H. Baubigny, *Compt. Rend.*, **135**, 22, 965-967, and **136**, 7, 449-451.

Examples of occlusion of zinc by manganese:

(*a*) To a solution (from zinc ore) containing 0.262 gram of zinc, 0.0212 gram of iron and 0.1043 gram of manganese in 35 cc., there was added 3.5 grams of ammonium chloride, 0.5 gram of ammonium persulphate and 7 cc. of ammonia; the solution was boiled, filtered and washed. The precipitate contained 0.01375 gram of zinc.

(*b*) A solution of the same volume containing the same amounts of zinc and iron, but no manganese, treated exactly like the foregoing, gave a precipitate containing 0.0033 gram of zinc.

(*c*) A repetition of the first experiment, using 150 cc. of water, instead of 35, gave a precipitate containing 0.0295 gram of zinc.

The following results of the precipitation of manganese by bromine from acetate solutions containing, in each case, 0.2265 gram of zinc and 0.2609 gram of manganese, have been communicated to me by Mr. Geo. C. Stone: "The manganese found was 0.3045, 0.2945, 0.2895, 0.2840, and 0.2864; in the sixth the manganese was not weighed. The zinc found in the same solutions was 0.1763, in the second it was not weighed, 0.1860, 0.1780, 0.1858 and 0.1795. As you will see, with a large proportion of manganese the error is a serious one."

The well-known method of separating manganese from iron and zinc by means of nitric acid and potassium chlorate does not appear to give satisfactory results in many cases. In our laboratory, recourse is now had to a separation of the zinc as sulphide for all control or umpire work upon material containing manganese and other interfering elements.

Calcium fluoride, which frequently occurs in zinc ores, does not appear to occlude zinc in the ordinary ammoniacal precipitate. Thus a crude ore from Illinois containing 24.24 per cent. of zinc as sulphide, 0.44 per cent. of iron, 31.37 per cent. of calcium carbonate, and 17.96 per cent. of calcium fluoride, gave 24.05 per cent. of zinc in the first filtrate and 0.25 per cent. in the second, with quite sharp end-reactions. An analysis in which the zinc was separated as sulphide gave 24.25 per cent. of zinc.

(5) *The Use of Hydrogen Sulphide for Separating Cadmium, etc.*—The inexactitude of this process may be inferred from the classic experiments of Fresenius, but in view of Dr. Low's advocacy of its use in technical analysis, it seemed advisable to

make some additional tests, following his directions precisely. These tests fully confirmed the statements of Fresenius, showing that it is impossible to separate even a small proportion of the cadmium without at the same time separating a very considerable proportion of the zinc.

Although it appears to be impracticable to separate cadmium completely from zinc by hydrogen sulphide, yet if the acidity of the solution is reduced so as to allow a complete precipitation of the cadmium along with nearly all the zinc, and the precipitate is afterwards treated with dilute hydrochloric or sulphuric acid, containing about 5.5 per cent. of absolute hydrochloric acid or 8 per cent. sulphuric acid, without heating, but with vigorous stirring or agitation, the zinc goes into solution while the excess of hydrogen sulphide, set free in the liquid, prevents any of the cadmium from dissolving. The development of the pure, bright yellow color of cadmium sulphide affords a visible means of controlling the operation with hydrogen sulphide water, if necessary. The detection and estimation of cadmium with accuracy, although not essential for most technical purposes, is, in some cases, *e. g.*, in oxide manufacture, of very great importance.

Items 6, 7 and 8 require only the following explanatory remarks: The brown-red color of uranyl ferrocyanide is more or less discharged by moderately strong acid, so that only the excess required to promote the formation of the insoluble double ferrocyanide of potassium and zinc should be present, and the amount of this excess must be the same in standardization as in titrating. If the amount of zinc present greatly exceeds 0.1 gram to 100 cc., some zinc chloride or normal ferrocyanide appears to be enclosed in the precipitate so that a low result ensues. Heat, as well as the presence of hydrochloric acid and ammonium chloride, promotes the transformation of the normal ferrocyanide into the insoluble double ferrocyanide. The completion of this reaction is extremely slow in cold solutions. Under the next item (9) attention will be drawn to a similar but much more pronounced delaying of the end-reaction due to the presence of cadmium.

(9) *Plus Errors Due to the Presence of Copper, Cadmium, Antimony, Manganese, Aluminum, Organic Acids, etc.*—In technical work the slightly higher results due to mere traces of such elements are disregarded, but when extreme accuracy is required, the cumulative effect of minute amounts of other metals must be

duly considered. Thus the presence of 0.06 per cent. of copper in a zinc blende gives no indication of its presence in an ammoniacal solution of 200 cc., yet it increases the zinc result by a little over 0.1 per cent. by actual test.

The erroneous statements found in various publications regarding the compounds formed when ferrocyanide is added to the solution of a cadmium salt have been made the subject of some research by the writer.

The research confirmed the results obtained by Dr. E. H. Miller,[1] which led him to conclude that the precipitates obtained under different conditions could be resolved into mixtures of two simple ferrocyanides: Cd_2FeCy_6 in which 3Zn equals 4Cd, and the zinc factor multiplied by 2.291 equals the factor of cadmium, and $K_2CdFeCy_6$ in which 3Zn equals 2Cd and the cadmium factor is 1.1454 times the zinc factor.

It also developed a peculiar reaction due to the presence of ammonium chloride, which led to the discovery of what is believed to be a new ferrocyanide of ammonium and cadmium.

When a quite acid solution containing cadmium, but no ammonium salt is titrated with ferrocyanide until the color reaction appears with uranium, and ammonium chloride is then added, the color reaction disappears and does not reappear until after a very considerable further addition of ferrocyanide. The ferrocyanide actually used corresponds to a factor ratio of zinc to cadmium as 1.0 to 1.245 and 1.0 to 1.243 upon duplicate trials. Th precipitate, when dried, was analyzed by distillation with caustic soda and found to contain Cd 32.62 per cent., NH_4 11.30 per cent., $FeCy_6$ 56.08 per cent., giving approximately the empirical formula $(NH_4)_2CdFeCy_6$. It is of a light bluish color when dry, is anhydrous and appears to be quite insoluble in hydrochloric acid.

Under the conditions existing in a zinc analysis, namely, the presence of about 4 per cent. by measure of strong hydrochloric acid and 3 per cent., or more, of ammonium chloride, if as much as 0.002 to 0.003 gram of cadmium and 0.2 to 0.3 gram of zinc are present in about 250 cc. of solution, the presence of the cadmium is shown at the end of the titration by the fading of the first faint coloration in the testing drops, which fading will extend to 2 or 3 drops, or proportionately more with larger amounts of

[1] This Journal, **22**, 541, and **24**, 226.

cadmium. A permanent end-reaction is obtained when about as much ferrocyanide has been consumed for each part by weight of cadmium as would be required for 0.62 part of zinc. This ratio corresponds with no definite compound of ferrocyanogen and cadmium, and varies with the conditions of the analysis. The accurate determination of zinc in the presence of cadmium, or of cadmium, either alone or in the presence of zinc, is therefore impossible by means of ferrocyanide.

Fortunately, however, we have in metallic aluminum[2] a means of quickly and completely separating cadmium, as well as the other metals of the lead group, from zinc by boiling in a moderately acid solution, from which the zinc can be precipitated by hydrogen sulphide after filtration and neutralization.

The effect of aluminum salts on the titration of zinc has been shown by Miller and Hall[2] to yield irregular results. We have found that 200 cc. of a solution containing 0.3032 gram of zinc and 0.299 gram of aluminum, both as chlorides, with the usual amounts of free hydrochloric acid and ammonium chloride, required 63.40 cc. of ferrocyanide instead of 61.22 cc., which would have been sufficient in the absence of aluminum.

Oxalic acid increases the amount of ferrocyanide required. Thus in five cases where lime had been separated as oxalate from a strongly ammoniacal zinc solution, the acidified filtrates required respectively 0.97, 0.40, 1.00, 0.35 and 0.65 cc. more than would have been required in the absence of oxalic acid.

(10) *The Decomposition of Ferrocyanide by Oxidizing Agents* Cl, Br, H_2O_2, N_2O_3, etc.).—When these are used for separating manganese, the usual procedure is to destroy the excess by means of a sulphite. We find it advantageous to use sodium sulphite in making up the ferrocyanide solution, thereby obtaining the additional advantage of rendering the latter quite permanent. Chlorates must be completely decomposed before titration, as they seriously affect the result even in the presence of sulphites (see footnote, page 9).

(11) *The Use of Too Much Hydrochloric Acid.*[3]—We found that 0.233 gram of zinc with 4 grams of ammonium chloride in

[1] If cadmium is to be precipitated by aluminum, the solution must be rather strongly acid and must be boiled or the precipitation will be very slow. If copper is to be precipitated, the solution must be free from ammonium salts.

[2] Miller and Hall: *School of Mines Quart.*, **21**, 270.

[3] Miller and Hall: *Loc. cit. ante.*

8 cc. of hydrochloric acid and 250 cc. of water required 47.30 cc. of ferrocyanide, while with 15 cc. additional of hydrochloric acid the same amount of zinc required 47.55 cc.

(12) *The Use of an Incorrect Standard.*—The value of 1 cc. of the ferrocyanide is usually determined by titrating the solution of a weighed amount of calcined zinc oxide, or, supposedly pure metallic zinc.[1] The stick zinc made by Merck and Schuchardt is almost absolutely pure when fresh, but soon acquires a coating of oxide which seriously diminishes its value.

A special grade of so-called "C. P." zinc in sheets has recently been place on the market, for use in standardizing. It is very convenient because its thickness is such that one square centimeter weighs almost exactly 0.1 gram (0.101 gram) and contains very nearly 0.1 gram of zinc. An analysis of a bright, but unwashed sample gave: Zinc, 98.86; lead, 1.09; iron, 0.02; oxygen, 0.03.

The actual value of any sample of fairly pure sheet zinc, if it contains no cadmium, can be accurately determined by standardizing against pure zinc by titration with ferrocyanide. In this way it is found that many of the expensive forms of zinc sold by the chemical dealers are in reality no purer than, and in some cases not as pure as, some of the high-grade spelters.

Some of the zinc oxides sold as "C. P." are also very impure. We find, however, that several of the German makes, when obtained in the original packages, contain no appreciable impurities, and, after calcination in a platinum dish in a perfectly clean, new muffle and cooling over sulphuric acid, can be kept for months in a tightly stoppered bottle without change.

A number of experiments were made to determine the rate at which zinc oxide gained or lost water and carbonic acid when exposed under different conditions, but the results varied so greatly for different samples exposed at the same time that the results were of no value.

At a meeting of chemists held in Joplin, Mo., in 1900, a proposal was made to test the stability of pure natural blende in fine powder, with a view to its use for standardizing.

Ten grams of a special sample, found by concordant analyses

[1] Metallic zinc for standardizing should be digested with ammonia and ammonium chloride, then washed thoroughly, first with water, then with pure alcohol and well dried. It will then keep for many weeks without sensible change, if not exposed to moisture or acid vapors.

by chemists in Europe and America to contain 65.51 per cent. of zinc, gained 0.004 gram in weight after exposure for two days over water charged with carbonic acid. After twelve hours' exposure over dilute hydrochloric acid it gained 0.0735 gram additional, after forty-eight hours 0.0985 gram, and after twenty days 1.0705 grams. Six days' desiccation over sulphuric acid reduced the total gain to 0.2590 gram. 5.32 grams of the original sample exposed, in a muffle, to a temperature of 400° for 45 minutes, lost 0.0304 gram in weight.

ANALYSES OF BLENDES.

The following analyses were made with the utmost care, using 5 to 10 grams of ore for the determination of the metals other than zinc, and are representative. They were not made in the ordinary course of commercial work, but especially to accompany this paper.

Ore.	Zinc.	Iron.	Lead.	Copper.	Cadmium.
Sphinx Mine, Neck City, Mo.....	65.77	0.55	0.00	0.077	0.135
Ore from Golconda, Ill	60.55	1.18	0.51	0.046	0.110
Average of 2270 car-loads from Webb City, Mo.....	57.08	2.60	0.90	0.050	0.337
Standard Mine, Fortuna, Mo.....	61.97	0.55	0.815	0.133	0.436
Maude B. Mine, Webb City, Mo....	55.70	4.90	trace	trace	0.227
Big Six Mine, Aurora, Mo.....	56.75	1.88	none	0 004	0.018
McKinley Mine, Prosperity, Mo....	57.20	1.25	5.29	none	0.550
Hudson Mine, Pleasant Valley, Mo.	62.05	0.61	none	0.030	0.322
Big Circle Mine, Oronogo, Mo.....	56.90	1.64	1.51	trace	0.110
Willard Mine, Mo.....	63.30	0.80	0.41	0.064	0.320
Gundling and Standard, Fortuna, Mo.	63.50	0.90	0.32	0.107	0.530
October Mine, Webb City, Mo.....	58.10	2.74	0.59	none	0.460
Majestic Mine, Webb City, Mo.....	57.05	1.82	1.61	none	0.330
Three Shaft, Carterville, Mo.....	60.20	2.08	0.89	0.090	0.140
Uncle Sam Mine, Aurora, Mo.....	61.20	0.75	none	0.010	0.590
Crittenden Co. ore, Kentucky.....	53.58	0.77	0.76	none	0.211
Underwriters Mine, Webb City, Mo.	57.95	1.60	1.62	....	0.710
Jack Rose Mine, Joplin, Mo.....	54.70	1.36	1.02	....	0.260
Blende from Kentucky Fluorspar Mines.....	53.50	0.77	0.76	none	0.211
Average of 2145 shipments, Joplin District.....	57.75	2.32	1.07	0.042	0.388

I desire here to express my obligations to Mr. Geo. C. Stone, of the New Jersey Zinc Co., Mr. C. V. Petraeus, of the Lanyon Zinc Co., and Dr. Edmund H. Miller, of Columbia University,

for valuable suggestions and assistance rendered in the preparation of this paper.

I append a description of the methods of analysis employed in our laboratory for the technical estimation of zinc.

THE VOLUMETRIC DETERMINATION OF ZINC AS PRACTICED IN THE LABORATORY OF WARING AND SON, WEBB CITY, MO.

(A) *Stock Solutions.*

(1) *Standard Potassium Ferrocyanide.*—21.63 grams of Merck's pure potassium ferrocyanide and 7 grams of sodium sulphite crystals are dissolved in pure, non-aërated distilled water, the solution made up to exactly 1 liter and thoroughly mixed. Usually 10 liters of solution are made at a time and kept in a 3-gallon demijohn from which it is siphoned to the burette as required. Theoretically, 21.544 grams of ferrocyanide is required per liter, but, owing to impurities in the so-called "C. P." salt, we find that from 21.55 to 21.80 grams are necessary. One cc. of this solution should be equivalent to 0.005 gram of zinc.

(2) *Standard Zinc Acetate.*—6.23 grams of pure, freshly ignited zinc oxide are dissolved in 60 cc. of 30 per cent. acetic acid with the aid of heat and, when perfectly cold, made up to exactly 1 liter. One cc. contains 0.005 gram of zinc. The acetate is much the most satisfactory salt of zinc for this purpose, though the sulphate or chloride can be used. The chloride causes the burette cock to stick, while the acetate is a lubricator.

(3) *Uranium Acetate (Indicator).*—Dissolve 4.4 grams of the pure salt[1] (Merck's or Schuchardt's) in 100 cc. of distilled water and 2 cc. of acetic acid. This amount is sufficient for 200 zinc determinations. If a pure acetate is not available, use the nitrate, 52 grams to the liter.

(4) *Standard Potassium Permanganate.*—Exactly 20.1 grams of the pure salt are dissolved and the solution made up to exactly 7 liters with pure aërated distilled water. One cc. of this solution should be equivalent to 0.005 gram of iron or 0.0025 gram of lime.

(5) *Stock Solution of Ammonium Chloride.*—200 grams of pure ammonium chloride are dissolved in a liter of distilled water

[1] The label "Uranium Acetate, Merck, highest purity," does not necessarily mean pure uranyl acetate, as the sodium uranyl acetate is so designated as well as the sodium-free salt. See *Proceedings Missouri Pharmaceutical Association*, 1903, pp 23-37.

and 10 cc. of ammonia. For use 30 to 50 cc. of this solution are added to a liter of water in a wash-bottle.

(6) *Dilute Hydrochloric Acid.*—One volume of the strong acid (sp. gr. 1.20) is mixed with three volumes of distilled water; used in a wash-bottle.

(7) *Dilute Sulphuric Acid.*—One volume of strictly pure strong acid is poured slowly, with constant stirring, into three or four volumes of distilled water and, when perfectly cold, made up to five volumes.

(B) *Standardizing.*

(1) *The Ferrocyanide Solution.*—Weigh out, as nearly as practicable, 0.3 gram of Merck's or Schuchardt's "C. P." zinc,[1] or exactly 0.37338 gram of "C. P." freshly ignited zinc oxide (equal to 0.3 gram of zinc), and dissolve in 25 cc. of the dilute hydrochloric acid, add 3 to 4 grams of pure ammonium chloride and dilute to 200 cc. with distilled water at about 60° C. Titrate at once with the ferrocyanide solution, running in about 58 cc. at once with vigorous stirring. Note the change at this point in the appearance of the precipitate, a change from bluish white, thickish skim milk, to nearly pure white, accompanied by a thinning of the solution and a separation of the $K_2Zn_3(FeCy_6)_2$ in flocculent form on standing for a minute, especially if the stirring has been vigorous. This appearance always occurs, at a temperature of about 60°, when the titration is within 2 or 3 cc. of completion. Run in 2 cc. more and the precipitate will lose its flocculent appearance and will remain suspended for a considerable time. Test two or three drops of the solution by running them off the end of the stirring rod on to a drop of the uranium solution placed on a perfectly clean white porcelain plate. The solution must be *thoroughly* stirred each time and the rod and sides of the precipitating vessel be washed with a jet of hot water, after each addition of ferrocyanide, before testing. The test should give no tinge of brown or even the slightest flash of discoloration. Run in the ferrocyanide now drop by drop, testing after each addition, until a distinct, though faint, flash of color is observed. When a definite reaction is obtained, allow the color to develop, which will require from two to three minutes. Frequently it will be seen that, in addition to the drop which first gave the reaction, from

[1] See note, p. 15.

one to five of the others develop a brown-red color. If this be the case, deduct from the burette-reading the fraction of a cubic centimeter corresponding to the number of drops that show a color, in order to obtain the correct reading The dilution coëfficient, *i. e.*, the amount of ferrocyanide necessary to give a reaction with uranium in a solution of the temperature and volume and containing the amounts of free acid and ammonium chloride that are in the solution being tested, at the end of the titration, is usually about 0.35 cc. and must always be deducted from the burette-reading. The standardization should always be made in duplicate or triplicate.

If the solution is found to be exactly standard, or within 0.25 cc. of the standard, it will only be necessary, when 0.5 gram of ore is taken for analysis, to deduct the dilution coëfficient from the burette-reading in order to obtain the percentage of zinc in the ore. If the variation from the standard is greater than 0.25 cc., divide the number of milligrams of zinc used for standardizing by five times the burette-reading (less the dilution coëfficient). To obtain the percentage of zinc in an analysis, the net burette-reading is to be multiplied by this factor, which should vary but little from unity.

The reactions between zinc chloride and potassium ferrocyanide occur as follows: At first the normal zinc ferrocyanide is formed; thus,

$$4ZnCl_2 + 2K_4FeCy_6 = 8KCl + 2Zn_2FeCy_6,$$

when about 45.5 cc. of the standard ferrocyanide solution has been added to a chloride solution containing 0.3 gram of zinc. If the temperature is low (20° to 25°), it will be found that a yellowish brown coloration is produced with uranium on the addition of more ferrocyanide. This coloration (which does not appear with hot solutions) will, however, fade gradually, but it will be yielded by the solution up to, nearly, the point at which the precipitate becomes flocculent, when it wholly disappears. The final, and permanent, coloration occurs when the following secondary reaction has been completed, as shown by Konick and Prost:[1]

$$6Zn_2FeCy_6 + 2K_4FeCy_6 = 4K_2Zn_3(FeCy_6)_2$$

whence $3Zn$ (196.23) : $2K_4FeCy_6,3H_2O$ (845.50) : : 5 : 21.5436.

[1] *Ztschr. angew. Chem.* (1896), pp. 460-461.

After a little experience, the coloration produced after the first reaction causes no difficulty, even with a cool solution, since the color is different and fades on standing instead of becoming more intense, and the solution retains the bluish skim-milk color which differs from the pure creamy white of the later reaction.

The presence of a trace of copper in the solution also affords an indication of the passing of the three-quarter point. The normal ferrocyanide of copper gives a light chocolate tint to the solution, if present in the merest traces in a zinc solution, but when the three-quarter point is passed the chocolate tint changes to a blue, which does not interfere with the final reaction. The presence of copper increases the apparent result by about 1.8 parts zinc for each part of copper.

(2) *Permanganate.*—This solution is standardized by means of ferrous ammonium sulphate as directed by Fresenius' and other handbooks. It is advisable to add a piece of pure zinc before solution of the ammonium salt, and a little acid, then when the solution is complete and cooled, to decant and wash before titration.

THE ZINC ANALYSIS.

The simple analysis, applicable to pure carbonate and blende ores, will be given first; then the modifications applicable to:

(*a*) Silicates and calcined ores.

(*b*) Impure zinciferous ores containing considerable zinc, with copper, cadmium, manganese, antimony, silver and other elements.

(*c*) Low-grade zinc ores, slags, furnace residues, etc.

In the case of pure blende or carbonate ore containing only zinc, lead, iron and rock, it is usual to take 0.5 gram of the finely ground and dried sample for analysis. With low-grade material, larger amounts should be used so that the quantity taken for the analysis should contain approximately 0.2 to 0.3 gram of metallic zinc.

Transfer the weighed ore carefully and completely to a flat-bottomed flask of 150 to 250 cc. capacity—the so-called "copper determination flasks" made by Whitall Tatum Company are excellent for this purpose, as are also small Erlenmeyer flasks. Add about 4 cc. each of strong nitric and hydrochloric acids, washing down with the acid any part of the ore that may have adhered to the neck of the flask, set it on the hot plate in the fume chamber and

boil until red fumes are no longer evolved. Add about 3.5 grams of granular ammonium chloride and continue boiling until the contents of the flask intumesce, becoming thick and pasty, avoiding too great a heat as the volatilization of the ammonium chloride with white fumes must be prevented. While the mass is still moist, but so nearly dry that it has stopped intumescing, remove it from the heat, add about 30 cc. of hot water, twirl the flask a few times to cause all the soluble matter to dissolve,[1] add 6 to 7 cc. of strong ammonia, boil for a minute, filter and wash out the flask four times with hot dilute ammonia and wash the precipitate, on the filter, four times more with the same solution. The washed ferric hydroxide always contains a considerable amount of zinc which cannot be removed by washing, so that it is necessary to dissolve and reprecipitate the iron. Set the funnel and precipitate in the neck of the flask in which the ore was dissolved, dissolve the precipitate by means of a spray of hot, dilute hydrochloric acid, using no more acid than is necessary; from 6 to 10 cc. should be enough. Place about 0.5 gram of ammonium chloride in the filter and wash three times with hot water and then once with dilute ammonia. Reject the insoluble residue. Add about 4 cc. of ammonia to the solution, boil, filter and wash as before.

Both of the ammoniacal filtrates containing the zinc should be perfectly colorless; if a blue tinge is perceptible, copper is present and must be removed as directed under modification (*a*). If no copper is present, add 15 cc. of strong hydrochloric acid, warm the solution to 50° or 60° and transfer it to a precipitating-jar of moderately thick glass. Titrate with ferrocyanide, adding at once within 10 or 15 cc. of the amount judged to be necessary. Note the appearance of the liquid as to the bluish skim-milk complexion, add 3 or 4 cc. at a time, stirring very thoroughly each time until the precipitate becomes flocculent, then less and less until the opaque, white, non-flocculent characteristic appears, then add 3 to 5 drops at a time, testing with uranium after each addition. When only from 2 to 5 drops of ferrocyanide are required to complete the precipitation, an experienced eye will detect a peculiar darkening of the test, not, however, showing any tinge

[1] If the appearance of the undissolved residue indicates the presence of gelatinous silica, the contents of the flask must be filtered into another flask and washed six or seven times with hot water, before adding ammonia (see remarks under modification (*a*)).

of color, so that the final reaction may be reached by means of single drops of the precipitant. For a beginner, it is best to reach a decided color reaction by means of 0.5 cc. additions and drop-tests, and then titrate back with standard zinc acetate solution added by single drops, testing after each drop. This must be continued until at least three or four drops have been tested without showing the faintest tinge of brown coloration, and then two or three minutes' time, at least, be allowed for the color to develop in the drop that marks the exact end-point. It will be noticed that when nearing the precise end of the reaction, a momentary darkening of the drop, as before stated exceedingly faint, will appear when the drops of zinc solution come in contact with the uranium acetate drop, immediately disappearing as the drops become mixed, so that for a minute or so the mixture is pure white, then the faint brown color begins to appear and grow darker until a distinct red-brown color is finally established. When the end-point is passed, no trace of momentary tint shows at the contact. The color reaction in this test, although requiring time to develop, is exceeding delicate and definite, and, with proper care in the preparation of the solution, duplicate and triplicate determinations will agree to a single drop, that is, to within 0.05 per cent. It is important that the volume of the solution to be titrated should be nearly 75 to 100 cc. for each 0.1 gram of zinc present. The sharpness of the end-reaction depends also in a great measure on the percentage of free hydrochloric acid in the solution; it should always be at least 3 per cent. by volume, of strong acid (sp. gr. 1.20).

Modification (a). For Ores Containing Soluble Silicates.—When soluble silicates are present in an ore, the method described above fails because a considerable portion of the zinc is precipitated as silicate when ammonia is added to an acid solution containing soluble or gelatinous silica; several solutions and reprecipitations will not bring all the zinc into solution unless the silica is first removed by filtration.

In the presence of soluble silicates, the following method gives satsfactory results. The weighed sample of pulverized ore is placed in a porclain casserole, moistened with a few drops of water and spread over the entire bottom with a stirring rod; a mixture of 1 cc. of nitric and 6 cc. of hydrochloric acid is added and the ore stirred, to prevent clotting, until complete gelatiniza-

tion has taken place. Evaporate gently, after stirring in 3 to 4 grams of ammonium chloride, until the mass is nearly dry, *i. e.*, until it is no longer quite wet, but will crumble on stirring. It is not necessary to carry the evaporation to complete dryness, nor is it advisable. Dilute with hot water, filter and wash seven times with hot water, catching the filtrate and washings in a 250 cc. flask. A little experience will enable one to stop the evaporation at the point where the gelatinous silica can be most rapidly filtered and washed; at this point not more than 0.005 gram of silica will remain in solution. The filtrate is now ready to be precipitated with ammonia and treated as already described. Should the ore contain manganese, it must be removed as described in the next section, before precipitating with ammonia.

Modification (*b*). *For Impure Ores Containing Zinc with Either Manganese, Copper or Cadmium, or All of These Metals with Other Elements.*—In the absence of cadmium, or when it is not to be estimated, the ore is to be decomposed as first described, or as in (*b*), if soluble silicates are present, increasing the proportion of nitric acid, if considerable sulphides are present. After the zinc is dissolved and the ammonium chloride added, add 0.03 gram of ammonium persulphate and 10 cc. of bromine water for each 0.01 gram manganese possibly contained in the solution, then 7 cc. of strong ammonia, and boil for two or three minutes before filtering. The manganese will be precipitated as hydrated binoxide along with the ferric hydroxide. When but little manganese is present, it is not necessary to redissolve the manganese hydroxide to obtain the whole of the zinc. If the precipitate is broken up by a jet of warm, dilute sulphuric acid, only the iron and zinc will be dissolved, so that only a small amount of sodium persulphate and bromine need be added before the second precipitation. When but little iron is present, it is well to dissolve by hot dilute hydrochloric acid, allowing, as before, what manganese hydroxide fails to go into solution to remain on the filter. When bromine is used as an oxidizing agent, any excess will show its presence by an orange or orange-red color when the solution is acidulated before titration. Any free bromine present must be removed by the addition of sodium sulphite or it will oxidize the first portion of ferrocyanide added in titration.

When the ore contains copper, the blue ammoniacal zinc solu-

tion should be neutralized by hydrochloric acid and an excess of 5 cc. added, then a gram or two, or even more, if much copper is present, of very fine, pure "Freiburg" test lead and the solution boiled for ten to twenty minutes, by which time all the copper will have been precipitated on the lead. When cool enough, the solution is decanted into the precipitating-jar, 8 cc. more hydrochloric acid added, and the titration for zinc proceeded with. The lead in the acid solution does not interfere in the slightest degree with the zinc determination. On the addition of ferrocyanide a chocolate-brown tint appears, if the copper was not completely separated. This color changes to a fine cobalt-blue towards the end of the titration, at which point the blue tint sometimes disappears altogether.

When cadmium is to be separated as well as copper, it is customary, in many laboratories, to evaporate the acid sulphate solution of the ore (without the addition of ammonium chloride or nitrate) to dense white fumes, cool, digest with water to dissolve basic sulphates, filter out lead sulphate and insoluble matter, dilute until the proportion of free sulphuric acid is less than 8 per cent., then to heat and pass hydrogen sulphide until all the cadmium and copper and, at least, as much zinc as of both cadmium and copper, have been thrown down as sulphides, filtering out the precipitate and finally dissolving the zinc and cadmium in hot dilute (1 : 4) hydrochloric acid, and again precipitating as sulphides after diluting until the amount of free acid is not over 7 per cent. by weight.[1] Or else to nearly neutralize the acid solution with soda, and then pour it into a solution of caustic soda according to Fresenius[2] to separate the cadmium as hydroxide. In either case, the zinc filtrates are combined and prepared for titration by adding ammonium chloride and hydrochloric acid as usual.

The following method, developed in our laboratory, gives exact results in a shorter time than any that we have experimented with. As it is available for all classes of zinc ores, affording a satisfactory control upon the accuracy of the usual technical methods, it will be described in detail.

The method depends upon the separation of the zinc from manganese, iron and aluminum by means of hydrogen sulphide, under

[1] See Fresenius, Section 162, pp. 537–538, American edition.

[2] Section 162, 105, p. 542.

slight pressure, in a solution very slightly acidified by formic acid; the metals of the copper group having been previously separated by metallic iron or aluminum with simultaneous reduction of ferric salts. The operations are:

(1) *Solution.*—The calamine, willemite, franklinite, blende and other soluble minerals, or ores containing them, are decomposed by hydrochloric acid or aqua regia, with subsequent treatment and evaporation with an excess of hydrochloric or sulphuric acid to thoroughly eliminate nitrous compounds. If zinc spinels or aluminates are present, the insoluble residue must be fused with a mixture of sodium carbonate and borax glass, the fused mass dissolved and the solution added to the main one. If much silica is present, spinels are decomposed by fusion with soda in a platinum crucible, any lead sulphate present having been extracted by ammonium acetate. In the absence of silica or boric acid, the spinels cannot be decomposed by fusion with soda alone. In such case they can be decomposed by prolonged fusion with an alkaline bisulphate. Silicates, such as cinders from oxide furnaces, unchilled slags and some natural silicates undecomposable by acids, must be fluxed or sintered with sodium carbonate before treatment with hydrochloric acid. It is not necessary, in any case, to evaporate to dryness to separate silica—it can be filtered off in the gelatinous state. This can be done very rapidly, after dilution with water, when the gelatinization has reached a maximum and before dehydration has begun. The gelatinous silica at this stage will not retain any traces of metals after a few washings.

(2) *Reduction.*—To avoid the effects of reactions like

$$Fe_2Cl_6 + H_2S = FeCl_2 + 2HCl + S,$$

and at the same time to remove copper, silver and bismuth before precipitating with hydrogen sulphide, the filtered solution, made fairly acid with hydrochloric or sulphuric acid, is boiled for fifteen or twenty minutes with a strip of clean sheet iron or steel. By this treatment all of the metals likely to be precipitated with zinc as sulphides are separated, except cadmium, which is not in the least degree reduced by metallic iron.

Mr. G. C. Stone has suggested the use of metallic aluminum for the reduction. This has the advantage of separating cadmium and lead along with the other metals of the copper group, since

both are completely precipitated by aluminum from a rather strongly acid boiling solution of sulphates or chlorides, so that, when zinc only is to be determined, the subsequent operations are very much shortened.

Reduction may also be effected by means of sodium sulphite or thiosulphate, when copper, or copper and aluminum are to be determined from the same weighed portion.

The reduction is followed by filtration, the filtrate being received in a flask of about 300 cc. capacity.

(3) *Neutralization.*—Add to the filtrates a drop of methyl orange, then run in, from a pipette, a rather dilute solution of sodium hydroxide, meanwhile constantly agitating the contents of the flask with a swirling motion, until the pink color barely, but permanently, changes to a light yellowish tint and the cloudiness, due to the separation of hydroxides, fails to clear up entirely. Then add, drop by drop, enough 50 per cent. formic acid (sp. gr. 1.12) to just restore the permanent pink color, and add up to half a cubic centimeter additional. Dilute the solution to 200 or 250 cc. (or so that it will contain not more than 0.15 to 0.20 gram of metallic zinc in 100 cc.) and heat to about 80°.

(4) *Precipitation.*—A rubber stopper, through which passes the delivery tube from a source of supply of hydrogen sulphide, is loosely placed in the neck of the flask and a moderately rapid stream of gas allowed to pass through the hot liquid. When the precipitation of the zinc as sulphide is well under way, the stopper is pushed in tightly. Absorption of the gas ceases when all the zinc is precipitated; the precipitate settles quickly, and the gas pressure rises rapidly when the operation is completed. When several precipitations are to be made at the same time, the flasks are arranged in succession in the usual manner and the first is removed when the precipitation is well started in the third, and so on, changing the gas connections as required. The outlet from the last flask is not closed until the precipitation is partially completed therein. Numerous experiments have shown that zinc can be completely precipitated and separated from iron, manganese and alumina under the conditions named, by the passage of only a very little more than the amount of hydrogen sulphide theoretically required. The use of a large excess is therefore unnecessary and is also undesirable.

(5) *Treatment of the Precipitate.*—When the preceding operations have been properly performed, the precipitated zinc sulphide will be pure white, pulverulent and very easily filtered and washed. Hot water only need be used for washing, no zinc will dissolve, or pass through the filter, as is the case with the slimy zinc hydrosulphide precipitated from cold solutions in the usual manner. Pour the contents of the flask upon a filter at once and wash with hot water. Spread the filter with its contents upon a large watch-glass or on the inner wall of a capacious beaker, and wash the precipitate into the bottom of the beaker by a jet of hot water. Wash the precipitating-flask and the lower end of the gas delivery tube with 10 cc. of strong hydrochloric acid, followed by hot water, pouring the acid and washings successively over the washed filter on to the precipitate in the beaker. When the volume of the acid solution has reached 125 to 130 cc., the solution is warmed gently to dissolve the zinc sulphide completely.

When cadcium is also present (*i. e.*, when the reduction has been effected by metallic iron) the zinc sulphide will dissolve completely before any cadmium sulphide is dissolved. By practice and experience, the point when all the zinc is dissolved and only the brilliant yellow cadmium sulphide remains, can easily be distinguished. The solution is then further diluted with an equal volume of hydrogen sulphide water, allowed to settle and the cadmium sulphide filtered off and estimated in the usual way by warming with acid ferric sulphate and titrating with permanganate. The iron equivalent of the permanganate used multiplied by 1.003 equals the cadmium. Properly performed, the result is accurate.

The solution of zinc sulphide in dilute hydrochloric acid is heated to 60° or more, made up to 200 or 250 cc. with hot water, a little ammonium chloride added, and it is ready for titration with ferrocyanide.

The method of separating zinc by hydrogen sulphide from nickel, cobalt and manganese, recommended by Fresenius,[1] is not applicable when iron is present, as iron is thrown down by hydrogen sulphide in the presence of sodium acetate.

Modification (c). For Low-grade Zinc Ores, Slags, Furnace Residues, etc., and for all purposes wherein it is required to determine small amounts of zinc with accuracy.

[1] American edition, Sec. 160, pp. 74 and 75.

Proceed exactly according to the method just described until the zinc sulphide precipitate has been washed, then, instead of dissolving the precipitate, dry and ignite it carefully in a clean muffle without separating it from the paper. No loss of zinc will occur, nor will basic sulphate be formed, if the wet precipitate is ignited at the mouth of the muffle until the paper is consumed, and the oxidation of the residue is then conducted at a low temperature (about 450°) until at the last, when it may be moved back to where the temperature is near the melting-point of silver. As much as 0.15 gram of zinc sulphide can be completely oxidized in this way in forty to sixty minutes. The calcination may be effected in a smooth shallow scorifier an inch and a half in diameter, from which the calcined oxide can be brushed into the scale pan without appreciable loss.

Lime and magnesia can be determined in the ammoniacal solution of zinc obtained after iron and alumina have been separated, according to the first of the above methods or its modifications, provided it is made very strongly ammoniacal, then heated to boiling before the addition of ammonium oxalate to precipitate the lime. The solution of ammonium oxalate should also be boiling when added to the zinc solution. Enough of the oxalate must be added to convert the zinc and magnesia to oxalates, as well as to combine with the lime: 1 part zinc requires 1.0447 parts ammonium oxalate; 1 part magnesium oxide, 3.9794 parts ammonium oxalate; 1 part calcium oxide, 2.8607 parts ammonium oxalate.

The filtrate from the calcium oxalate is then to be cooled and treated in the usual manner with phosphate to precipitate magnesia. No zinc will be thrown down, if sufficient ammonia and ammonium chloride are present. The zinc in the filtrate cannot be determined by titration, but must be precipitated as sulphide; or as phosphate, by rendering the cold solution slightly acid with sulphuric or hydrochloric acid, adding a *large* excess of ammonium sodium hydrogen phosphate, neutralizing very carefully with ammonia drop by drop, adding a drop or two additional, then about 1 cc. of acetic acid and warming gently until the flocculent precipitate of $ZnNH_4PO_4 + H_2O$ has settled completely as a dense crystalline powder, which, after washing with hot water, may be dried at 100°-105° and weighed as $ZnNH_4PO_4$

containing 37.28 per cent. Zn,[1] but the better way is to ignite and weigh as $Zn_2P_2O_7$, containing 42.77 per cent. Zn. In this case the filter-paper should be burned first to ash, then the ash and dried precipitate ignited gently at first, then for a few minutes at a bright red heat.

The flocculent $ZnNH_4PO_4 + H_2O$ is very soluble in the mineral acids as well as in ammonia, but after crystallization it is much less soluble in the latter. It is only slightly soluble in acetic acid; an excess of 1 cc. in 100 cc. of solution does not dissolve an appreciable quantity. It is somewhat soluble in all ammonium salts, if only a small excess of phosphate is present. The addition of 1 cc. of a 10 per cent. solution of sodium ammonium phosphate for each 0.005 gram of zinc is sufficient to entirely prevent its solution in ammonium chloride or sulphate, or in the acetate, unless the latter is present in enormous quantity. It is, however, always slightly soluble in the oxalate. Therefore, for very accurate work, lime and magnesia, if present in the zinc solution, are preferably separated together as phosphates, after adding a large excess of ammonia and reprecipitating; then the combined filtrates are to be slightly acidulated and proceeded with as above. The crystalline zinc ammonium phosphate is quite insoluble in hot or cold water.

For this elegant and accurate, but too little known, method I am indebted to Mr. Geo. C. Stone, who has carefully worked out its details, including the properties of the precipitate. Hundreds of filtrates from zinc phosphate, separated as described, have been tested by him with ammonium sulphide, without showing zinc.

THE ORGANIC MATTER IN SOILS AND SUBSOILS.

By F. K. Cameron and J. F. Breazeale.

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INTRODUCTION.

The relative amount of organic matter in a soil or subsoil has long been regarded as an important characteristic. Popularly, and with some reason, it has been generally held to furnish an indication of the fertility of a soil. It has a real importance, since it affects the texture or structure and water-holding capacity of

[1] It can also be accurately titrated with ferrocyanide after solution in hydrochloric acid with addition of ammonium chloride. Also, according to P. H. Walker (This Journal, 23, 468), its zinc content may be determined alkalimetrically.