temperature must not exceed 85° , because of the possibility of molybdic acid being precipitated. The contents of the flask were vigorously stirred for 5 minutes. The yellow precipitate of ammonium phosphomolybdate was filtered off and washed with acid ammonium sulfate solution until 2 or 3 cc. of the wash water did not give a brown coloration on the addition of a drop of ammonium sulfide: 7 cc. of ammonium hydroxide of sp. gr. 0.90 and 15 cc. of water were poured into the flask in which the precipitate was formed, to dissolve any adhering precipitate: the solution was then poured on the precipitate in the filter. The filtrate containing the ammonium molybdate and ammonium phosphate was next prepared for the Jones reductor. The filter was washed with water until the filtrate had a volume of about 60 cc.: 10 cc. of sulfuric acid (sp. gr. 1.84) were added. (If a precipitate forms on the addition of the sulfuric acid, it should be redissolved with ammonium hydroxide and the same amount of sulfuric acid added a second time.)

The solution was then passed through a Jones reductor charged with amalgamated zinc. It was passed through a second time after the addition of 2 cc. more of sulfuric acid. This was followed with 200 cc. of water. The solution collected from the reductor was titrated at once with $N/10$ potassium permanganate.

TEST EXPERIMENTS

In order to show the relative accuracy of the proposed method, two different samples of phosphor-tin were used in making the following series of determinations of tin and phosphorus: Twelve different portions of Sample I were analyzed for phosphorus and tin, six by the recommended procedure and six by standard procedures described in the body of this paper. This series was then followed by a similar series of analyses in which Sample II was used.

TABLE V—RESULTS OF ANALYSES OF PHOSPHOR-TIN

Sample No.	No.	PERCENTAGES TIN FOUND		PERCENTAGES PHOSPHORUS FOUND	
		Electrolytic Method	Proposed Volumetric Method	Cyanide Method	Proposed Evolution Method
I	1	96.32	96.38	2.97	3.03
	2	96.34	96.40	2.98	3.02
	3	96.38	96.35	2.98	2.99
	4	96.38	96.36	2.96	3.04
	5	96.36	96.40	2.99	3.01
	6	96.40	96.35	2.95	3.02
II	1	96.50	96.45	3.10	3.12
	2	96.46	96.52	3.07	3.11
	3	96.52	96.50	3.09	3.11
	4	96.44	96.48	3.06	3.10
	5	96.50	96.45	3.08	3.13
	6	96.48	96.50	3.07	3.12

SUMMARY

The need of a method formulated specifically for the analysis of the alloy, phosphor-tin, has been shown, and attention has been called to the fact that the related literature apparently does not contain such a method.

A volumetric method has been developed and is proposed in the foregoing discussion. The tests to which this method has been subjected indicate that it is not only easy of execution but that it is also rapid and accurate.

The method provides for the carrying out of the determinations in a train of flasks. The alloy is dissolved in hydrochloric acid in the first flask, from which

all air is excluded by means of a current of illuminating gas or carbon dioxide. The tin dissolves as stannous chloride and the phosphorus is liberated as phosphine which is absorbed by solutions in the train of three flasks. The tin is titrated at once with an oxidizing solution. The phosphine is converted into phosphoric acid by the absorbing solutions from which the acid is precipitated as phosphomolybdate which is then reduced in a reductor and finally titrated.

The time required for making the two determinations, after the sample is weighed, need not exceed 45 minutes. Other methods, adapted to phosphor-tin analysis and giving the same order of accuracy, required hours for their execution.

The proposed method provides for the detection of impurities in the alloy. It is, therefore, as well adapted for careful assay work as for "control" analyses.

As a result of the study of various absorbing agents it has been shown that potassium permanganate solutions are satisfactory absorbents for phosphine. And furthermore, it appears that the oxidizing and absorbing power of the reagent is increased in a marked degree by the addition of nitric acid.

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THE ELECTROMETRIC TITRATION OF ZINC¹

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Of all the troubles to which the zinc chemist is heir, none perhaps is more vexatious than the trickiness and general unreliability of even the better methods of zinc analysis. Mr. Keith's² report discloses, for instance, that analyses of the same sample made by some of the best known zinc chemists of the country, all using the same method of analysis (the "Beale"), varied among themselves by as much as 4 per cent of the total zinc content. Of course such variations are far beyond the errors of the personal equation and can be accounted for only as being due either to loss of zinc in the processes leading to the final titration (such as for example might be due to absorption on the Fe-Mn precipitate), or to the interference of the various substances with the end-point of the ferrocyanide titration. Of these two sources of error the last is undoubtedly the most serious, as, at least in the author's experience, the loss of zinc in any of the better known commercial methods is very slight.

Assume, therefore, that we have carried through the preliminary more or less complete separation of SiO_2 , Fe, Mn, Cd, etc., according to any of the regular methods. We will then have left a solution containing besides all our zinc (hoffentlich) more or less free chlorine, bromine, nitric acid, hydrochloric acid, manganese, copper, lead, iron and cadmium, and no one knows what else, all in amounts depending enormously on even the slightest variation in our procedure. Our problem is now to find the best way of determining

¹ Presented at the *Symposium on the Chemistry and Metallurgy of Zinc*, 54th Meeting American Chemical Society, Kansas City, April 10 to 14, 1917.

² Keith, "Zinc Ore Analysis," Leadville Publishing and Printing Co., Leadville, Colo.

the zinc in this mixture. Unfortunately, there is, with the possible exception of Hg_2SCN , no specific reagent which will precipitate zinc without at the same time precipitating traces at least of most of the other elements. The best substitute for a specific reagent is undoubtedly potassium ferrocyanide, but unfortunately this reagent, besides precipitating almost any of the heavy metals, has the added disadvantage that it is a reducing agent, and thus will react with whatever bromine, chlorine, or nitric acid is present, and so will give too high results unless extreme care is taken in the preliminary elimination of all oxidizing agents, heavy metals and, especially, manganese. Besides this the end-point of the ordinary ferrocyanide titration obtained either by the use of uranium, molybdenum or iron, is always uncertain, especially in the poor light of the ordinary laboratory, and, moreover, the whole titration is tedious and uncertain, due to the large blank correction necessary. It is thus, perhaps, no wonder that zinc analyses vary so conspicuously among themselves.¹

The most rational way to correct this state of affairs is not so much to improve the methods of preparation of the zinc solution (though undoubtedly precautions, such as the addition of SO_2 , should be taken to remove any free oxidizing agents) as to change the conditions of the ferrocyanide precipitation by carrying it out in solutions containing from 10 to 20 per cent hydrochloric acid. In these solutions zinc-ferrocyanide is only slightly soluble, but lead, manganese, iron and copper are very soluble and even cadmium is fairly soluble. At this concentration of acid, however, the ordinary indicators are comparatively useless, as would be indeed almost any chemical indicator. For this reason electrometric methods similar to those used with so much success in the analysis of iron, vanadium, chromium, etc., immediately suggest themselves:

First, because outside of their being almost the only ones possible under these conditions, they are, under any conditions, the most convenient and accurate methods available. One does not have to depend on the time-consuming and always inaccurate outside indicator, nor on the inaccurate and, in my experience, unreliable internal indicator, such as ferrous iron. One simply notes the point of sudden deflection of a galvanometer needle, a point which can be determined, but with little care, to a fraction of a drop.

Second, this method is also the quickest and most certain. There is no danger of overrunning and the titration can be finished in less than one-third the time of the older methods.

Third, the electrometric end-point is not affected by the color of the solution, by the lighting of the room, by the amount of acid or neutral salts present, and, in fact, at least in 10 per cent acid, is not affected by iron, lead, manganese (up to 50 mg.), or small amounts of copper and cadmium, all of which (except lead) have marked effects, especially on the uranium end-point.

The method as finally worked out requires no complicated apparatus: a cheap galvanometer, a slide wire resistant, some sort of standard electrode such as a calomel electrode (made from a bottle, a cork and a piece of bent tubing, a sodium chloride solution, and a few g. of mercury and calomel), a piece of platinum wire (for the platinum electrode), some copper wire for connections, and a couple of dry cells complete the needed extra equipment, though a voltmeter is a great convenience. If this apparatus seems too complicated to make, it can be purchased already made up for the determination of chromium, iron, vanadium, etc. A detailed description of the apparatus, the theory of it and the general methods of using it will be found in the *Journal of the American Chemical Society* in several places.¹

Having the apparatus set up, the operation is simplicity itself. The two electrodes are dipped in the beaker containing the solution to be analyzed (which solution should be hot, should contain at least 10 per cent strong hydrochloric acid, but no free oxidizing agents nor more than a trace of cadmium); by adjusting the slider of the resistance the pointer of the galvanometer should be brought to zero and the titration begun. As the ferrocyanide is slowly added with constant stirring the pointer will swing slowly until the end-point is almost reached; at the end-point the direction of the swing will be reversed. From this point on the ferrocyanide is added drop by drop until one drop causes a sudden very large but permanent deflection. This is the end-point. Or, if one has a voltmeter in the set-up, one can simply set the slider so that the voltmeter reads 0.24 volt and titrate until the galvanometer indicates zero current. This end-point is accurate, even with 20 per cent (strong) hydrochloric acid, to 0.1 cc. of the usual ferrocyanide solution.

Using this method, the preliminary operations for the purification of the ore lose their customary importance. Almost any of the best known methods can be used. My own method is to dissolve the ore in the minimum strong hydrochloric acid, add a pinch of KClO_3 , add quickly 100 cc. dilute NH_4OH , make up to 250 cc., filter an aliquot, and acidify. Add 10 per cent excess hydrochloric acid, add SO_2 until saturated, boil out the SO_2 with heat and a stream of air (or add test lead) and titrate. In ordinarily pure ores simple solution in strong hydrochloric acid and the addition of the test lead and aluminum works very nicely. Of course, if extreme accuracy is desired or if the ore contains large amounts of cadmium, some standard method such as Breyer's² is to be preferred for the preliminary separations. The electrometric end-point should, however, replace Breyer's or the uranium end-points under all conditions as much more accurate and convenient, especially for small traces of zinc (where one has zinc solutions free from cadmium, manganese, etc., to analyze smaller acid concentrations should be employed).

¹ My attention was called to the need of an electrometric method for the titration of zinc by Mr. Hyman Storth at the Bureau of Standards.

¹ Hildebrand, *J. Am. Chem. Soc.*, **35** (1913), 847; Forbes and Bartlett, *Ibid.*, **35** (1913), 1527; Kelley and Conant, *Ibid.*, **38** (1916), 341.

² Breyer, *Orig. Commun. 8th Int. Cong. of Applied Chem.*, **25**, 7.

While no attempt to give a complete table of experimental results is made here, certain more significant results have been collected in Tables I and II:

TABLE I

Accuracy of titrations with ferrocyanide of total zinc in solutions containing various known quantities of Zn^{++} , Fe^{++} , Mn^{++} , Pb^{++} , Cu^{++} and HCl using the electrometric end-point (E. M. F.), the ferrous ferrocyanide end-point of Breyer (iron), the usual end-point with uranium nitrate as an outside indicator (uranium).

HCl (a)	CONTENT OF SOLUTION IN MG.					MG. OF ZINC FOUND		
	Zn	Mn	Fe	Cu	Pb	E. M. F.	Iron	Uranium
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
15	0.0	0.0	0.0	0.0	0.0	0.05	..	1.0
2	0.5	0.0	0.0	0.0	0.0	0.50	0.34	0.95
3	5.0	0.0	0.0	0.0	0.0	5.01	4.98	5.45
5	50.0	0.0	0.0	0.0	0.0	50.01	50.08	50.57
2	0.5	0.5	0.0	0.0	0.0	0.59	0.71	1.55
10	0.5	0.5	0.0	0.0	0.0	0.49	0.6*	0.7*
10	5.0	0.5	0.0	0.0	0.0	4.98	5.1*	5.3*
10	5.0	5.0	0.0	0.0	0.0	5.01	..	..
10	5.0	50.0	0.0	0.0	0.0	5.05	0.0	5.7*
10	5.0	0.0	5.0	0.0	0.0	5.09	5.11	*
15	5.0	5.0	5.0	5.0	0.0	5.08	*	*
15	5.0	5.0	5.0	5.0	5.0	5.10	*	*

* End-point very uncertain.

(a) HCl content in cc. 35 per cent HCl per 100 cc. of solution.

TABLE II

Content of the same Cd-free ore by different methods showing results in per cent zinc and approximate time taken (ore contained 7 per cent Mn).

METHOD	Reference	Per cent Zinc	Time
Breyer standard	{ Loc. cit. E. M. F. end-point	31.04	12 hrs.
"Beale"	Loc. cit.	31.74	8 hrs.
New Jersey Zinc Co.	See below	31.12	6 hrs.
American Zinc, Lead Smelting Co.	See below	31.32	5 hrs.
Author's long method	See text	31.10	4 hrs.
Author's short method	See text	31.6	2 hrs.

NEW JERSEY ZINC CO. METHOD (Courtesy of Mr. G. C. Stone)—

Weigh out 0.5 g. of ore within 0.5 milligram. Transfer to a 250-cc. beaker. Add 15 cc. of hydrochloric acid (sp. gr. 1.20), cover and boil until all is in solution that can be dissolved by hydrochloric acid alone. If there are insoluble particles remaining, other than silica, and always with green sulfide ores, add 5 cc. of nitric acid (sp. gr. 1.42).

In case the hydrochloric acid treatment alone is necessary, boil down to about 5 cc. and remove from the hot plate.

If nitric acid is used, evaporate to dryness, leaving on the hot plate until there is no odor of acid or until a little ammonia in a beaker produces no cloud of ammonium salts when held near the assay. Remove from the plate, cool, add 5 cc. of hydrochloric acid (sp. gr. 1.20) and boil until all is in solution. If brown or green fumes are evolved it indicates that the evaporation to dryness was incomplete. In this case evaporate to dryness again with the hydrochloric acid, cool, add 5 cc. of strong hydrochloric acid as before and boil.

From this point on, the treatment is the same whether nitric acid was used in solution or not.

Wash off both sides of the cover glass and the sides of the beaker with a fine jet of cold water, using as little as possible. Be particularly careful to keep the volume down in the cases of ores carrying manganese. Add 5 g. of ammonium chloride crystals. Add saturated bromine water according to the manganese contents of the ores.

If there is no manganese, add 2 or 3 cc. to insure complete oxidation of the iron. If this is neglected the iron is incompletely precipitated by the subsequent treatment with ammonia. With small amounts of manganese, 15 to 25 cc. of bromine water are needed.

When the manganese is high, the volume of the ore solution must be less than 10 cc. Shake the bottle of bromine water violently with an excess of bromine and quickly pour 25 cc. into the ore solution before the suspended free bromine can settle.

Allow time for the ammonium chloride to dissolve completely, then add 15 cc. of ammonia water.

In the case of the high manganese ores great care is necessary on account of the excess of bromine. If the ammonia water is poured in carelessly the reaction with the free bromine which

has settled to the bottom of the beaker is very violent, and may cause loss of solution or injury to the hands of the operator. The best method of manipulation is to incline the beaker at an angle, keeping the cover glass in place and to pour the ammonia water in slowly through the lip of the beaker, allowing it to run down the side of the beaker and float as a separate layer on the ore solution. Now place the beaker on a warm (not hot) part of the plate, on two or three layers of asbestos paper if there is no gradation of heat on the plate. The ammonia will then gradually diffuse into the solution, precipitating the iron and manganese completely without any violent reaction.

Bring the contents of the beaker to a boil. Allow to boil for one minute to insure the coagulation of the precipitate. Do not allow to boil longer than one minute, or there is danger of re-solution of a part of the manganese. Wash the cover glass off with a hot jet of the wash solution when removing it from the beaker.

Filter while hot, allowing all the solution to run through the filter before commencing washing. Transfer as much of the precipitate as possible to the filter, using the jet to loosen it from the beaker, and carefully wash the entire inner surface of the beaker. Then wash the filter and precipitate thoroughly three times more with a jet of the hot wash solution, containing 50 g. of ammonium chloride and 50 cc. of ammonia water per liter.

Wash the precipitate from the filter into the beaker in which the original precipitation was carried out with a small quantity of the wash solution: add a few drops of hydrochloric acid to redissolve the iron and manganese. With high manganese ores it will be found necessary to heat to boiling before the manganese will dissolve. With these same ores, if the volume is over 10 cc. concentrate by evaporation to less than 10 cc. Precipitate the iron and manganese again as with the first precipitation except that it is unnecessary to use ammonium chloride crystals. The chloride contained in the solution used for washing the precipitate from the paper is sufficient for the small amount of zinc remaining. The bromine may also be omitted on the second precipitation, with ores free from manganese, as the iron is all in the ferric condition. Where manganese is present, bromine must be used in the second precipitation, observing all the precautions necessary with the first. Ten cc. of ammonia water are sufficient on account of the smaller quantity of free acid. Filter and wash beaker, filter and precipitate as before, combining the filtrates from the two precipitations. With ores very high in iron, manganese or alumina, at least one additional separation of these constituents must be made by the same method. Experience must be relied on to determine exactly how many separations are necessary with any given ore.

Heat the solution to boiling and test, if from a manganiferous ore, by adding a few cc. of bromine water. If more manganese comes down, throw the solution away and start a new assay, as the manganese cannot be separated quantitatively from so large a volume of solution without the expenditure of more time than would be required for a new assay. If no manganese comes down, boil gently for a few minutes to eliminate bromine.

Add hot water until the volume is a little less than 250 cc. Add 4 drops of an ammonium sulfide solution made by saturating with hydrogen sulfide a mixture of 2 parts ammonium water (sp. gr. 0.90) and 1 part water by volume. If there is much copper, more sulfide may be necessary.

Add hydrochloric acid cautiously until the precipitated zinc sulfide just dissolves, then add 10 cc. excess of the 1.20 sp. gr. acid and titrate with standard potassium ferrocyanide solution (containing 44 grams per liter), using 10 per cent uranium nitrate solution as an external indicator, on a paraffin-coated spot plate. The solution must be violently stirred while titrating.

AMERICAN ZINC, LEAD SMELTING CO. METHOD (*Courtesy of Dr. John Johnston*)—Weigh 0.5 gram into a flask of 200 cc. capacity. Add 10 cc. hydrochloric acid and boil nearly to dryness. Add 5 cc. nitric acid and take to dryness. Overheating or baking should be avoided. The best time to remove the flask from the hot plate is when it is stained red all over. Care should be taken to avoid spurting. Cool, and add 10 cc. hydrochloric acid and boil to half its volume. Add 50 cc. hot water and 10 cc. ammonia. If manganese is present add 20 cc. saturated solution of bromine water. Boil and filter through 11 cm. filter, which should leave about one-third of the funnel exposed, into a beaker 375 cc. capacity. Wash three times with hot water. Redissolve precipitate into original flask with hot dilute hydrochloric acid, 1 part acid to 3 parts water. Wash well with hot water. Add 10 cc. ammonia as before, and the same amount of bromine water, if manganese is present. Boil and filter through the same paper into the same beaker. Wash three times with hot water. Make the filtrate neutral with hydrochloric acid, using litmus paper as indicator, and add 6 cc. hydrochloric acid in excess. If copper is present add 20 g. test lead and boil until all copper is thrown down. Heat to 70° C. and titrate with a standard solution of potassium ferrocyanide. Run the solution in rather slowly and stir constantly. A slight color change will be noted in the beaker when the precipitation is almost complete. This should not be ignored, since if it does not occur there is a possibility of error. Use a 1 per cent solution of ammonium molybdate for outside indicator.

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A NEW METHOD OF SEPARATING ZINC FROM CADMIUM AND THE LATTER'S DETERMINATION IODOMETRICALLY¹

By ERIC JOHN ERICSON

Further research in the development of the writer's method for complete spelter analysis has demonstrated the possibility of separating the bulk of the remaining zinc from cadmium by crystallization as zinc sulfate. The exact composition of the latter has not yet been ascertained. In one analysis of the crystals only 15.50 per cent was found, while the formula $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ calls for 22.73 per cent.

Although a small trace of cadmium is entrained in the zinc sulfate or zinc-ammonium sulfate, for technical purposes only one crystallization is deemed necessary, in view of the large sample (19.2 grams) of spelter taken originally.

The procedure in spelter analysis is as follows:

Referring to earlier publications² for details for removing and determining lead, the filtrate from the latter is boiled until nearly neutral and a white precipitate appears. Then add 50 cc. dilute sulfuric acid (1:3), boil down to about 80 to 100 cc. volume and allow to stand over night. In the morning the bulk of the zinc will be found crystallized out as sulfate. Decant the clear solution and wash three times with cold water, allowing each washing to drain. Dilute the filtrate to 200 cc. and pass in hydrogen sulfide until all cadmium is precipitated: usually 15 to 20 minutes is sufficient with a fairly rapid evolution of gas. Allow the precipitated cadmium sulfide several hours time to settle before filtering off. Determine

cadmium by any of the methods mentioned in the above-mentioned papers.

Cadmium may also be determined iodometrically according to von Berg's¹ method (modified), by transferring to an Erlenmeyer flask, adding about 125 cc. of distilled water, a measured excess of *N*/10 iodine solution and then 30 to 50 cc. dilute hydrochloric acid. Shake and titrate with sodium hyposulfite until slight iodine excess is indicated; then add a few cc. starch solution and finish titration until disappearance of the blue color. The difference is due to cadmium: 1 cc. *N*/10 iodine solution = 0.00562 gram cadmium.

The new zinc-cadmium separation has been applied successfully to zinc ores also. Before its introduction it was a difficult matter to detect and determine accurately the small amounts of cadmium usually occurring in these ores.

PROCEDURE—Dissolve 5 grams ore in nitric or hydrochloric acid, according to the nature of the ore, fume off with 20 cc. sulfuric acid, add water, boil and filter. To the filtrate add an excess of ammonia, boil and precipitate iron and alumina. Dilute to 500 cc., filter and pipette off an aliquot portion representing 3 or 4 grams; evaporate to low bulk and until small white precipitate appears; then add sulfuric acid and boil down to 80–100 cc. Remove from hot plate and allow zinc to crystallize out. Decant solution and precipitate cadmium as previously directed. Redissolve on filter with hot hydrochloric acid, neutralize filtrate with ammonia and add about 10 grams trichloroacetic acid: dilute to 200 cc. and precipitate once more with hydrogen sulfide. A pure cadmium sulfide is now obtained, which may be determined by any of the methods previously described, but the most accurate is undoubtedly the gravimetric determination as sulfate.

I think that the above separation can be applied in brass analysis in detecting small amounts of cadmium. Recently, attention was called to the difficulty of detecting and determining small amounts of cadmium,² and the need of more accurate methods. This applies particularly to methods of separation, since the actual determination does not offer any unusual difficulties.

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THE CHEMICAL EXAMINATION OF NATURAL BRINES³

By O. R. SWEENEY AND JAMES R. WITHROW

The proper analysis of natural brines has always been important. They are used by chemical manufacturers to make comparisons with a view to reaching decisions as to prospective yields of salt, bromine and other products. The war-time elevation of the price of bromine from 30 cents to as high as \$6.50 per lb., as well as a similar elevation of other products derived from natural brine, has given rise to search for additional sources of these products and a careful scrutiny of many of the brines encountered in oil, gas and coal

¹ Presented at the *Symposium on the Chemistry and Metallurgy of Zinc*, 54th Meeting American Chemical Society, Kansas City, April 10 to 14, 1917.

² *Eighth Intern. Congr. Appl. Chem.*, 1, 183, and *THIS JOURNAL*, 5 (1913), 401.

³ Sutton's "Volumetric Analysis," 10th Ed., p. 172.

² *Eng. Mining J.*, Mar. 3, 1917, p. 392.

³ Read before the Industrial Division, Kansas City Meeting of the American Chemical Society, April 12, 1917.