

Samarium. Analysis of the sulphate.

1.36567 grm. $\text{Sa}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, gave 1.09770 $\text{Sa}_2(\text{SO}_4)_3$. $\text{Sa} = 150.76$.
1.09770 $\text{Sa}_2(\text{SO}_4)_3$ gave 0.65046 Sa_2O_3 . $\text{Sa} = 150.66$.

Mean, 150.71. As the material was not entirely free from europium this value is too high.

Gadolinium. 0.88884 Gd_2O_3 gave 1.48257 $\text{Gd}_2(\text{SO}_4)_3$ and 1.83903 $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Hence $\text{Gd} = 155.78$, which is somewhat too low.

Erbium. 1.09395 Er_2O_3 gave 2.53997 $\text{Er}_2(\text{SO}_4)_3$. $\text{Er} = 167.14$.

Ytterbium. 1.067279 Yb_2O_3 gave 2.69209 $\text{Yb}_2(\text{SO}_4)_3$. $\text{Yb} = 173.08$.

Baxter and Griffin¹ have shown that the oxalates of the rare earths, under certain conditions, carry down ammonium oxalate. This possibility should be borne in mind in any determination of atomic weights by the oxalate method.

Wyrouboff and Verneuil² in a long paper upon cerium, reproduce their determinations of 1897, and defend them against criticisms. No new determinations are given.

Some additional information upon thorium, berzelium and carolinium has been published by Baskerville³. The report is one of progress, without final results.

Miscellaneous Notes.

Bradbury⁴ has pointed out certain relations between the atomic weights of several elements, but his results do not seem to have any great importance. There is also a memoir by Hinrichs⁵ in which he reiterates his well known views in favor of whole-number atomic weights, and criticizes the modern determinations.

[CONTRIBUTION FROM THE COMMITTEE ON UNIFORMITY IN
TECHNICAL ANALYSIS III].

REPORT OF THE SUB-COMMITTEE ON ZINC ORE ANALYSIS.⁶

BY GEO. C. STONE AND W. GEO. WARING.

Received January 6, 1907.

In 1903 your Committee prepared three samples of zinc ore: A, a pure blende from Joplin. B, a mixture of franklinite, willemite, calcite, etc., from Franklin, N. J., and C, an impure blende from Colorado containing a good deal of iron, copper and lead. These were analyzed by forty-two chemists, and the results reported to the New York Section in 1904

¹ This Journal, 28, 1684.

² Ann. chim. phys., (8) 9, 349.

³ 4th Ann. Rep. Carnegie Institution, p. 136; and 5th Rep. p. 144.

⁴ Chem. News, 94, 157 and 245.

⁵ Chem. Cent., 1906, I. 197. Abstract from the *Moniteur Scientifique*, which I have not seen.

⁶ Read at the New York Meeting of the American Chemical Society.

and printed in a report of the Committee on Uniformity of Technical Analysis¹.

The results were very bad ; those on sample A varied from 55.97 to 59.79 per cent. zinc ; on B, from 12.20 to 39.22 ; and on C from 28.90 to 38.86.

The methods used were divided into eight classes :

1. Low's original method. In this the ore is decomposed by a saturated solution of potassium chlorate in nitric acid, evaporated to dryness, taken up with ammonia and ammonium chloride, the filtrate acidified with hydrochloric acid and titrated with potassium ferrocyanide.

2. The Hinman-Low method. In this the ore is first decomposed by hydrochloric acid and then treated as in the last.

3. The Wintersteen method. In this the ore is decomposed by evaporation with seventy-five to one hundred times its weight of hydrochloric acid and treated as in the Low method, but the titration is performed in the alkaline solution after adding citric acid and ferric chloride ; acetic acid is used as indicator.

4. The Joplin method. The ore is decomposed by aqua regia, the iron precipitated twice by ammonia and ammonium chloride, the filtrates acidified and titrated with ferrocyanide.

5. The same as the last except that the solution is treated with lead to remove copper, or with aluminum or hydrogen sulphide to remove lead copper and cadmium.

6. Methods in which the copper, etc., are separated as in the last, the iron by barium carbonate or by ammonia, or as basic acetates, and the manganese by an oxidizing agent. The zinc is either titrated or weighed.

7. Methods in which the copper and iron are separated as in 6 and the zinc precipitated as sulphide from an acetic acid solution. The zinc is either weighed or titrated.

8. Waring's method. The ore is decomposed by acid or fusion and the silica removed. The acid solution is then boiled with aluminum to reduce the iron and precipitate the lead, copper, cadmium and bismuth, neutralized exactly, slightly acidified with formic acid and the zinc precipitated by hydrogen sulphide under slight pressure. The zinc is finally determined either gravimetrically or volumetrically.

Method 1.—On sample A the fourteen results varied from 57.30 to 59.12 the correct result being about the average. Sample B, thirteen determinations, all low, from 12.20 to 14.73, the actual amount being about 18.00. Sample C, fourteen results from 30.20 to 33.83 ; most of these were low.

¹ This Journal, 26, 1644, (1904).

Method 2.—On samples A and C there was but one determination each; the results were fair. Sample B, eight determinations, varying from 17.20 to 19.57; only two were good.

Method 3.—The variations on all three samples were very large.

Method 4.—The results on sample A were good, but on samples B and C they were worthless, as this method does not separate the manganese and copper which these ores contained.

Method 5.—No results on sample A or B. Sample C, eighteen results, most of which were fair, although there were three or four at each extreme that were very bad.

Method 6.—None on A or C. On B the results were very irregular, from 16.90 to 23.30, only five out of sixteen being near the truth.

Method 7.—Most of the results on all three samples were fair and a large proportion were good.

Method 8.—Three determinations on A, five on B, and three on C, all good.

These results show the unreliability of the separation of manganese and zinc by oxidizing agents; they also show that there is danger of obtaining high results in titration owing to the presence of undecomposed potassium chlorate, etc.

The method of titration used in No. 3 cannot give accurate results, as the zinc value of the ferrocyanide varies with the amount of zinc present so that it is impossible to get correct results unless the solution has been standardized with exactly the amount of zinc contained in the sample analyzed.

The only method that gave uniformly accurate results was No. 8, and at the conclusion of the report we said:—“Method 8. This method is applicable to all ores and zinciferous materials, and it is only the fact that it has not been tried by more persons that prevents us from recommending its general adoption - - - - We would like to have as many as possible try this method to see if it is as successful in other hands as in those of its originator.”

A number of chemists having expressed their willingness to co-operate, a new sample was prepared by grinding together three ores similar to those used before, with enough cadmium sulphide to give about 0.6 per cent. of cadmium in the mixture, and this sample “D” was sent out for analysis.

Some of the first results reported showed that some analysts had difficulty in getting correct results. Mr. Waring and Mr. Weber of the Bureau of Standards made a number of experiments and traced the trouble to two sources, the principal being the necessity and difficulty of exactly

neutralizing; and sometimes to a partial oxidation of the iron after it had been reduced by aluminum and before the precipitation by hydrogen sulphide. They therefore proposed the following modified method:

Modified Waring Method.

After decomposing the weighed sample by acids alone or aided by fusion as the case may require, all the zinc is to be brought into solution as sulphate. If nitric acid was used in the decomposition, all traces of it must be expelled by evaporation with hydrochloric and sulphuric acids successively or by two evaporations with sulphuric acid, finally to abundant evolution of fumes of sulphur trioxide. Dissolve the mass in 25 to 40 cc of water, add sufficient sulphuric acid to bring the free acid in the solution up to 10 or 15 per cent. Introduce a piece of heavy sheet aluminum and boil 10 minutes, or to complete reduction. Filter and wash through a filter containing a piece of aluminum into a beaker containing a stirring rod or strip of the same metal, cool, add a drop of methyl orange and neutralize carefully with sodium bicarbonate to a light straw color. Add, drop-wise, dilute formic acid (20 per cent. strength) until the pink color is just restored, then 5 drops more. (Dilute hydrochloric acid, one part strong acid to 6 parts water, may be substituted for formic acid when ammonium sulphocyanate¹ is to be introduced). Dilute to about 100 cc. for each 0.1 gram Zn possibly present, add, if much iron is present, 2 to 4 grams ammonium sulphocyanate, remove the strip of aluminum, heat nearly to boiling and saturate with hydrogen sulphide. Allow the pure white zinc sulphate to subside for a few minutes, then filter and wash with hot water. Transfer precipitate and filter to a capacious beaker, heat with 8 or 10 cc. of strong hydrochloric acid and 30 or 40 cc. of water until the zinc is all in solution. Determine the Zinc as pyrophosphate, containing 42.91 per cent. zinc; or by titration with ferrocyanide. The use of ammonium heptamolybdate² in one per cent. solution as an indicator instead of uranium acetate or nitrate is recommended, provided all free hydrogen sulphide has been previously expelled from the solution by heating. If a blue color still appears in the test drop, add a crystal or two of sodium sulphite to the zinc solution, to decompose any remaining hydrogen sulphide.

The following table gives the results received on Sample D. They have been grouped by methods as before. In addition we have added a column for the modified method and one to include some additional methods of each of which there were only one or two determinations; this has been headed miscellaneous.

¹ Zimmermann Annalen, 99, 1.

² Nissenson and Kettembeil, Chem. Ztg., 77, 951-955.

TABLE I.

Method 1.		Method 2.		Method 3.		Method 6.	
Chem.	% Zn.	Chem.	% Zn.	Chem.	% Zn.	Chem.	% Zn.
19	31.62 V	17A	30.94 G	I	31.49 V	44	31.31 G
..	31.68 V	..	31.12 V	..	31.89 V	..	31.32 G
..	31.70 V	17B	31.00 G	..	31.91 V	..	31.36 G
..	31.66 V	..	31.25 V	39	30.60 V	..	31.40 G
32	30.87 V	34	33.80 V	..	30.80 V	47	31.59 V
..	30.97 V	34A	33.70 V	..	31.59 V	..	31.64 V
46	31.95 V	..	33.80 V	..	31.47 V	49	31.47 G
..	31.40 V	44	31.40 V	..	31.55 V	50	31.02 V
54	30.30 V	..	31.50 V	..	31.80 V	..	31.05 V
..	30.50 V	50	31.52 V	50	28.81 V	53	31.50 V
..	30.60 V	58	31.54 V	55	31.90 V
..	30.80 V	31.63 V	..	32.01 V
..	31.54 V
..	31.63 V
Method 7.		Method 8.		Modified.		Miscellaneous.	
		Original.					
50	31.60 V	I	32.24 G	I	31.42 V	19	31.10 V
..	31.70 V	..	32.30 G	..	31.46 V	..	31.16 V
57	31.48 G	..	32.31 G	..	31.38 V	50	29.49 V
..	31.51 G	..	32.33 G	..	31.51 G	..	29.40 V
33	31.10 V	..	35.53 V	..	31.69 G	52	31.47 G
..	32.56 V	3	31.53 V	..	32.13 G
..	32.37 V	..	31.63 V	3	31.61 V
..	32.34 V	..	31.68 V	56	31.48 G
..	32.34 V	19	31.58 V	..	31.37 G
..	32.49 V	..	31.59 V	..	31.44 G
..	32.53 V	56	31.32 G	..	29.55 G
..	II	31.40 V	..	31.39 G	..	29.60 G
..	31.40 V	24	31.80 V	..	26.45 G
..	24	30.56 V	..	31.80 V	33	30.24 V*
..	26	31.53 V	..	32.00 V	*Cu separated	
..	32	30.71 V	32	31.40 V	as thiocyanate,	
..	31.05 V	33	31.40 V	then Zn as sul-	
..	33	31.37 V	..	31.41 V	phide by H ₂ S.	
..	31.46 V	..	31.41 V		
..	31.50 V	..	31.77 V		
..	34	31.40 V	51	31.82 V		
..	38	31.55 V	..	31.82 V		
..	44	31.30 G	..	31.82 V		
..	31.50 V	..	31.45 V		
..	48	32.88 V	58	31.43 V		
..	32.75 V	59	31.40 V		
..	32.61 V	45	31.40 V
..	49	31.45 V	60	31.50 V
..	51	30.77 V	..	31.29 G
..	30.87 V	..	31.70 G
..	30.97 V	..	31.23 V
..	30.82 V	61
..

Method 7.		Method 8. Original.		Modified.		Miscellaneous.	
Chem.	% Zn.	Chem.	% Zn.	Chem.	% Zn.	Chem.	% Zn.
..	30.77 V
..	30.87 V
..	30.82 V
..	54	31.20 V
..	31.50 V
..	56	31.27 V
..	31.35 V
..	31.37 V
..	31.41 V
..	31.44 V

The chemists up to and including number 42 are those who reported the results given in the first series. The G or V following the result signifies gravimetric or volumetric respectively. The results are very much better than the first series. Method 1 still shows a tendency to give low results. Method 2 gives good results for four out of the six analysts who used it. Method 3 is still very irregular. Methods 4 and 5 are not represented. Methods 6 and 7 are, as a rule, good. With method 8 (original) two chemists report very high results, three very low, and the remaining ten are all within two tenths of one per cent. of the most probable result. With method 8 modified there are 31 results by 13 analysts; 11 of the analysts and 19 of the results are within two tenths of the most probable result; the other two analysts are about four tenths high. Of the miscellaneous method, No. 19 did not state what method he used; both his results are rather low. No. 50 does not describe his method clearly enough to permit of classifying it. No. 52 used a method that is practically the same as 8 for the result 31.47; the other result was obtained by another modification of the same method; in both cases the zinc was weighed as zinc ammonium phosphate. The first three results by No. 56 were obtained by separating cadmium, etc., as sulphide, and precipitating and weighing zinc as sulphide. His last three results were obtained by separating cadmium and copper with caustic soda¹. No. 3's result was by method 4.

In the Bureau of Standards Dr. H. C. P. Weber has made a number of analyses of this sample by several methods, and Dr. Noyes says "I feel very confident that the final value, 31.41, must be very close to the actual content of zinc. This is based on the air-dry ore."

Since our former report Dr. Nissenon has made his report to the International Congress of Applied Chemistry at Rome. In this report he gives a complete and excellent review of the methods that have been proposed for determining zinc and has made a number of analyses to compare different methods. He has tried the method which we have called No. 7,

¹ Low. Tech. Meth. Ore Analysis, 1905, p. 216.

weighing the zinc as sulphide, an electrolytic method and the titration both with ferrocyanide and sodium sulphide, and finds that he gets about equally good results with all and therefore makes no recommendations. In this country the sodium sulphide method has never met with favor and is not likely to on account of the rapidity with which the solution changes its value. In some works where it is used they find it necessary to run a standard with each ore.

We greatly regret that no determinations have been made of this sample by any electrolytic method, as the published results indicate that such methods are both rapid and accurate.

From the results given above we strongly recommend the modified Waring method for use in all cases where accurate results are required and for all check analysis.

The following notes on the method may be of assistance. Under the conditions described the precipitation of cadmium is complete, but traces of copper remain in solution unless the boiling is continued for a very long time; this prolonged boiling is not necessary as the copper is afterwards precipitated as sulphide with the zinc and does not redissolve with the latter.

In neutralizing, if the solution is strongly acid, it is better to nearly neutralize with sodium or potassium hydroxide and finish with bicarbonate. This not only saves time but lessens the chance of loss by foaming.

It is not necessary to pass the hydrogen sulphide under pressure if the solution is diluted as already directed. The gas should be passed through the solution until a drop of the liquid blackens a drop of cobalt or nickel sulphate or chloride made alkaline with ammonia. After a little experience it is not necessary to make even this test. It is very important that the zinc solution should be quite hot during the precipitation of the sulphide, therefore it is advisable to begin nearly at the boiling point and to pass the gas rapidly. If the heating of the solution has taken much time, the excess of formic acid may volatilize (if this reagent has been used). In such cases enough more must be added to make the solution acid.

We most strongly recommend that zinc be determined gravimetrically by weighing as pyrophosphate, except where the operator has had much and recent practice with the ferrocyanide titration. While the latter is capable of giving very accurate results it will only do so when *all* the conditions are *exactly* the same both in standardizing and during the final titration, and it is necessary to have considerable experience with the method to be sure of accuracy.

In regard to the indicator to be used, whether uranium nitrate or acetate or ammonium molybdate, and the method of applying the test, whether on paper, on a porcelain cavity plate, flat plate or a paraffin-coated

plate, each chemist should make experiments and decide which suits him best. All these reagents and methods have given good results in different hands, and men who are entirely successful with one, often have great difficulty in obtaining good results with some of the others.

For a full description of the details of the determination of zinc as pyrophosphate and for the ferrocyanide titration, see the paper by Mr. Waring in this Journal, **26**, 9, (1904).

In conclusion we wish to express our thanks to all of those who have taken part in the work and without whose cordial co-operation it could not have been carried on.

(CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY).

A NECESSARY MODIFICATION OF VOLHARD'S METHOD FOR THE DETERMINATION OF CHLORIDES.¹

BY M. A. ROSANOFF AND ARTHUR E. HILL

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I. On the Determination of Chlorides.

Volhard's method for the determination of chlorides is well known. It consists in acidifying the given solution with nitric acid, adding a ferric salt (say iron-ammonium alum) as an indicator, precipitating the chloride with a measured but excessive amount of a standard silver nitrate solution, and without filtering out the silver chloride, determining the excess of silver nitrate by titration with a standard solution of ammonium sulphocyanate. As long as the solution contains any silver, the ammonium sulphocyanate produces only a white precipitate of silver sulphocyanate. When the silver is gone, the solution is colored red by the sulphocyanate of iron.

A somewhat extensive experience in using this rapid method gradually forced upon us the feeling that in its present form it is inaccurate. The more carefully the titration is carried out, the less distinct the end-point often seems to be. A historical investigation showed that others have had similar experience with the method. Some time after the appearance of Volhard's first paper² Brügelmann reported³ that the end point in question was indistinct, explaining it, however, on the assumption that it was the free nitric acid present that was destroying the color by oxidizing the sulphocyanate. The interfering factor was more clearly discerned by Drechsel,⁴ who found that sulphocyanate of iron is decomposed

¹ Presented before the New York Section of the Am. Chem. Soc., December 7, 1906.

² J. pr. Chem. **9**, (N. F.) 217 (1874).

³ Z. anal. Chem. **16**, 1 (1877).

⁴ J. pr. Chem., **15**, 191 (1877); Z. anal. Chem. **16**, 351 (1877).