for the mixture with no sodium was raised to the same value as was obtained with the first ore. By this time, however, the mixes had been rotated for many hours in the kilns and had, therefore, become thoroughly pulverized. When we, therefore, ground the ore very fine before using it the results were likewise improved. The state of division is not, however, the sole factor in the difference between the two ores for we have worked with ore coarser than the second and obtained excellent results. A more important factor appears to be the ease with which the ore becomes pulverized in the kilns (hardness).

In view of the facts stated, we therefore made another set of experiments in which we used recovered and residual manganese dioxide with new potassium hydroxide. The former was obtained from the same manufacturer who had furnished us with the recovered alkali described in the second section. The ratio of alkali to manganese dioxide was again 2.28 moles of the former to one of the latter. When the old manganese dioxide, as we may call the material for brevity, was used just as it was received, it gave uniformly low yields—from 25 per cent to 35 per cent of the theoretical—while we should have obtained about 85 per cent. Since it is well known that manganese dioxide absorbs (or perhaps combines with) relatively large amounts of caustic alkalies, we suspected that the old dioxide might be contaminated with considerable sodium hydroxide. We therefore washed it very thoroughly with water and in some cases boiled it with dilute nitric acid. When the recovered and residual dioxide was fresh it responded very well to this treatment; material which had been kept for some time, and especially material which had dried out, was not much improved. These results point to the conclusion that it was the absorbed sodium hydroxide which was responsible for the deteriorating of the dioxide and which becomes more difficult to remove as the material dries out. Since the first section of the paper shows how large amounts of residual dioxide can be avoided and as it is not necessary to convert the manganate into permanganate by processes in which large amounts of dioxide are reprecipitated, it did not seem necessary for us to follow up this point further.

SUMMARY

1—It is found that when manganese dioxide is heated with potassium hydroxide in a current of air to produce potassium manganate, the reaction frequently stops before the maximum oxidation stage has been reached. This can be avoided by remoistening and reheating the mix; the use of moistened air also is helpful.

2—The yield of potassium manganate varies greatly with the proportion of potassium hydroxide in the mixes. At the temperatures at which these experiments were carried out and with the pyrolusite used, practically all of the manganese dioxide is converted into manganate when 2.5 moles of potassium hydroxide are used for each mole of manganese dioxide.

3—The conclusions of Sackur that in this reaction mangani-manganates and not manganates are obtained

and that the maximum yield attainable is, therefore, only 60 per cent, is thus proved to be incorrect.

4—Larger amounts of alkali, however, cause the manganate to decompose into a mangani-manganate, similar to, if not identical with, that postulated by Sackur.

5—The substitution of sodium hydroxide for potassium hydroxide greatly lowers the yield if the proportions between alkali and manganese dioxide named are employed. What the effect of other proportions would be is as yet undetermined. Care must be taken, therefore, not to allow sodium to accumulate in the recovered caustic when the operation is carried out continuously.

6—It is very important to pulverize the ores very finely and to keep them finely divided in the kilns in order to obtain the highest possible yields. Some ores are more difficult to handle in this respect than are others.

7—The residual manganese dioxide sometimes deteriorates on repeated use. This may be caused by absorption of impurities from the solution. If the dioxide before it has had time to dry out is thoroughly washed with water or boiled with dilute nitric acid, its effectiveness for the process may be restored.

This work is to be continued along the lines suggested. A number of similar problems connected with the preparation of barium manganate remain to be solved and work on these has also been begun.

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THE DETERMINATION OF ZINC AND COPPER IN GELATIN¹

By GEORGE S. JAMIESON
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One method used for the determination of zinc and copper in gelatin is based upon the complete destruction of the organic matter by digestion with nitric and sulfuric acids.² After the digestion is completed, water is added, and the solution is made slightly alkaline with ammonium hydroxide. Then a measured quantity of hydrochloric acid is added. The copper is precipitated as sulfide and filtered. The filter containing the copper sulfide is digested with nitric and sulfuric acids until a colorless solution is obtained. The copper is finally titrated by the well known iodide-thiosulfate method. When the hydrogen sulfide has been removed from the filtrate containing the zinc, ammonium chloride is added along with ammonium hydroxide to make the solution alkaline. Enough hydrochloric acid is added to render the solution acid to methyl orange. After adding a large excess of sodium or ammonium acetate, the zinc is precipitated with hydrogen sulfide and filtered. The zinc sulfide is dissolved in hydrochloric acid and the resulting filtrate is boiled to remove the hydrogen sulfide. A small amount of ferric chloride is added and a basic acetate precipitation is made in the usual manner in

¹ Published by permission of the Secretary of Agriculture.

² Methods of analysis, A. O. A. C., 1916, 175.

order to separate any phosphates present from the zinc. The zinc is precipitated from the filtrate as sulfide and after filtration is ignited to the oxide. It is well known that the digestion of gelatin with nitric and sulfuric acids requires almost constant attention during the entire process which generally takes 2 hrs. and sometimes longer for completion. In addition to the digestion, the long analytical procedure makes the method unsatisfactory.

Several years ago C. R. Smith decomposed gelatin with hydrochloric acid in connection with the determination of arsenic¹ and suggested that this method of decomposing gelatin could be used to advantage for the determination of the other metals in place of the tedious digestion process. Mr. Smith and a number of other chemists have employed the hydrolysis method for the determination of zinc and copper in gelatin. Since the method of separating the zinc and copper from the hydrolyzed solution is somewhat different from that employed in the digestion method, it will be briefly described. A small amount of magnesia mixture and an excess of sodium phosphate solution are added along with enough ammonium hydroxide to make the hydrolyzed gelatin solution alkaline. Then the zinc and copper are precipitated together as sulfides and filtered. The crystalline precipitate of ammonium magnesium phosphate serves to collect the metallic sulfides so that they can be readily filtered. The precipitate is treated with a cold solution of 1 : 10 hydrochloric acid which has been saturated with hydrogen sulfide in order to dissolve the zinc sulfide and leave the copper sulfide on the filter. The zinc and the copper are determined as described above.

It is believed that the following method will be found much simpler than those now used. The size of the sample taken for analysis varies from 20 to 50 g., according to the amount of zinc and copper present. The samples are weighed into 500 cc. beakers and treated with 100 cc. of water and 15 to 30 cc. of hydrochloric acid, depending upon the amount of gelatin taken for analysis. The covered beakers are heated for an hour or two on the steam bath. During the first part of the heating, the solutions are agitated several times in order to loosen any lumps adhering to the bottom of the beakers. After hydrolysis the solutions are made very slightly alkaline with ammonium hydroxide and allowed to cool to about 40° C. Then hydrogen sulfide is passed into the solutions for 2 min. While passing in the hydrogen sulfide, the solutions should be stirred several times with the delivery tube in order to facilitate the separation of the sulfides in the form most suitable for filtration. When the sulfides have settled for about 10 min., they are filtered on a 9 cm. filter and washed several times with a very dilute solution of colorless ammonium sulfide. The wash solution is prepared by passing hydrogen sulfide for several minutes into 250 cc. of water which contains 0.5 cc. of 1 : 1 ammonium hydroxide. In the case of high-grade gelatin it is recommended that about 2.5 mg. of iron should be added to the hydrolyzed gelatin before making the solution alkaline.

¹ *J. Assoc. Official Agr. Chemists*, [2] 1 (1915), 244.

It is found that the ferrous sulfide greatly facilitates the precipitation and the filtration of small quantities of zinc and copper sulfides. The iron is conveniently added in the form of a standard solution which contains 2.49 g. of ferrous sulfate in 1000 cc. (1 cc. = 0.5 mg. of iron). If the directions given above are closely followed in making the hydrolyzed gelatin solution very slightly ammoniacal, there is no danger of leaving any weighable amount of copper sulfide dissolved in the ammonium sulfide in the filtrate. The sulfides are dissolved by pouring a small quantity of very hot 1 : 1 nitric acid around the upper edge of the filters. The filters are washed very thoroughly with water at room temperature. The filtrate is evaporated with 10 cc. of 1 : 3 sulfuric acid until all the nitric acid is expelled. When the sulfuric acid is cool, 30 cc. of water are added, and the solution is filtered to remove the silica. The filtrate, which should have a volume of about 100 cc., is warmed to about 50° C. and hydrogen sulfide is passed into the solution for at least 5 min. in order to precipitate the copper completely. The copper sulfide is filtered on a Gooch crucible and washed with hot water saturated with hydrogen sulfide. During the filtration and washing of the precipitate a very gentle suction is employed, otherwise there is the danger of having some of the copper sulfide pass through the crucible. When the washings have thoroughly drained, the Gooch crucible is placed inside of a porcelain crucible and dried over a small flame for a few minutes. Then the flame is gradually increased to its capacity. At this point the outer crucible is removed and the Gooch crucible heated directly in the oxidizing part of the flame for 15 min. After cooling and weighing, the crucible is heated again as hot as possible for 5 min. more in order to be certain that all the copper is converted into the oxide. The filtrate containing the zinc is heated until the hydrogen sulfide is expelled. After adding about 5 cc. of ammonia in excess of that required to neutralize the sulfuric acid in the solution, 15 cc. of 50 per cent formic acid are added and a rapid stream of hydrogen sulfide is passed into the solution for 5 min. to precipitate the zinc sulfide. It is important to stir the solution with the delivery tube while passing in the hydrogen sulfide until the larger part of the zinc is precipitated. The solution containing the zinc sulfide is heated on the steam bath for about half an hour. The zinc sulfide is filtered on a Gooch crucible and washed with a 2 per cent solution of ammonium thiocyanate. During the filtration and washing of the precipitate, it is best to use either no suction or at most a very slight suction. When all of the precipitate is in the crucible and the wash solution has largely run through, the suction is increased until it is sufficient to drain the crucible properly. The zinc sulfide is dried and ignited to convert it into the oxide in the same manner as the copper sulfide is treated. After weighing, the crucibles containing the oxides of zinc and copper are treated with hydrochloric acid, thoroughly washed with water, and ignited in order to prepare them for subsequent analyses.

Several samples of commercial gelatins of various

grades were analyzed by the hydrolysis method described above as well as by the digestion method for the sake of comparison. In the digestion analyses it should be noted that the copper was determined by weighing the oxide in place of the volumetric method given above. Also the zinc was precipitated as sulfide in the presence of ammonium formate and formic acid instead of ammonium acetate and acetic acid.

In conformity to the usual custom, the results of the analyses are stated in terms of milligrams of metal per kilo of gelatin or parts per million.

No.	HYDROLYSIS METHOD		DIGESTION METHOD	
	Cu P. p. m.	Zn P. p. m.	Cu P. p. m.	Zn P. p. m.
1.....	..	1341.0	..	1341.0
1.....	..	1341.0	..	1340.0
1.....	..	1341.0	..	..
2.....	..	126.0	..	122.0
2.....	..	128.0	..	..
3.....	32.0	96.4	32.0	96.4
3.....	26.6	104.0	32.0	96.4
4.....	20.0	64.0	20.0	68.0
4.....	24.0	56.0	20.0	56.0
5.....	24.0	77.9	24.0	80.3
5.....	22.4	80.3	24.0	80.3
5.....	20.0	80.3	..	76.0

The copper was separated but was not determined in Samples 1 and 2 because at first it was intended only to investigate the determination of zinc.

In order to test the method further, measured quantities of standard solutions of zinc and copper were added to weighed amounts of Sample 5. The hydrolysis and analyses were made as described above with the following results:

SAMPLE TAKEN	Cu Added	Zn Added	Cu Found	Zn Found
Grams	Mg.	Mg.	Mg.	Mg.
20	2.5	2.8	2.5	2.7
20	3.0	3.1	3.1	3.2
20	2.5	4.7	2.4	4.7
20	2.0	3.1	1.9	3.2

It should be observed that the amount of zinc and copper in 20 g. of Sample 5 gelatin as determined by averaging the results obtained by previous analysis, has been deducted from the results given above. The results obtained with these trial analyses show that the method is accurate.

In order to obtain satisfactory results, it is most important that the directions be followed in every detail. Furthermore, great care must be taken to eliminate by filtration any non-volatile matter which may separate during the course of the analyses, before proceeding to make the final precipitation of the zinc or copper sulfides. Also, the Gooch crucibles used must be prepared so that they will not lose weight during the filtration and ignition of the sulfides.

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THE DEOXYGENATING EFFECT OF THE EFFLUENT FROM THE MILES ACID PROCESS OF SEWAGE TREATMENT

By F. W. MOHLMAN

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Experiments with the Miles acid process of sewage treatment were conducted at the New Haven Sewage Experiment Station under the direction of Prof. C. E. A. Winslow, from June 1, 1917, until May 1, 1918, in comparison with three other processes which have been considered for New Haven conditions.¹

¹ Eng. News Record, 79 (1917), 18.

Some very interesting facts were established during this work regarding the Miles acid process.

The Miles patent, No. 1,134,280 claims that the Miles process "(1) consists in introducing—an inorganic acid as the sole effective agent" and "(3) consists in introducing sulfurous acid into the sewage."

Sulfurous acid seems to have a selective toxic action on bacteria which is more intense than is obtained by the same hydrogen-ion concentration of sulfuric acid. The effect of the sulfurous acid is augmented by the germicidal power of the bisulfites formed from the bicarbonates. Therefore, from the standpoint of effective disinfection, sulfurous acid is preferable to sulfuric. It also has the decided advantage of being cheaper, when made as needed, by burning sulfur or pyrites and conducting the gas into a part of the sewage, which can then be used for acidifying the remaining sewage.

We have applied compressed sulfur dioxide to the sewage as it flowed into a settling tank through a galvanized iron pipe about 20 ft. long. The settling tank was 16 ft. long, 4 ft. wide, and 4 ft. deep. The detention period was 4 hrs. when treating 10,000 gal. of sewage per day. After acidification the sewage contains bisulfites and some free sulfurous acid. It also contains lime and magnesium soaps, which are attacked by the acid, liberating the free fatty acids. As the sewage passes through the tank, part of the bisulfites and sulfurous acid is oxidized to bisulfates and sulfuric acid. In the effluent there is a mixture of sulfurous acid, sulfuric acid, bisulfites, RHSO_3 (R indicating Na, K, Ca, Mg, or Fe), and bisulfates, RHSO_4 . The oxidation takes place at the expense of the dissolved oxygen in the sewage, and some oxygen is also supplied by absorption of atmospheric oxygen from the surface of the liquid. The oxidation may easily be followed by determining total sulfur dioxide in both bisulfites and sulfurous acid by titration, using an excess of iodine solution. By titration with standard sodium hydroxide, using methyl orange as indicator, all of the sulfuric acid but only half of the sulfurous acid is determined. This is due to the fact that the reaction $\text{H}_2\text{SO}_3 + \text{NaOH} = \text{NaHSO}_3 + \text{H}_2\text{O}$ takes place, and NaHSO_3 reacts neutral to methyl orange. To get accurate results as to the total acidity, all sulfurous acid should first be oxidized to sulfuric acid or else the sulfur dioxide in the sulfurous acid must be determined. Titration with standard sodium hydroxide using phenolphthalein as indicator includes the acidity due to bisulfites as well as that due to sulfurous acid and sulfuric acid, as NaHSO_3 reacts acid to phenolphthalein. By a combination of the three titrations the exact state of oxidation of the sulfur dioxide may be followed. These facts must be remembered in determining the acidity of the Miles effluent, as erroneous results may be reported when titrating with methyl orange when the effluent contains unoxidized sulfur dioxide. We have usually attempted to carry the free acidity to 50 p. p. m. (as CaCO_3).

Preliminary tests made on February 14, 1918, showed a total content of 118 p. p. m. of sulfur dioxide