and by Myers, in the references cited above, was used. The anode was a spiral of heavy platinum wire, 1 cm. in diameter. It was made to rotate about 600 times per minute. A solution of copper sulphate, when acted upon under these conditions, with a current of 2 amperes and 4 volts, lost its color in fifteen minutes. This led to the following quantitative determinations of copper.

Copper present. Gram.	Volts.	Amperes.	Time. Minutes.	Volume of liquid. cc.	Copper found. Gram.	Separation of poles. cm.
0.2405	10 to 5	0.01 to 2.0	30	40	0.2401	2
0.2405	10 to 5	0.01 to 2.0	20	25	0.2401	1
0.4810	10 to 5	0.01 to 2.0	25	25	0.4805	1

The copper sulphate solution was neutral at the beginning of the decomposition, hence the low current in the early stages of the precipitation. The more concentrated the solution the more rapidly did the metal separate. It seems probable from other experiments that 0.5 gram of copper can be deposited in fifteen minutes. The several trials made with a nickel sulphate solution indicate that from 0.25 to 0.5 gram of that metal can also be precipitated *with a mercury cathode and rotating anode* in about the same period of time.

Mention is here made of these observations as experimentation in this particular direction will be undertaken immediately. Should success attend the same, as there is every reason to believe, one rather expensive factor in electro-analysis will be eliminated, *viz.*, the platinum dish, cone or cylinder.

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COMPOSITION OF THE FOUR SULPHIDES OF MANGANESE.[1]

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LITERATURE.

THE composition of the two commonly known sulphides of manganese has been investigated by several workers. The results obtained have been so conflicting that it is impossible to decide from the literature whether either of these sulphides is anhydrous or not, much less to give the exact composition. The reason for this discrepancy, as we shall attempt to show, has been the failure

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[1] Read before the New York Section of the American Chemical Society, April 8, 1904.

to recognize the existence of a gray and a red sulphide of manganese.

F. Muck reported that the green sulphide is crystalline (eight-sided plates) and that its composition corresponds to the formula $Mn_2\begin{matrix}S\\O\end{matrix}\Big|\begin{matrix}S\\H_2\end{matrix}$, and states that he found 7.43 per cent. of water. The theoretical percentage of water, according to the formula given, is 9.38. Muck appears to think that the green sulphide is an oxysulphide containing a molecule of hydrogen sulphide. He seems to have come to this conclusion from the observation that sulphur is given off on heating the sulphide in a stream of hydrogen or carbon dioxide. We have frequently made the same observation, but have attributed it to the presence of free sulphur, which, as is well known, is not completely dissolved by carbon disulphide. Muck prepared the green sulphide by the ammonium oxalate method given on page 1623. He does not give the composition of the pink sulphide.

Alexander Classen,[1] who prepared the green sulphide by digesting the pink sulphide with excess of ammonium sulphide, states that the green modification is anhydrous.

Cleremont and Guiot,[2] who conducted a very extensive investigation on this subject, found that the green sulphide, when dried at 105° in a stream of hydrogen is anhydrous, while the pink variety, dried under the same conditions, contains about 9 per cent. of water. They ignited the material in hydrogen and called the loss water. They do not mention extracting free sulphur before ignition and since samples prepared by us contained from 4 to 14 per cent. of free sulphur they are not justified in stating that the 9 per cent. lost is water.

Völker[3] prepared the pink sulphide by a very laborious method. He passed hydrogen sulphide through a very dilute solution of manganous acetate. He removed the acetic acid liberated by evaporating down the filtrate until the free acid was volatilized. The residue was then diluted with water and hydrogen sulphide again passed. He states that the sulphide so obtained can be washed and dried without decomposition, while that precipitated by means of ammonium sulphide can not. He determined the

[1] *Ztschr. anal. Chem.*, **16**, 319.

[2] *Gazz. chim. ital.*, **23**, 560 (1893).

[3] *Ann. Chem. Pharm.*, **59**, 38.

water by mixing the sample with dry lead carbonate and heating in a glass tube. He obtained the following results:

	Manganese.	Sulphur.	Water.
1	60.45	37.68	2.08
2	59.09	38.33	2.44

He states that the material varied in color from light to dark red, the first sample being darker than the second.

Antony and Donnini,[1] two Italian chemists, state that "both sulphides are identical in composition and it is erroneous to consider the green sulphide to be an oxysulphide or an anhydride, and the pink a hydrate." They conclude that both sulphides are anhydrous, both are crystalline. The only difference which they can discover, besides the color, is in specific gravity. They find that the green sulphide has a higher specific gravity than the pink modification. They dried the pink sulphide at 70° in an atmosphere of carbon dioxide and extracted the free sulphur with carbon disulphide. Their dried sample was red. On heating a sample to 320° in an atmosphere of carbon disulphide a loss of only 0.21 per cent. was noted.

COMPOSITION OF THE PINK SULPHIDE.

The first sample of the pink sulphide was prepared by precipitating the manganese from a neutral solution of manganous chloride with ammonium sulphide. It was washed by decantation with water containing ammonium sulphide. To prevent oxidation the washing was completed in an atmosphere of hydrogen sulphide, but in about fifteen minutes the precipitate began to change color from pink to green. In forty-five minutes this change was complete. In the subsequent preparations the washing, as well as drying, was carried out in an atmosphere of hydrogen. The hydrogen was carefully freed from oxygen by passing the gas through a red hot tube containing metallic copper.

When filtering off and washing the sulphide, a few minutes' exposure to the air was sufficient to completely convert the material on the surface into the brown sesquioxide. When partially dried, the pink sulphide oxidizes still more rapidly when exposed to the air. One sample had been placed in a desiccator and partially dried by heating in the air-bath after the air had been displaced by hydrogen. On opening the desiccator to remove a large

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[1] *Bull. Soc. Chim.*, 1877, p. 353.

amount of water which had collected on its sides, a blue flame was noticed on the partially dried sulphide. On extinguishing the flame the pink material had become white. This material proved to be manganous sulphate. Usually the oxidation produced the brown sesquioxide.

This brown material is readily reconverted to the pink sulphide by treatment with hydrogen sulphide. At first this was done with the dried material. The transformation was quite rapid and was accompanied by a very noticeable increase in temperature. After such a treatment the sulphide was again dried, and the sulphur liberated from the hydrogen sulphide was extracted by means of carbon disulphide. In the later preparations the brown material was removed by allowing a little hydrogen sulphide to pass through the apparatus with the hydrogen. The free sulphur was removed with carbon disulphide as before. No sample of the pink sulphide was obtained which was free from sulphur. The amount present has varied from 4 to 14 per cent.

The drying was conducted on the steam-bath, a partial vacuum of one-half atmosphere being maintained. The drying required from six to eight hours. The bulk of the sulphide decreased, during the drying, to about one-fourth of the original bulk. It was found free from all impurities except sulphur. The dried material is quite stable, requiring no special precautions for its preservation. It can be heated in the air to 100° without oxidation. On heating it to 205° it began to oxidize quite rapidly. It was then heated in an atmosphere of hydrogen to 360°, when it gradually changed to the green modification.

Several samples, prepared in the manner just described, were analyzed. The method employed consisted in extracting the free sulphur with carbon disulphide and then igniting the residue with sulphur in a stream of hydrogen. In this manner the amount of anhydrous manganous sulphide was obtained. The loss was assumed to be water. The following percentages were obtained: 9.30, 6.73, 8.54, 10.58, 8.98, 5.55.

A serious error in this method of determining water was found in the fact that it was impossible to extract all of the free sulphur with carbon disulphide, a portion of it being present in the modification, insoluble in carbon disulphide. We do not believe that this or other errors of analysis account for the great divergence in the results obtained. We believe that the differences were due to the fact that we did not have a product of uniform composition. This became more evident as the work continued.

As the pink sulphide, prepared as just described, showed a tendency during the washing to change color more or less rapidly, another method of preparation was adopted. Instead of precipitating with ammonium sulphide, colorless sodium sulphide was used. Muck, as well as Cleremont and Guiot, have found that in the presence of this reagent the pink modification could not be changed to the green sulphide. The washing and drying were carried out in the same manner as before. The product obtained differed markedly from that previously obtained. It was not pink, but *brick-red.* We consider this product a distinct sulphide of manganese different from the so-called pink sulphide.

The Penfield method of determining water was also adopted. The tubes used were about 8 inches long. Before sealing the end they were heated with the Bunsen burner to dry them. The weighed amount of manganese sulphide was first introduced. Enough anhydrous lead oxide was then introduced to form a layer about ¾ inch long. This amount of lead oxide is sufficient to absorb all of the sulphur given off from the weight of manganous sulphide employed. The water was then expelled in the usual manner by heating with the Bunsen burner. While the tube was cooled with a moist cloth it was fused off and the portion containing the water was weighed. The water was then expelled and the tube again weighed, the difference being the weight of the water. The method was checked by determining the percentage of water in crystallized barium chloride. As the red sulphide contained only a small amount of water, about 7 mg. being the maximum amount weighed, portions of barium chloride containing 7 mg. or less of water were taken. The following results were obtained: 14.54, 14.46, 14.79 per cent., the average being 14.60 per cent., while the theoretical percentage is 14.71.

The percentages of water found in three samples of the red sulphide were 0.74, 0.77 and 0.74. These results agree fairly well with those of Antony and Donnini, who found 0.21 per cent. of water in the "pink" sulphide, which they say was red when dried. Völker found as low as 2.08 per cent. of water and states that this sample was dark red. As he states that his samples varied in color, his product must have been a mixture, as we soon discovered our "pink" product to have been. Our earlier results agree with those of Cleremont and Guiot, who found about 9 per cent. of water.

It was very gratifying to discover in the next series of preparations the cause of these varying results. This appears to be the presence of a *third or fourth sulphide of manganese* which, from its color, is called the *gray* modification and which contains a considerable amount of water. This sulphide is mentioned by Roscoe and Schorlemmer, who state that its formula is $3MnS.H_2O$, in which the theoretical percentage of water is 6.45. The reference to the literature is erroneous and we have been unable to find the original article. The existence of this sulphide seems to have been overlooked by all the other investigators of the sulphides of manganese.

We obtained it in a sample of the "pink" sulphide which had been exposed during the drying process to more than the usual amount of hydrogen sulphide. This sample was composed of lumps which were gray on one side and red on the other. Some of the pieces which contained the least amount of the red material were selected and the amount of water determined. 2.96 per cent. was found. A portion, which represented a fair average sample of the mixed material, was analyzed and was found to contain 1.76 per cent. of water. It will be observed that this is about two-thirds of the amount present in the impure gray material, and more than twice as much as we have found in the red sulphide. On powdering a portion of this mixed material a product was obtained which has the characteristic flesh color of the so-called pink sulphide of manganese. This sulphide should, therefore, be regarded as composed of varying amounts of the gray and red sulphides of manganese. The various percentages of water found by the other investigators, as well as by ourselves, may be explained by assuming that they had products containing different proportions of these two sulphides. It may also be assumed that the reason why the manganese sulphide produced by sodium or potassium sulphide cannot be converted into the green modification, while that produced by ammonium sulphide will undergo this transformation, is found in the fact that varying amounts of the gray sulphide are present in the latter product.

As we have frequently observed, when the pink precipitate is digested to produce the green sulphide the color first changes to gray. Further effort will be made to obtain the gray modification free from the red and to determine the amount of water present in the pure substance.

COMPOSITION OF THE GREEN SULPHIDE.

The first sample of the green sulphide which was analyzed was prepared by heating the pink modification in an atmosphere of hydrogen to 360°. The temperature was taken by means of an air thermometer. The transformation was quite gradual, being complete after about one hour. The amount of water found in this sample by the Penfield method was 0.97 per cent. Antony and Donnini state that they effected this transformation by heating the pink modification to 320° in a stream of carbon dioxide and that the transformation was complete in one-half hour. Invariably on igniting the pink sulphide with sulphur in a stream of hydrogen a green anhydrous product is obtained.

The remaining samples of the green sulphide which were analyzed were made by the method used in the quantitative determination of manganese given in the next article. The precipitate was washed by decantation and dried in a stream of hydrogen at 100°. This sulphide is much more stable in the air, so that samples have been dried in the air at 100° without the formation of any brown oxide whatever. Sulphur was present in all samples obtained, the lowest percentage found being about 1, while the highest was 4 per cent. The amount of water was determined by Penfield's method, these samples giving 1.18, 1.21 and 0.86 per cent. respectively. On drying these samples at 105° to constant weight, which required from four to six hours, water was lost, so that the percentage present after drying was 0.76, 0.51 and 0.55 per cent. respectively. Our results on the green sulphide are in substantial agreement with all other investigators except Muck, who states that 7.43 per cent. of water is present. Other workers find the green sulphide anhydrous or nearly so.

SUMMARY.

Three sulphides of manganese exist, two of which, the red and green, are anhydrous, while the gray sulphide contains a considerable amount of water. The pink sulphide is a mixture in varying proportions of the gray and red sulphides.

The difference in color between the red and green modifications must be due to a difference in molecular structure, the green being probably the more complex. This view is supported by the following facts:

(*a*) The pink or red modification is invariably first formed by precipitation, the green being a transformation product of one of these sulphides.

(*b*) The green modification is more distinctly crystalline and larger-grained.

(*c*) The green sulphide is by far the most stable substance.

Although we have never obtained either sulphide free from sulphur, which can be extracted by carbon disulphide, we do not believe that this sulphur forms part of the molecule of either sulphide, as the properties of neither modification seem to be modified when this sulphur is extracted.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, N. Y.]

DETERMINATION OF MANGANESE AS THE GREEN SULPHIDE.[1]

By J. C. Olsen, E. S. Clowes and Wm. O. Weidmann.

Received September 19, 1904.

Two sulphides of manganese have been generally known up to the present time. One of these is pink or flesh colored, while the other is green. These sulphides differ markedly in their physical properties. The pink variety is finely divided, stays suspended in the liquid and passes through the pores of the filter-paper very persistently. The green sulphide is much larger grained, so that it settles readily from the mother-liquor and can be readily filtered and washed.

In quantitative work, therefore, it is very desirable to obtain the green sulphide. As manganese can be weighed with the greatest accuracy as sulphide, this method of determining the element would be much more largely used, if the green modification could be invariably obtained on precipitation. This method of deter-

[1] Read before the New York Section of the American Chemical Society, April 8, 1904.