of Mineral Analysis," 1868; "Table for Qualitative Analysis in Colors," 1870; edited Elderhorst's "Manual of Blowpipe Analysis," 1873; fourth and fifth editions of the same, 1875–76; edited "Manual of Blowpipe Analysis and Determinative Mineralogy," 1880; compiled "Semi-Centennial Catalogue of the Rensselaer Polytechnic Institute," 1874, and edited "Proceedings of the Semi-Annual Celebration" of the same institution, 1874; edited "Biographical Record of the Officers and Graduates of the Rensselaer Polytechnic Institute," 1886.

In 1857 he received the degree of A.M. and Ph.D. from the Georgia Augusta University, Göttingen; in 1864 the honorary degree of A.M. from Amherst College; in 1880 the honorary degree of M.D. from the Union University of New York, and the same year the honorary degree of LL.D. from Beloit College, Wisconsin. He has been elected fellow of the American Association for the Advancement of Science, fellow of the London Chemical Society, fellow of the Society of Chemical Industry, England, member of the American Chemical Society, corresponding member of the New York Academy of Science, member of the American Institute of Mining Engineers, member of the Troy Scientific Association, honorary member of the Albany Institute, member of the Norske Turistforenings, Christiana, Norway; elected member of the University Club, 1883, and of the Union League Club, New York City, 1886.

W. P. MASON.

# METHODS FOR THE DETERMINATION OF MANGANESE.[1]

By W. S. Thomas.

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FOR some time no satisfactory method for the rapid determination of manganese has been in use in this laboratory; all proposed schemes have been, from time to time, successively tried and none have withstood the tests under all conditions.

With the great demand now made for chemical analyses by which metallurgical and manufacturing processes are controlled, it has been no small part of the chemist's work to devise rapid methods for making these determinations, so necessary for the information of the metallurgist and manufacturer.

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[1] This and the paper following it are reprinted from the Bulletin of the Missouri Mining Club, published at the Missouri School of Mines, Rolla, Mo.

In order to supply this need, every rapid method now in use and generally known or published, has been introduced into the course of instruction known as Technical Analysis in this laboratory.

During the past two years the determination of manganese has been attempted by using a method published in the *Journal of Analytical and Applied Chemistry* by A. H. Low, but so far as the method has been applied in this laboratory it has proven of no value, owing to the low results obtained.

For the purpose of arriving at a satisfactory conclusion in regard to the Low method, a series of experiments were begun, using manganese carbonate, and manganese sulphate, from which most of the water of crystallization was driven off and the sample kept in a corked tube. In order to check the volumetric work the metallic content of both salts was carefully determined by gravimetric analyses, in which the manganese was precipitated as manganese ammonium phosphate, ignited, and weighed as pyrophosphate.

This method gave very closely agreeing results by duplicate analyses of the respective salts, the filtrate in each case being tested for manganese by means of ammonium sulphide and only mere traces of manganese found.

A standard solution of potassium permanganate was made in which 6.312 grams of potassium permanganate were dissolved in two liters of distilled water, and a solution of 11.46 grams of $C_2H_2O_4 + 2H_2O$, (oxalic acid), in one liter of distilled water, kept well corked and away from the light.

In obtaining an experimental standard, ten cc. of the oxalic acid solution were taken and five cc. of sulphuric acid added, and the whole titrated with standard potassium permanganate, one cc. = 0.0056 gram of iron, the strength of the oxalic acid being calculated from the data obtained.

It was found that ten cc. of oxalic acid reduced 20.1 cc. of the standard potassium permanganate, one cc. of which equals 0.0011 gram manganese, based on the equation $10FeSO_4 = K_2Mn_2O_8$. Therefore one cc. oxalic acid equals 0.002211 gram manganese.

By calculation based upon the equation (Low's)

$$C_2H_2O_4,2H_2O + MnO_2 + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O,$$

126 parts of oxalic acid equal fifty-five parts of manganese. Knowing the weight of oxalic acid in one cc. of solution and introducing this into the proportion, one cc. of oxalic acid solution was found to be equivalent to 0.005 gram manganese.

From these two methods we obtain two entirely different strengths, neither of which give satisfactory results, as will be seen by calculations based upon titrations, made according to Low's instructions.

A half gram of manganese sulphate, which gave 34.64 per cent. manganese by gravimetric analysis, was taken and made up to 500 cc.; fifty cc. were taken for each titration, zinc oxide was added in the usual way, and bromine water to precipitate the manganese as manganese dioxide, the excess of bromine boiled off, solution filtered, the precipitate well washed with hot water, and the filter with its contents replaced in the flask where the precipitation was made; fifty cc. of dilute sulphuric acid added and a measured volume of oxalic acid run in from a burette; the excess of oxalic acid determined by treating with the standard potassium permanganate. Nine titrations by Low's method gave the following results:

| No. | $C_2H_2O_42H_2O$ added. | Excess of $K_2Mn_2O_8$. |
|---|---|---|
| 1 | 10 cc. | 13.6 cc. |
| 2 | 10 " | 13.6 " |
| 3 | 10 " | 13.4 " |
| 4 | 10 " | 13.6 " |
| 5 | 10 " | 13.8 " |
| 6 | 10 " | 13.5 " |
| 7 | 10 " | 13.8 " |
| 8 | 10 " | 13.8 " |
| 9 | 10 " | 14.0 " |

Taking a mean of the excess as 13.6 cc. of potassium permanganate, and multiplying by 0.0011 (one factor of the strength of the permanganate) and dividing by 0.002219 the strength of one cc. of oxalic acid in terms of potassium permanganate, we obtain the amount of oxalic acid oxidized by the 13.6 cc. of potassium permanganate, which, subtracted from ten cc. gives the number of cubic centimeters of oxalic acid oxidized by the manganese dioxide derived from the sample. Multiplying this by 0.0055+ and correcting for one gram, we obtain 35.64, which is one per cent. above the gravimetric result as the per cent. of manganese in the sample. The factor $2\frac{1}{2}$ used in this calculation is obtained by comparing the two equations:

$$2C_2H_2O_4,2H_2O + 2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 4CO_2 + 8H_2O$$

$$5C_2H_2O_4,2H_2O + K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O,$$

from which is readily seen, that the strength of one cc. of oxalic acid in terms of potassium permanganate is $2\frac{1}{2}$ of its strength in terms of manganese dioxide, from which we can derive a strength for oxalic acid based on experiment and not on calculation, as set forth in another place.

Titrating the same sample of manganese sulphate by Volhard's method, in which the strength of the potassium permanganate in terms of iron equal to 0.0056 gram, is multiplied by the factor 0.2946, which is obtained by comparison of the equations:

$$10FeSO_4 + 8H_2SO_4 + K_2Mn_2O_8 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3$$

$$3MnO + K_2Mn_2O_8 = 5MnO_2 + K_2O$$

(in which $K_2Mn_2O_8 = 10FeO$ and $3MnO$ respectively) the following results were obtained: One-half gram of substance taken and made up to 500 cc. and fifty cc. taken for each titration.

| No. of titration. | Cubic centimeters of $K_2Mn_2O_8$ used. |
|---|---|
| 1 50 cc. solution. | 10.3 |
| 2 50 cc. solution. | 10.3 |
| 3 50 cc. solution. | 10.3 |

Multiplying this result by 0.2946 and correcting for one gram we get thirty-four per cent. manganese or 0.64 per cent. less than by the gravimetric analyses.

The methods were both tried upon a sample of manganese carbonate, which gave, by means of manganese pyrophosphate, forty-five per cent. of manganese. Several samples of one-half gram were taken and a few titrations made from each with the following results. Six titrations by Low's method gave

| No. | $C_2H_2O_42H_2O$ added. | Excess of $K_2Mn_2O_8$. |
|---|---|---|
| 1 | 10 cc. | 12.9 cc. |
| 2 | 10 " | 12.6 " |
| 3 | 10 " | 13.0 " |
| 4 | 10 " | 12.3 " |
| 5 | 10 " | 12.3 " |
| 6 | 10 " | 12.9 " |

Throwing out No. 3, the average volume of potassium permanganate reduced by the excess of oxalic acid equals 12.6 cc. and applying the same calculations as before, we obtain 41.03 per cent., or four per cent. less than by gravimetric analyses.

Eight titrations by Volhard's method gave the following results:

| No. | Solution. | $K_2Mn_2O_8$ added. |
|---|---|---|
| 1 | 50 cc. | 13.5 cc. |
| 2 | 50 " | 13.5 " |
| 3 | 50 " | 13.5 " |
| 4 | 50 " | 13.4 " |
| 5 | 50 " | 13.5 " |
| 6 | 50 " | 13.4 " |
| 7 | 50 " | 13.5 " |
| 8 | 50 " | 13.5 " |

When corrected for one gram these titrations give 44.54 per cent. manganese, or 0.46 per cent. less than the gravimetric analyses.

The results obtained with Low's method are in one case approximate, but, when the same manipulations are applied to as much as one-half gram of substance, the result is nearly fifty per cent. too low. Theoretically the method is perfect, but I have been unable to obtain the theoretical results in practice, and in so far as this is the important feature, the method has proved worthless in my work.

Volhard's process is very rapid and simple in its application. The manganese should be in the form of a proto salt, which is the form obtained by the procedure in decomposing an ore. Iron is removed by means of zinc emulsion, $3ZnO + Fe_2Cl_6 = Fe_2O_3 + 3ZnCl_2$, which converts the iron into insoluble ferric oxide by vigorous shaking.

This having been done, the solution, precipitate and all, is made up to 500 cc.; fifty cc. is taken out by means of a pipette, placed in a twelve-ounce flask, 250 to 300 cc. of hot water added, heated to boiling, standard potassium permanganate run in, and the solution shaken after each addition of potassium permanganate. A bulky brown precipitate of manganese dioxide is formed and the pink color of the solution is destroyed until the manganese is all oxidized to manganese dioxide, when a drop of the permanganate imparts a pink color to the solution. A few trials will enable the operator to ascertain this point with accuracy and rapidity.

This work was conducted more for the purpose of ascertaining the values of the methods when working with the rapidity which is required in actual practice, than for absolute accuracy, to 0.01 or 0.001 per cent. I have no doubt that Volhard's process can be made to check closer than 0.64 or 0.46 per cent. respectively, of the metallic content of an ore, but in practical metallurgical analyses, it is not always practicable to exercise the necessary precautions. The method is capable of wide application, and where rapidity is essential, is sufficiently accurate in most, if not all cases.

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# THE WET ASSAY FOR COPPER.

BY R. S. DULIN.

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IT seems difficult for the metallurgical chemists of this country to settle upon a uniform method for the rapid determination of copper. We should have a standard method, applicable for all commercial work, which would be fairly accurate under as many possible varying conditions, so that results obtained from the same ore, by different chemists, should be substantially uniform. For about nine months past I have been engaged upon an extended series of experiments, having for their object a determination of the chief causes for variation and error in the methods most generally employed and for the purpose of finding a modification of common methods which would be an improvement upon those now used. At the same time I have made myself conversant with much of the current literature upon the subject and the observations herein offered, while based upon my individual experiments, are corroborated, in most part, by the published results of others.

There are at present three well-recognized methods employed in the United States for the determination of copper. Each method has its own advocates, and it is perfectly fair to say, that either method in the hands of a skilled chemist, thoroughly understanding the reactions of the methods, working with all due care, will yield substantially the same results. The methods referred to are :