

HAMPE'S METHOD OF DETERMINING Cu_2O IN METALLIC COPPER.

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Having occasion to make a series of determinations of Cu_2O in copper in some suites of specimens in the National Museum, representing the process of refining pig copper to tough pitch metal, the Hampe* method was selected as being the best so far proposed.

The method is based upon the reaction between Cu_2O and AgNO_3 , discovered by H. Rose,† and consists in treating the material to be analyzed with neutral solution of AgNO_3 in the cold for several days, when, according to Hampe, the following reaction takes place between Cu_2O and AgNO_3 : $3\text{Cu}_2\text{O} + 6\text{AgNO}_3 + 3\text{H}_2\text{O} = 4\text{CuO}$, N_2O_5 , $3\text{H}_2\text{O} + 2\text{CuN}_2\text{O}_6 + 6\text{Ag}$, whereby two-thirds of the copper is converted into an insoluble basic nitrate, and remains with the silver precipitated, while one-third goes into solution as normal nitrate. On filtering off the residue and determining the amount of copper contained in it, we can easily calculate the percentage of Cu_2O in the metal. The following series of results, calculated on Hampe's formula:

Cu_2O in Cu					
No. 1.	0.136	0.140	2.542	3.862	8.209
No. 2.	0.222	0.128	2.537	3.897	7.897

showed the method to be quite satisfactory as far as the agreement of duplicates goes.

Rammelsberg‡ investigated the matter slightly and found that only 28.80 per cent. of the copper went into solution. He assigned the following somewhat unusual formula to the insoluble nitrate: $\text{Cu}_{10}\text{N}_6\text{O}_{35}$. Hampe§ has replied that Rammelsberg's investigation was too limited, being confined to a single determination, and proper precautions were not taken, while his own work was very elaborate and extended, and his deductions based upon many determinations. Rammelsberg used pure Cu_2O ; Hampe used both Cu_2O || and metallic copper containing a known amount of Cu_2O , but with the latter material the amount of Cu_2O present was so small that the unavoidable errors of determination would completely mask the difference between 28.8 per cent. and 33.33 per cent.

Since, however, in the actual use of the method for determining Cu_2O in copper there is always a large excess of uncombined copper present

* Zeit. f. Berg-, Hütten- u. Salinen-Wesen, 1873, Vol. XXI, p. 218.

† Pogg. Ann., Vol. CI, p. 513.

‡ Ber. Deutsch. Chem. Ge., 1877, p. 1780.

§ Zeit. f. Anal. Chem., Vol. XVII, p. 127.

|| Hampe's Cu_2O always contained CuO .

which might possibly affect the reaction, it seemed desirable to take up the subject for further investigation.

That the free copper influences the reaction is readily shown by the fact that the filtrate from the residue of Ag and $H_6Cu_4N_2O_{12}$ contains much nitrite of copper.

More recently Wells* in a different connection has fully established the Hampe formula as representing the reaction between pure Cu_2O and $AgNO_3$.

In all ordinary cases, such as the determination of Cu_2O in tough pitch metal, the determination of Cu_2O in the native copper of Lake Superior by Monroe,† and the test cases, using Cu containing Cu_2O , of Hampe, mentioned above, the unavoidable errors of the work are so great that it is immaterial whether the constant of solution is 28.8 or 33.33, but in the case of the series I had under investigation, where in one sample 8 per cent. of Cu_2O was found by the Hampe constant, such a difference could not be tolerated.

For the purpose of this investigation, therefore, a series of samples was prepared corresponding exactly with the material to which the method would be applied; that is, metallic copper containing Cu_2O , but containing a large amount of Cu_2O . It was necessary that the samples should contain nothing else.

A tolerably pure $CuSO_4$ was dissolved in hot water till a strong solution was obtained; it was, however, neither boiling nor saturated. This solution was cooled with agitation, and a crop of small crystals obtained. These were separated from the mother liquor, redissolved, and the operation repeated twice. The final crop of crystals gave an absolutely pure $CuSO_4$.

A solution was made of the pure crystals, and the copper precipitated by the electric current. In order to obtain the copper in suitable form, the plan used in refining copper commercially by the current was adopted. A strip of ordinary sheet copper was coated with paraffine wax, and then graphite was sprinkled on it; this prepared strip was used as the first cathode. When a thin film of copper had deposited, the strip was taken from the bath, and the film of pure copper removed, the coating of wax making this quite easy to do. The thin sheet of pure copper was then used as the cathode, and the electrolysis of the solution continued, until a suitable amount of copper had been precipitated.

In this way some 200 grams of absolutely pure copper were prepared.

This pure copper was next melted in a scorifier, in a gas muffle, and allowed to absorb O from the air. In this operation the greatest care had to be exercised to avoid contamination of the metal, especially by

* H. L. Wells and S. L. Penfield. *Gerhardite and Basic Cupric Nitrates*, the chemical work by the former. *Am. Jr. Sci.*, Vol. xxx, p. 56.

† *Trans. A. I. M. E.*, Vol. viii, p. 414.

Fe. I am greatly indebted to Dr. H. G. Torrey, assayer of the United States Mint at New York, for making these fusions for me with such great care that only small amounts of Fe could be found in the metal after fusion.

55.853 grams of the pure metal were melted in a scorifier and allowed to absorb O until it had covered itself with the melted oxide; the resulting button, freed as much as possible from the melted oxide, weighed 45 grams.

Drillings from this button were crushed to an approximately uniform size, thoroughly mixed, marked off into squares, and samples for analysis made up by taking some from each square.

0.8318 gram were dissolved in HNO_3 , converted into sulphate, and the copper precipitated by two Bunsen cells, yielding 0.8162 gram copper or 98.12 per cent.

2.0795 grams treated in this way yielded 2.0400 grams copper or 98.10 per cent. In the solution after the precipitation of the copper from the latter were found 0.00028 Fe=0.013 per cent.

2.7428 grams, determining the amount of copper going into solution, as well as that made insoluble by treatment with AgNO_3 , yielded a total of 2.6918 grams copper=98.14 per cent.

The average of these three copper determinations is 98.12 per cent., adding to this the Fe, we have 98.135 per cent.; subtracting this from 100, we have 1.867 as the percentage of O present. 1.867 per cent. O=16.67 per cent. Cu_2O . We have therefore the composition of this material:

	Per cent.
Cu	83.317
Cu_2O	16.670
Fe.....	0.013
	100.000

For the Cu_2O determination absolutely pure AgNO_3 was dissolved in H_2O using 100 c. c. H_2O to 3 grams AgNO_3 . The Cu containing Cu_2O was weighed out, and the cold solution added, using 200 c. c. or 6 grams AgNO_3 for each gram of the material. For the first few hours the mixture was repeatedly stirred, after which it was allowed to stand, with occasional stirring, for three to four days, being kept in a cool place all the time.

The residue, consisting of basic nitrate of copper and metallic silver, was filtered and thoroughly washed. It was then treated with quite dilute H_2SO_4 , avoiding an excess. This dissolved the copper and, owing to its fine state of subdivision, a small portion of the silver also. The solution was filtered, evaporated, the silver precipitated by HCl , filtered again, and evaporated till fumes of H_2SO_4 were given off. The residue was taken up by H_2O , the solution filtered, and the copper pre-

cipitated by the battery, using two Bunsen cells, coupled zinc to zinc, and carbon to carbon. The following results were obtained :

	Per cent.
2.7081 grams gave 0.3507 Cu	=12.95
2.7428 grams gave 0.4355 Cu	=15.88
2.1279 grams gave 0.3106 Cu	=14.59
Average.....	14.47

Multiplying this by the Hampe constant, we have 24.44 as the per cent. of Cu_2O that should be present according to his formula, but the direct oxygen determination shows only 16.67 per cent. to be present.

If we assume that all the copper present as Cu_2O in the metal was transformed into the insoluble nitrate by the action of the AgNO_3 we have 14.47 per cent. Cu = 16.29 per cent. Cu_2O , which is sufficiently close to 16.67 per cent., as found by the O determination, to warrant the assumption as being true.

Thirty grams of the above material were mixed with an equal weight of the pure copper, and the mixture thoroughly melted, when it was removed from the muffle.

The method of examination was enlarged and slightly modified in certain points suggested by the work upon the first sample, with the hope of obtaining more closely concordant results.

The drillings were crushed fine and thoroughly mixed, then the whole was spread out and marked off into twelve squares, and four of these squares were taken for each analysis. Especial attention was given to securing uniformity in the samples weighed out, since some of the differences in the first set of results are due to differences in the samples taken.

The silver separated by the reaction was determined, and the iron remaining in the solution after the separation of the copper was also determined. The following results were obtained :

Sub. taken	Insol. Cu	Sol. Cu	Fe	Ag ppt	Total Cu	O	Fe	Insol. Cu	*
					<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	
3.0846	0.3406	2.6976	trace.	9.4538	98.495	1.504	trace.	11.042	
3.3337	0.3768	2.9052	10.1969	98.509	1.491	11.300	
3.2479	0.3521	2.8479	0.00007	9.9700	98.525	1.475	0.002	10.840	
				Average	98.507	1.493	11.06	

Per cent.	Per cent.
1.493	O = 13.33 Cu_2O
11.06	Cu = 12.455 Cu_2O

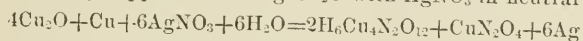
Dividing the total amount of silver precipitated, 29.6207 grams, by the total amount of material taken 9.6662 grams, we have 3.0643 grams as the amount of silver precipitated by 1 gram of the material. Theoretically, 1 gram of a mixture containing 86.67 per cent. copper and 13.33 per cent. Cu_2O should precipitate 3.1544 grams silver, thus

showing a deficiency of 0.0901 gram in the amount of silver precipitated, which indicates that 2.645 per cent. of the copper entered into the reaction without precipitating a corresponding amount of silver. Expressed atomically we have :

Cu present as Cu_2O	11.837 ÷ 63.4 = 0.1867	4.477
Cu not precipitating silver.....	2.645 ÷ 63.4 = 0.0417	1

While these results are not as close as could be desired, yet considering the difficulties in the case arising out of the fact that all the experimental errors are thrown upon the 1.493 per cent. of O, they show that for every 4Cu in the Cu_2O entering into the reaction, one Cu did not reduce its corresponding amount of Ag. Taken in connection with the discovery of nitrite of copper in the filtrate from the silver and basic nitrate, these figures clearly establish the reaction as follows :

Reaction on treating copper containing Cu_2O with AgNO_3 in neutral solution.



Five grams of the first fusion were mixed with 55 grams of the pure copper and thoroughly fused. Treated in the same way as the second sample, this material yielded the following results :

Sub. taken.	Insol. Cu	Sol. Cu	Fe	Ag ppt.	Total Cu	O	Fe	Insol. Cu	
						<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	
3.2626	0.2471	2.9501	0.000490	10.3304	98.915	1.070	0.015	7.58	
3.5278	0.2781	3.2092	0.000455	11.1430	98.890	1.097	0.013	7.88	
3.3826	0.2966	3.0479	0.000560	10.6036	98.873	1.116	0.017	8.77	
					Average	98.893	1.092	0.015	8.08

Per cent. *Per cent.*
 1.092 O = 9.75 Cu_2O
 8.08 Cu = 9.10 Cu_2O

The composition of the material is therefore :

Per cent.
 90.235 Cu
 9.750 Cu_2O
 0.015 Fe

 100.000

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Performing the same calculations upon these figures as in the preceding case we have :

Silver precipitated by 1 gram of material.

	Grams.
Calculated.....	3.2217
Found.....	3.1531

Deficiency0.0686

$0.0686\text{Ag} = 2.01$ per cent. copper not precipitating Ag

Cu present as Cu_2O $8.658 \div 63.4 = 0.1366$ 4.309

Cu not precipitating silver $2.01 \div 63.4 = 0.0317$ 1

The conclusion arrived at from these figures is that, when copper containing Cu_2O is treated with a neutral solution of AgNO_3 in excess in the cold, all the Cu_2O is converted into the insoluble basic nitrate $\text{H}_6\text{Cu}_4\text{N}_2\text{O}_{12}$.