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THE DETERMINATION OF OXYGEN IN COMMERCIAL COPPER.

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THE only conventional method with which I am acquainted for the determination of oxygen in commercial copper consists in dissolving the metal in a solution of silver nitrate, and estimating the oxide of copper, which is supposed to be left as a basic nitrate, by solution in standard sulphuric acid and titration of the excess of acid by sodium carbonate. As commonly formulated, this method includes no precautions for ensuring regularity of action between the copper and silver nitrate, although, granting all other assumptions, such regularity is essential for the attainment of accuracy. In a recent investigation on the atomic weight of copper, the conditions requisite for the regularity of the reaction in question have been laid down. The

condition of most moment is that the solution shall be kept at a low temperature, preferably at 0°C. , for otherwise a smooth exchange between copper and silver does not take place, but an oxidation of the copper at the expense of the NO_3 group occurs, with the result that the residue of silver left after the reaction has been brought to a close contains basic cupric nitrate, not owing its presence to oxygen existing in the copper under analysis, but due to the nitrate of silver used as a reagent.

On observing the precaution of conducting the operation in a vessel buried in chips of ice, no difficulty arising from irregularity of interaction is experienced. Solution proceeds slowly, but eventually reaches the limit set by the relative quantities of the substances concerned. It is usual to employ a weight of copper somewhat greater than can be dissolved by the quantity of silver nitrate taken. A single strip of the metal is convenient, because the recovery and re-weighing of the undissolved portion is then an easy matter; when several small pieces are used, one may be overlooked in the mass of spongy silver which is precipitated. An additional precaution may be taken by filling the flask in which the reaction is carried out with CO_2 , so as to avoid possible oxidation of the copper during solution, and, for the same reason, using boiled-out water. The conscientious operator having done all this and more, soon becomes aware that the method is entirely worthless. In point of fact, the more carefully he excludes chance oxidation, the more erroneous are his results, for the method, when skilfully worked, fails to find any oxygen whatever in ordinary commercial copper, although that body is certainly present. The reason will be given in a later portion of this communication.

Having purged the silver nitrate method from accidental errors with the incidental discovery that its indications depended wholly on their occurrence, I turned my attention to other methods that seemed feasible on *a priori* grounds. Thus copper, in the form of thin turnings, was heated in a glass combustion-tube in a stream of hydrogen; the reduction was, however, only superficial. Next, copper, in the form of small bars, such as could be cut out of fire-box plate, was heated in an atmosphere of nitrogen, and sulphur vapour was then passed over it. Reaction readily occurred, and it was easy to convert the whole of the bar into a sulphide which approached the composition Cu_2S when the temperature was fairly high, but always contained rather more sulphur than corresponded with this formula. In adapting this method to practical requirements, the copper was placed in a boat in a combustion-tube, and the sulphur (recently fused) in another boat a little behind that containing the copper. Nitrogen, prepared from ammonium chloride and potassium nitrite, washed, dried, and purified by passage over red-hot copper, was caused to expel the air in the tube containing the boats in which were respectively the sulphur and the copper. When the displacement of air was complete, the portion of the tube in which was the boat containing the copper was heated, and then that in which was the sulphur boat. Sulphur vapour was driven gently by the stream of nitrogen over the heated copper, which forthwith began to glow. Excess of sulphur was caught in a cool part of the tube beyond the copper boat, and any flowers of sulphur that might be formed were filtered off through an asbestos plug. The exit end of the combustion-tube was connected with an absorption apparatus containing ammonia and hydrogen

peroxide. That portion of the sulphur which had been oxidized to SO_2 by the oxygen in the copper was caught in the absorption-tube, and finally estimated as barium sulphate.

Owing to the ease with which the reaction between copper (even in pieces of large section) and sulphur takes place, a simplification of the above method was devised. A weighed rod of copper and an excess of sulphur (recently fused) were placed in a narrow piece of combustion-tube, closed at one end, which was then exhausted and sealed. On heating this tube to a temperature just short of the softening-point of the glass, the copper and sulphur combined; on the completion of the reaction, the tube was allowed to cool, and any gas which it contained collected over mercury and analysed.

Both methods yielded small and varying quantities of SO_2 , but as their working was improved and accidental presence of oxygen excluded, the quantity tended to a minimum. In short, much as in the silver nitrate method, the indications of the process disappeared when its errors were eliminated.

A little reflection allows these facts to be grouped under one head. The oxygen in commercial copper is generally assumed to exist as cuprous oxide dissolved in the metal. No doubt this is substantially true in ingot copper refined and containing no appreciable amount of impurity save oxygen, but not brought to tough-pitch. In copper intended for structural use, on the other hand, impurities other than oxygen, notably lead, are almost invariably present. There is no reason to suppose that the oxygen of such tough-pitch copper is present as cuprous oxide. Lead oxide or more complex bodies, such as lead arseniate, probably account for a considerable fraction. When copper containing oxygen in this form is dissolved in silver nitrate, the oxygen-bearing substances remain as a sludge with the spongy silver, and are substantially unattacked by the dilute standard sulphuric acid used to estimate the total basicity of the residue. The assumption on which the silver nitrate method is based is to the effect that all oxygen in the copper appears as basic cupric nitrate, a substance readily attacked by dilute sulphuric acid. Lead oxide or arseniate, on the other hand, in the refractory state which from their origin (in a mass of melted copper) they would naturally assume, would be but superficially attacked by weak sulphuric acid, and thus saturation of the acid in amount corresponding with the oxygen-contents of the copper could not occur. A similar influence appears to limit the reaction of copper containing oxygen in other forms than that of cuprous oxide when it is heated with sulphur. At the low temperature at which copper and cuprous oxide are attacked by sulphur, the more stable oxygen compounds—*e.g.*, lead oxide—are but little affected, and the oxygen is not eliminated as SO_2 . Doubtless it would be possible to decompose such oxides by means of sulphur at a higher temperature, but the practical difficulty caused by the softening of combustion-tubing at such a temperature then intrudes.

The method, after many trials, was abandoned, and a return made to the obvious and simple plan of reducing the copper in hydrogen. As mentioned above, only superficial reduction was obtained at any temperature below the softening-point of a glass combustion-tube. Fine division of the copper was thought undesirable, both from the risk of surface oxidation and from the difficulty of preparing filings or saw-

dust free from contamination. Recourse was had to the use of a temperature well above the melting-point of copper, the adoption of a porcelain tube set in a small injector furnace being therefore a necessity. Preliminary trials showed that it was not feasible to fuse copper in hydrogen and estimate the oxygen by loss of weight, for during the process the metal is spattered about with such violence that mechanical loss can hardly be avoided. It became necessary, therefore, to weigh the water produced by the action of hydrogen upon the melted copper, and the apparatus shown in the figure was finally adopted. The following are the principal parts: A hydrogen-generator containing zinc and sulphuric acid (not hydrochloric, lest vapours of that acid pass over with the hydrogen) is connected with a wash-bottle of copper sulphate solution followed by a sulphuric acid drying-tube. The oxygen of any air that may be entangled in the zinc or acid of the hydrogen-generator is eliminated by passing

the gas through a bulb-tube of platinized asbestos gently heated. Any water there formed is caught in a second sulphuric acid drying-tube, and the pure dry hydrogen (containing at worst a trace of nitrogen) enters a porcelain tube set horizontally in a small furnace of the injector pattern driven by a blast from a Root's blower (or bellows). The copper in which the oxygen is to be determined is cut in stout strips or bars to fit a small porcelain boat; 10 to 15 grammes may be conveniently taken. The porcelain tube, the boat, and all corks and connecting-tubes are thoroughly dried, and placed in position while so hot that they can scarcely be handled with comfort. Error due to adhering moisture is thus avoided. The exit end of the porcelain tube is connected with a weighed sulphuric acid tube protected by a sulphuric acid guard-tube. (I have laid emphasis on the use of sulphuric acid tubes throughout; they cannot be replaced by any less thorough means of drying; calcium chloride, as always for exact work, is "useless, dangerous, and ought to be abolished.") The inlet-tube is a $\perp$, with the right-hand horizontal limb closed by fusion. The vertical limb is that entering the rubber cork of the porcelain tube. This little

device makes it possible to look along the axis of the porcelain tube, and observe the behaviour of the copper during the process of reduction. The phenomena which occur are these: The copper suffers no visible change up to and including the time when it is at a bright red heat. No sensible action of the hydrogen upon the oxygen in the copper takes place up to this point, for no water appears in the exit tube. Just before fusion, when the metal is softening, small bubbles and excrescences appear on the surface of the copper, and evidently eject some gas. It seems probable that hydrogen is occluded by the copper at a temperature just short of fusion, and that the bubbles are due to the escape of water-vapour from the action of this hydrogen upon the oxygen of the copper. However this may be, it is certain that the appearance of these bubbles is immediately followed by the formation of water, which partly condenses in the glass exit tube, and is swept on into the weighed absorption tube in the usual manner. The bubbles soon cease to form, and the copper remains in tranquil fusion with a brilliant surface. The whole reaction is over in a couple of minutes, and the furnace can be shut down. Hydrogen is passed for another five minutes, to ensure the displacement of any water which may have lodged in the exit tube. During cooling, the copper again passes through a volcanic period, and finally solidifies with a rugose surface. This second spitting (which in outward form resembles the "sprouting" of silver) is probably due to expulsion of absorbed hydrogen; it is certainly not identical in nature with the first, for it is not attended by the formation of water. The violent motion of the melted copper during these two periods of disturbance causes a rain of tiny globules of copper, which coat the porcelain tube in the neighbourhood of the boat, and sometimes cause the two to adhere after cooling. This scattering of the copper is the effectual reason for the impracticableness of determining oxygen by loss of weight on heating in hydrogen.

Nothing now remains but to displace the hydrogen in the weighed tube with air, and to allow it to cool for weighing. Hydrogen is supplied continuously to the porcelain tube while it cools, so that all copper therein is brilliantly clean when the tube is opened. By thus avoiding casual oxidation the tube can be kept corked indefinitely, and used on the next occasion without any precaution save a preliminary warming.

I have had the method in use for a considerable time, and find it satisfactory in every way. It is applicable to copper-tin alloys, but not to brass, on account of the difficulty with which zinc oxide is reduced.

DISCUSSION.

Mr. BEVAN inquired what proportion of oxygen commercial copper usually contained.

Mr. HEHNER asked if Mr. Blount could suggest any explanation of the difficulty in obtaining a cuprous sulphide of constant composition to which he had referred. In Rose's well-known method for the determination of copper, which, as far as his experience went, always gave satisfactory results, pure Cu_2S was readily obtained.

Mr. BLOUNT said that the amount of oxygen present in commercial copper depended upon the proportion of other impurities. In a high-class tough-pitch copper containing over 99 per cent. of Cu, with, say, 0.15 per cent. of arsenic and a

similar quantity of lead, one might expect to find about $\frac{1}{10}$ per cent. of oxygen. In copper which was considerably under-poled, or in the condition in which it came direct from the refiners, the proportion of oxygen would be considerably greater.

With regard to Mr. Hehner's question, in the method which he (Mr. Blount) had described, the temperature was considerably lower than that reached in Rose's method; although a very fair approximation to Cu_2S could be obtained by carrying the heating as far as a combustion-tube would stand, the copper could not be said to be completely converted into Cu_2S ; an excess of sulphur always remained. For the purposes of the method described in the paper, it was, however, not necessary to take any special precautions to get the copper to that point.