

and metallic sodium in the other. The weight and appearance of the peroxide remained unaltered.

This result differs from that of Dulk (*loc. cit.*), the brown oxide of lead being decomposed into oxygen and the red oxide.

V. 4.057 grms. of PbO_2 was used in this experiment, but instead of sodium, anhydrous cupric sulphate was placed in the other bend of the tube. Neither the lead peroxide nor the copper salt changed in appearance, nor the former in weight.

II. ON THE ESTIMATION OF TANNIC ACID IN TANNING MATERIALS, ETC.

BY NELSON H. DARTON.

As the exact determination of the proportions of tannic acid is a problem of comparatively difficult solution many methods have been proposed to facilitate this, but, as a rule, have yielded very discordant results when compared with the actual weights of the leather formed from it. Thus tanners have lost all faith in chemists generally. Some prominent tanners have informed me that they have sent spent barks containing less than one per cent of tannic acid to chemists in this city and they have returned results of from 7 per cent. to 4 per cent. These results were generally obtained by Hammel's hide method or that of Lœwenthal, as modified by Neubauer, or even by the old gelatin method, which is now seldom used.

In my intimate connections with the tanning trade I seriously felt the defects in and want of a proper method, and not being able to find one of sufficient accuracy sought out one that would answer the conditions of speed and accuracy, and this I will detail below, merely mentioning that in numerous and exhaustive trials I have found it to yield results as near as within $\frac{1}{4}$ per cent of the actual value. Lœwenthal's modification of his own method is not nearly as accurate as this, as I will show in a subsequent paper.

The bark, etc., is taken dry and finely cut, powdered or crushed. 20 grammes of this is weighed out, placed in a flask with sufficient water and the tannic acid thoroughly exhausted by repeated treatments with boiling water. The filtrate is mixed with about 25 cc. of dilute sulphuric acid and again filtered after making the bulk up to one litre. Standard solutions are then prepared. The first of tannic acid containing two grammes to a litre. The pure tannic acid must be used. 2nd, a solution contain-

ing to a litre 1.5 grammes of permanganate of potassium, 3rd, a solution of indigo carmine of such a strength that it must require twice as much of the permanganate solution as an equal bulk of the tannin solution, that is about 3 grammes to a litre. 4th, a 10 per cent solution of ammonio-sulphate of copper in ammoniacal water. 5th, a dilute sulphuric acid, one of acid to five of water. A convenient measure of the indigo is taken, say 20cc. It is diluted to about $\frac{2}{3}$ of a litre, acidulated with the acid and titrated with the permanganate. Another amount of the indigo and the same of tannic acid solution are taken and titrated as before. This is then repeated, using the decoction of the bark. About 60 cc. of the last is then taken and about the same of the copper solution, these are mixed together, some ammonia solution added and the mixture filtered from the tannate of copper which precipitates. An equivalent amount of this filtrate is titrated as before and from these data the amount of tannic acid calculated by the following formula.

The amount of permanganate used for the indigo and tannin together, less that used by the indigo, is to the permanganate used for the decoction, less that necessary for the indigo present and an equivalent amount of the filtrate noted, as the amount of tannic acid present in the litre of standard solution, is to the quantity of tannic acid in 20 grammes of the bark (a litre of decoction). The process may be executed in about one half hour after the decoction is obtained, but as eight or ten of the determinations may be carried on at once without loss of time it is by far the shortest method known.

This process has been in constant use in my laboratory for some time back, and as I have much of this work constantly to attend to I have thoroughly tested its value and am assured the main error is not over $\frac{1}{4}$ per cent. as I will show in my subsequent paper.

This method, somewhat extended, is applicable to the determination of the gallic acid at the same time. It is simply in treating a portion of the filtrate from the tannate of copper with a solution of bichloride of mercury, and after filtering this off and separating the excess of Hg, titrating the filtrate, using the calculations similar to the above, the amount of gallic acid may be readily arrived at. The relation of the permanganate to a gallic acid solution for the first member of the equation should be previously ascertained, although it differs but slightly from the tannic acid.

I then proceeded to investigate the purity and properties of the tannate of copper upon which the whole of the method depends. Two tannates of copper were prepared, one from the pure

tannic acid, the other from the decoction of hemlock bark and the two were compared, the first, from the pure tannic acid, contained 27.72 per cent. of copper oxide and the other 27.58 per cent., within 99.5 per cent. of each other. By combustion they both yielded essentially the same formula. In both cases they were in black lustrous masses quite insoluble in cold but partly soluble in hot or boiling water, from which it is deposited on cooling. In alcohol, gallic acid solutions and in presence of alkalies they are very insoluble but quite soluble in diluted acids.

III. ON A CONVENIENT AND ACCURATE FORM OF WEIGHING FLASK TO DELIVER AS A BURETTE.

BY NELSON H. DARTON.

In many volumetric processes, the end reaction is so sharp that the small amount of solution required to produce it is too small to be perceptible in the reading of an ordinary burette. Readings to 0.05 cc. are as close as can be usually seen. Differences of temperature, which affect both the bulk of the solution and the capacity of the burette, are also sources of error which must be avoided if we wish to attain great precision.

In cases where extreme accuracy is required, the method of weighing, instead of measuring the amount of solution used, is to be preferred.

Two or three forms of apparatus for this purpose have been proposed, but they all are open to two objections. 1st. That the delivery tube is too large to deliver less than 0.05 cc., or if fine enough to deliver it, a sufficient amount cannot be delivered conveniently at the start to bring the solution upon which one is working near to the point of change, and 2d. that regulating the admission of the air to the apparatus distracts the operator's attention at the critical moment.

I have constructed and used an apparatus which is not open to the above objections. Two forms are used. The first for liquids which may suffer an alteration of standard by contact with organic substance, as cork or rubber, consists of a flask with a Gay-Lussac delivery tube with a fine delivery jet. The stopper is perforated for a glass tube, connecting by a short rubber tube with another tube drawn to a fine point to regulate the admission of air to the flask. A small pinch cock on the rubber tube completes the control of the air supply, and consequently of the delivery from the flask. With the