When the present paper was nearly completed, a short note by A. J. Field[1] was found. He states that Collischonn's method is unsatisfactory, but quotes no experimental evidence, and his failure to obtain concordant results is probably due to non-observance of the precautions to be adopted, and more possibly due to adding varying amounts of acid for the back titration. He states, however, that "if after the addition of the iodine solution, the mixture is shaken for 5 minutes, a low result is obtained, while shaking for 20 minutes gives a higher result, the percentage varying with the length of time of agitation." This is quite contrary to the experiments recorded above, but two additional experiments were nevertheless run to test the point. An acetone solution was titrated, the iodine solution being added to the acetone caustic soda solution, without shaking, and the stoppered bottle was then shaken vigorously while standing, for 5 minutes, and for 20 minutes, respectively. The net amounts of iodine used were identical—22.26 and 22.26 cc. The theoretical amount of iodine used when carrying out the titration under the conditions specified in this paper, that is, running in the iodine solution with continual agitation, was 22.26 cc.

Summary.

(1) It has been shown that Messinger's method for the analysis of acetone gives accurate and concordant results under proper conditions.

(2) The influence of standing, method of adding the iodine solution and shaking, effects of excess acid, and dilution have been studied and found not to influence the results under proper conditions.

(3) Methyl alcohol and ethyl alcohol both use up a certain amount of iodine solution.

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[CONTRIBUTION FROM THE MINNESOTA AGRICULTURAL EXPERIMENT STATION.]

A SIMPLE HYDROGEN ELECTRODE.[2]

BY C. H. BAILEY.

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The considerable number of hydrogen electrodes that have been described in the literature suggests either that these devices have not been wholly perfected, or that electrodes suited to one purpose may not be adapted to other uses. Moreover, several of the forms that have been proposed are expensive; most of them are somewhat complicated and fragile and their construction presents an impossible undertaking for the average amateur glass blower.

This laboratory has had occasion to make a large number of hydrogen-

[1] *J. Ind. Eng. Chem.*, 10, 552 (1918).

[2] Published with the approval of the Director as Paper No. 180, of the Journal Series of the Minnesota Agricultural Experiment Station.

ion determinations, especially of the water extracts of plant material. Several types of electrodes have been tried, and most of them laid aside as being unsuited to this purpose. In the first place, certain of our preparations were so low in electrical conductance as to diminish the sensitivity of the potentiometer set-up. This was due to the considerable distance in most types of electrodes between the platinized electrode and the point of contact with the saturated potassium chloride solution as well as to the manner of making this contact. Again, as stated by McClendon and Sharp,[1] the platinized electrodes should be wholly immersed in the extract, and with certain electrodes this could be accomplished only by tipping them at an awkward angle, making even more difficult the contact with the potassium chloride solution. It appeared desirable to develop, if possible, an electrode which would be simple in construction and operation, have a short interval between platinized electrode and contact with the potassium chloride solution, and permit of complete immersion of the platinized electrode.

After several trials an electrode was constructed which appeared to meet all these requirements. As shown in Fig. 1, it is made by blowing a small bulb in the closed end of a 7 mm. tube, which is then bent at the angle shown, about 50 mm. below the top of the bulb, and fitted at the open end with a solid glass stopper. Spare stoppers of about this size can be found in most well-established laboratories. Those which taper considerably are preferable. A gas-carbon mold is made which is slightly smaller than the stopper, and the glass at the open end of the tube is softened and flowed about the mold until it has approximately the correct internal dimensions. The stopper is then ground into its seat by the use of a mixture of carborundum powder (150 mesh), turpentine and camphor.

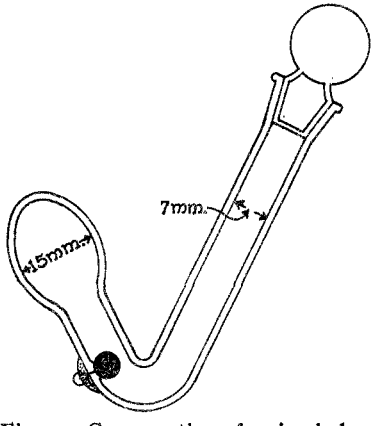

Fig. 1.—Cross-section of a simple hydrogen electrode.

The metal electrode is made by cutting a round piece of thin gold plate 5 mm. in diameter. Such gold plate is obtainable from dental laboratories and is preferable to platinum foil since the time for saturation with hydrogen ions is comparatively short. To this is soldered with gold a piece of No. 30 (0.010 in.) platinum wire about 15 mm. long. This can be done by carefully heating the middle of the wire in a small flame, and melting on one end a small bit of the pure gold foil previously cut in a strip and bent about the end of the wire. This gold is then heated just to

[1] *J. Biol. Chem.*, **38**, 534 (1919).

a molten state, the round bit of foil placed under it, and the two pounded together by tapping with a light hammer. The gold used as solder, and the portion of the wire nearest the foil, are then beaten thin.

The opening in the tube through which the wire lead from the electrode passes is then prepared. This is most conveniently done by heating a piece of No. 18 platinum wire about 2 cm. from the end, and holding it against the tube. The hot wire can be gradually forced through the glass wall, leaving a small, smooth opening. It is not difficult to then maneuver the wire lead of the metallic electrode through the hole thus prepared. Low melting-point or soft glass can be flowed in around the wire, completing the mechanical part of the job.

No. 25 (0.018 in.) platinum wire can be used for the lead and external contact, if it is plated with gold and beaten thin near the foil. The electrode is drawn well into the glass at the time the soft glass is fused in around the wire. In this way there are no heavy platinum parts exposed within the tube, and consequently no delay due to the slowness with which such parts are saturated with hydrogen ions. The heavier platinum wire which passes out through the glass wall is more substantial than fine wire and less apt to break off close to the glass.

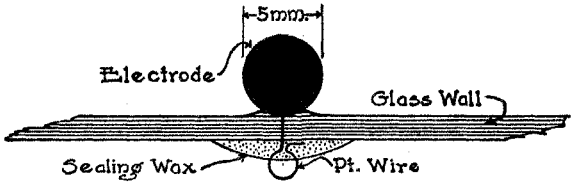

Fig. 2.—Detail of metallic electrode and connections.

A convenient way of reinforcing the platinum lead wire outside the tube is shown in detail in Fig. 2. The wire is bent forward for a short distance, then curved in a loop, and finally bent back close to the glass. The lower part of the loop and loose end of the wire are surrounded with a small lump of sealing wax, which must adhere tightly to the glass tube. Metallic connection to the potentiometer can easily be effected by catching a small hook at the end of a coiled copper wire to the open end of the platinum loop just without the sealing wax. Electrodes thus prepared have appeared more rugged than those in which the free end of the wire has not been secured. If the wire breaks in will generally be at the outer surface of the sealing wax, and by paring the latter, contact may be established with the free end of the wire previously embedded in the wax, and the electrode thus used for a considerable time.

The gold foil is platinized in the customary way, and the electrode is used in the following manner. Sufficient of the liquid under examination is placed in the open arm to completely fill it. The tube is then tilted so that the liquid flows into the bulb end, displacing the air. This is repeated until the bulb arm is completely filled, and the open arm to a depth of about 10 mm. above the top of the bend. A slender glass tube

leading from the hydrogen generator or tank is then placed in the open arm so its lower end about reaches the lower part of the bend, and hydrogen is gently bubbled into the bulb, displacing the liquid, which rises in the open arm. Sufficient hydrogen is admitted to fill the closed arm. If the open arm is not level full of the liquid, it is completely filled, and the stopper carefully seated in such a manner as to permit the excess liquid to be forced out as it is inserted. All air is thus excluded from the tube. It is vigorously shaken for two minutes and then tilted so enough liquid flows into the closed arm to just cover the foil. The stopper is removed, and by a series of quick flips part of the liquid in the open arm is thrown out. The outer surfaces of the tube are then rinsed with distilled water and dried.

To complete the circuit the platinum wire loop is connected to the potentiometer as previously described, while a slender siphon tube filled with saturated potassium chloride solution is dipped into the open arm. This siphon is made by drawing out one end of a 3 mm. (i. d.) glass tube to a slender tip about 10 cm. long. The tube is bent to a V shape just above the tip, and the large end cut off to a length of about 6 cm. The completed siphon is filled with saturated potassium chloride solution, and finally several fragments of filter paper, previously soaked in potassium chloride solution, are forced into the fine tip by means of a needle. This filter paper prevents the potassium chloride solution from actually siphoning over to an appreciable extent while the readings are being taken. The tip can be brought very close to the platinized foil, thus reducing the electrical resistance of the cell. The other end dips into a vessel filled with saturated potassium chloride solution, which in turn is connected to the calomel electrode. This scheme is adapted from the suggestions made by Van Slyke and Baker.[1]

Hydrogen electrodes made and used as described have proven very useful in determining the hydrogen-ion concentration of water extracts of foods, such as wheat flour. It comes to equilibrium promptly, and is easy to fill and clean. About 10 cc. of the extract is sufficient to rinse and fill the cell, and even less may be made to serve if care is taken. When used with the potentiometer in this laboratory the complete set-up is sensitive to 0.25 millivolt.

The writer's obligations to Dr. R. A. Gortner for his services in constructing several of these useful electrodes are gratefully acknowledged.

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[1] L. L. Van Slyke and J. C. Baker, N. Y. (Geneva) Sta. *Technical Bull.* 65 (1918).