LXXIV. A NEW TYPE OF MICROBURETTE.

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DURING the last decade several microburettes have been described, notably those of Benedetti-Pichler [1926], Kirk [1933], Linderström-Lang and Holter [1931; 1933], Rehberg [1925], Schilow [1927], Schwartz [1933] and Widmark and Orskov [1928]. Till a year ago, none of them, with the possible exception of that of Pincussen [1927], was specially designed for serial titrations. Two different types have been described during the last year, which are specially designed for this purpose.

That of Conway [1934] is simple, easy and cheap to make, and accurate. Though entirely suitable for the purpose for which it was designed, it can only be used with one solution.

The tapless microburette of Links [1934] is more complicated but it can be used with different solutions; it is not difficult to clean and has most of the advantages of the screw-controlled type. It can be used with any solution as the latter does not come into contact with the mercury.

The burette described below was designed before the description of either Links's or Conway's apparatus came to the attention of the author and had been, in fact, partly constructed. It is not as accurate as some other types, but as it has been in use for several months with satisfactory results, and as it can be made from the material usually available in the laboratory, its description may be of some interest.

Some of its main advantages are as follows:

1. The readings are taken at a mercury-air surface.
2. The titrating reagent only comes into contact with pyrex glass, paraffin wax and paraffin oil, and once prepared is never exposed to the air.
3. A large number of titrations can be carried out without refilling.
4. The titrating reagent can be changed almost instantaneously.
5. No cleaning is necessary when changing reagents.
6. Calibration is simple and direct.
7. The burette can be used for small quantities.

PRINCIPLE.

The apparatus is similar in principle to the measuring device of Hahn [1929]. The various titrating fluids are contained in small bottles, each of which is fitted with two tubes, a delivery tube (with a titrating point) and a second tube which connects the bottle to the burette proper. An exactly measured volume of liquid paraffin is displaced from the burette into the bottle, from which in turn an equal volume of titrating fluid is delivered.

CONSTRUCTION.

1. *Stock bottles.* For stock bottles, 2 oz. "Kali" bottles are chosen and coated inside with paraffin wax. An ordinary cork is bored to carry a 5 mm. tube, *H* which ends flush with the bottom of the cork, and a delivery tube of pyrex

glass bent twice at right angles and passing to the bottom of the bottle. The cork is boiled in paraffin wax for a time, then the tubes are fitted, and the cork is forced as tightly as possible into the neck of the bottle while the wax is still hot. The solution with which the bottle is to be filled is sucked up the delivery tube (by applying suction to *H*), and when it is nearly full, pure paraffin oil is poured down the tube *H* in such a way as to exclude all air.

2. *Burette proper.* The general scheme of the apparatus will be seen from Fig. 1. *B* is a length of graduated thermometer tubing, calibrated by weighing a thread of mercury of known length. It is connected at one end with the pressure-

Fig. 1.

regulating mechanism *C*, and at the other, through the bulb *D*, with an ordinary three-way stopcock *E*. The second tube of the stopcock expands into the reservoir *F*, and the third is connected with a shallow U-shaped piece of capillary tubing *M*; to this is attached the tube *H* of the stock bottle. The reservoir *F*, tube *M*, tap *E*, and the upper half of the bulb *D* all contain paraffin oil. The lower half of *D* and the burette stem *B* contain mercury, as does the pressure-regulating mechanism *C*. When *C* is lowered, and *F* is connected to *D*, the mercury column in *B* will flow towards the zero mark; when *C* is raised, and the tap is turned through 180 degrees, the mercury will travel along the scale in the opposite direction and expel an equivalent volume of titrating fluid from the titrating point.

3. *Stand.* Absolute rigidity is essential for the proper functioning of the burette. This is obtained by clamping the stock bottle against the two V-shaped wooden chocks *V* and *V'*, by means of the flexible copper strip *T*, which is tightened by the butterfly nut *R*. (The blocks are allowed a certain amount of horizontal play to allow proper alignment of *H* with *M*, before tightening *R*.) The slide track, etc., for the pressure-regulating mechanism was constructed from curtain rail fittings obtained from a sixpenny store.

4. *Titration point.* This can be drawn from the delivery tube itself, though such an arrangement is extremely inconvenient if the tip gets damaged. A separate tip can, of course, be fitted with a properly ground joint, but after a certain amount of experiment, the joint described below has been found to be entirely satisfactory. The delivery tube of the stock bottle is first drawn out so that it will fit snugly into some pyrex tubing (Fig. 2, *a*). This latter tubing is then drawn out to a capillary from 4 to 6 inches long and is cut close above the drawn out part (Fig. 2, *b*); *a* is then moistened with water and dipped into carborundum powder, and the tip is roughly ground on. (It is not necessary to do more grinding than will prevent the sharp edges from splintering.) What grinding there is should be at the tip of *a* and not at the shoulder. Both parts are then thoroughly

cleaned and dried, and the titrating tip is drawn down to the requisite fineness. A blob of vaseline is placed on *a*, and *b* is gently warmed, so that on fitting it on to *a*, the vaseline will flow into the annular space between the two tubes. Finally a piece of rubber tubing which has been moistened inside with paraffin is pushed over the joint; it is easy to arrange that the rubber is in a state of tension, thus holding the tip firmly in position (Fig. 2, *c*).

The tip must be protected when not in use, and the titrating fluid must be prevented from syphoning over. This can be done in the following way. A piece of thin rubber tubing is placed over the shoulder of the titrating point so as to act as a cushion. The mouth of the pyrex tube (Fig. 2, *d*) is held against this, so as to make an airtight joint, by an elastic band which passes over the horizontal part of the delivery tube (this and the copper stirrup by which it is attached to the pyrex tube are not shown on the diagram). The protecting tube contains a small amount of titrating fluid covered by a layer of paraffin oil.

Fig. 2.

Fig. 3.

MANIPULATION.

The stock bottle is loosely clamped in position by the strip *T*, and the tube *H* and its rubber connection are filled with paraffin. (A small wash-bottle containing paraffin is convenient for this purpose.) Whilst the tube *M* is being pushed home, the tap *E* is momentarily opened. The butterfly nut is then tightened, and the protecting tube is removed from the titrating point. A small amount of the reagent is run out of the titrating point, and the mercury in *B* is brought back towards the zero mark by lowering *C* and connecting *D* to *F*.

The titration is carried out by raising *C* and turning the tap through 180 degrees. As there are no drainage errors, it does not matter how fast the first part of the titration is carried out; towards the end-point, however, *C* is lowered so that there is only a slight positive pressure, sufficient to expel the fluid from the titrating point only when the latter is immersed in the liquid being titrated. The fluid is prevented by surface tension from escaping when the tip is withdrawn. This principle has been used by Schilow, Schwartz, Linderström-Lang and others, and by its means the end-point can be very carefully controlled.

Use of burette for small samples.

Fig. 3 shows an arrangement which is used for solutions of which only a small quantity is available. In this case the bottle merely acts as a stand, the tube *H* being continuous with the delivery tube. It is used as follows: a short piece of

pyrex tubing wide enough to fit over the delivery tube is drawn out to a titrating point. It is then filled with paraffin and attached to the delivery tube as shown by a rubber sleeve. The tube *H* is attached to the burette as usual, and the tap *P* is opened. The required fluid is then sucked up the titrating point by lowering *C*, the tap *E* being in the appropriate position. The titration is then carried out in the usual way and the titrating tip is discarded when finished with.

This attachment has been found useful when dealing with enzyme solutions *etc.*, for not only can the whole of the solution be used, but the exact volume of it is known before measuring it out. The ability to use all the available solution is not often an advantage, but as far as the author knows, such a property has not been claimed for any other microburette, though a number could easily be adapted for this purpose.

ACCURACY.

The burette in use has a scale approximately 25 cm. long and a capacity of 0.1 ml. It is divided into a hundred parts, each division representing 1.0 μ l. To test the accuracy of the apparatus, twelve samples of approximately decinormal sulphuric acid were accurately measured out and titrated against decinormal NaOH from the burette, using methyl red as indicator. The following results were obtained:

Tube no.	Volume of N NaOH required (μ l.)	Deviation from mean	% error
1	51.6	0.2	0.4
2	51.7	0.1	0.2
3	51.8	0	0
4	51.9	0.1	0.2
5	52.1	0.3	0.6
6	51.7	0.1	0.2
7	52.1	0.3	0.6
8	51.8	0	0
9	51.8	0	0
10	52.2	0.4	0.8
11	51.6	0.2	0.4
12	51.4	0.4	0.8

These results leave much to be desired, but it must be remembered that the scale is comparatively short, and in the above titrations, which were selected at random, only half of it was being used.

At first the tap *E* was lubricated with a paraffin-rubber composition, but it was found that this soon became softened and dissolved by contact with the liquid paraffin, and a certain amount of creep was liable to occur. This difficulty was got over by using an aqueous starch-glycerol lubricant, prepared as follows: 0.5 g. of Kahlbaum soluble starch is stirred up with 0.2 ml. of 5 % mercuric chloride solution and 0.7 ml. of water and heated in a boiling water-bath for 10 minutes; 0.5 ml. of glycerol is then added and stirred in whilst the mixture is still hot. It thickens considerably on standing and should not be used till 3 or 4 hours after preparation.

The rubber joints at each end of the tube *M* slowly swell and absorb paraffin. The actual rate of absorption has no disturbing effect on the titration, but the tubing, which of course is thick-walled, must be renewed when it becomes too loose fitting.

Note. A second burette has been constructed which is similar in all respects to the above, except that two calibrated tubes are incorporated instead of one. They are of 0.5 and 0.05 ml. capacity respectively and are connected to bulb *D* through a two-way tap, so that either can be used.

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