table on page 688. Only the corrected figures and legends are recorded: reference is made to both publications, the first number being that assigned in *Bulletin* **94**, and the second, the Bureau of Soils number assigned in articles which appeared in THIS JOURNAL.[1]

To report in the conventional manner the results obtained in the examination of the various brines submitted for analysis was a concession to the supposed wishes of the laymen interested to whom the statement of results as ions conveys but slight information. This concession was made against our best judgment, since to report the various basic and acid radicles as combined is to abandon for the moment the best conception of the state of salts in solution. To calculate such analytical data to the saline combination is to juggle figures. As the basis for the conventional combination the respective solubilities of the component salts, which anciently were regarded as entities, have been taken. This, likewise, is a false basis, since the solubility of each salt when alone in solution is different from its solubility when in solution with the other salts. The latter solubility is determined by the equilibrium conditions obtaining for each system studied. The conventional combinations should represent, if anything at all, the solids precipitated on evaporation from the system studied, and should be recorded in the order of their precipitation. This could be determined only by an examination of the system under consideration.

The value of the results previously published is scarcely diminished by the errors introduced in the calculations previously published. However, the fact that the system of calculation from ionic to saline form is based on erroneous conceptions and therefore itself is erroneous does not excuse avoidable errors in the application of the system. For that reason it is desired to substitute the recalculations herewith presented.

BUREAU OF SOILS, U. S. DEPARTMENT OF AGRICULTURE
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[1] *Loc. cit.*

LABORATORY AND PLANT

A MODIFIED BURETTE CALIBRATING PIPETTE AND CERTAIN POINTS IN THE USE OF SUCH INSTRUMENTS[1]

By C. W. FOULK

Received March 23, 1915

Some months before this article was prepared for publication, the writer was told by the "Trouble Man" of a large chemical firm that the laboratory and factory control difficulties he was called upon to adjust were frequently caused by inaccuracies in the volumetric ware employed, and he added that in his opinion many young chemists and not a few old ones were unaware of this source of error. The "Trouble Man" must take the responsibility for his statement about chemists, but the author is willing to testify regarding the general depravity of uncertified volumetric ware. During the last ten years the calibration tables of several hundred burettes have been examined and errors of 0.1 cc. or more have been found the rule rather than the exception. Occasionally the corrections reach a truly surprising value. For example, at least three otherwise innocent looking burettes have been found with errors of over 0.4 cc. in the first 20 cc. of the scale. It, therefore, cannot be too strongly emphasized that all such measuring instruments must be calibrated before using.

If only one or two burettes are to be examined the method of weighing the water delivered from successive intervals is the simplest since it involves no special apparatus. If, however, a larger number are to be calibrated or if from time to time a few must be tested, some form of calibrating pipette will be found an advantage on account of the time saved and the simplicity and directness of the procedure. Several such pipettes have been described[2] but in every case an important point has curiously enough been overlooked, namely, the use of the two-way glass cock as an automatic zero adjustment. A modification employing this time-saving scheme will be described in this paper and in addition the general principles and procedures involved in the use and calibration of these calibrating pipettes will be given. It so happens that in previous articles there is not very good agreement as to the details of determining the capacity of the pipette itself and in some cases the methods of calculating the final values obtained for the different points on the burette scale are unnecessarily long. Many recent text-books also do not refer to the use of such calibrating instruments and, therefore, there is perhaps some justification for presenting in this place a more complete account of their advantages and use.

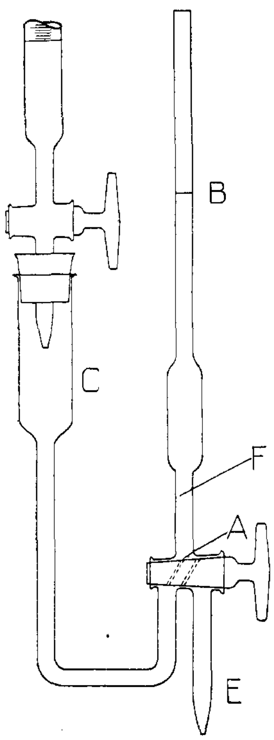
The instrument illustrated here is in its general operation like others that have been described, *i. e.*, it is a device for accurately measuring successive portions of water as they may be drawn from the burette under examination. It differs, however, from the previous instruments by its using the two-way glass cock as a zero adjustment instead of the usual mark on the lower stem. The enlargement at C may also be looked on as an improvement, since it furnishes a convenient place for attaching the clamp for holding it and also permits the use of a rubber stopper for connecting to the burette, which makes a more satisfactory joint than the gum tubing that would otherwise have to be employed.

All of the previously described pipettes of this sort have had a mark on the lower stem which served as a zero point, to which the water was adjusted before a portion was drawn out of the burette for measurement and at which the outflow was stopped when the pipette was emptied to make room for the next portion from the burette. The accompanying figure will illustrate this form of pipette if a mark around

[1] Pipettes of the design described in this article and provided with a 0.01 cc. division scale on the upper stem can be secured from the Kauffman-Lattimer Co., Columbus, O.

[2] Arndt, *Centralblat*, **1856**, p. 865; Scheibler, *J. prakt. Chem.*, **76** (1859), 177; Ostwald, *Ibid.*, N. F., **25** (1882), 452; Morse and Blalock, *Am. Chem. J.*, **26** (1894), 479.

the stem be imagined at F. That such a mark is redundant and that the two-way cock can serve as a self-adjusting zero can be seen by reference to the figure, in which the cock is represented in the position of allowing the flow of liquid to take place from the burette into the pipette. It will be seen that, if the pipette has previously been filled and emptied, the flow will begin at the top of the boring through the plug of the cock as indicated at A. Furthermore, since the operation of the cock is such that the connection with the burette is closed before the outflow through the tip can begin and the outflow through the tip is closed before the inflow from the burette can begin, it is evident that, after the pipette is emptied and another portion of liquid is to be drawn from the burette, its flow will also begin at the top of the boring at A and so on for all succeeding portions. This makes the point A a zero mark to which the adjustment of liquid is automatically regulated by the position of the cock. Moreover, this zero point is more accurate than a mark around the lower stem would be on account of the smaller diameter of the boring.



GENERAL POINTS IN THE USE OF SUCH CALIBRATING PIPETTE

First, there can be no question of the accuracy of the method. Owing to the smaller bore of the stem of the pipette the readings are ten times more delicate than on the burette. In other words, differences of 0.001 cc. can be noted in the pipette as readily as 0.01 cc. in the burette. An error might possibly be introduced by carelessly allowing a considerable difference in temperature to occur between the water as measured in the burette and in the pipette. Ordinary care will, however, prevent such differences so that it is safe to assume the temperature of the water to be the same —within the limits required by the nature of the work. A similar assumption is made by the Bureau of Standards in its method of calibrating flasks by delivering into them measured volumes of water from standard pipettes.[1]

Secondly, there can be no question of the time saved by the use of these calibrating devices because adjusting the meniscus in the pipette when drawing off a portion of water from the burette is a brief operation compared with making a weighing, and finally because there are no temperature corrections to calculate. The pipette when once calibrated for the standard temperature (20°) for glass apparatus, may be assumed to retain a constant volume so far as ordinary laboratory temperature changes are concerned.

THE CALIBRATION OF THE PIPETTE

It is evident that the capacity of the calibrating instrument itself must be determined with great care and that this must be done by weighing the water required to fill it. From this weight and the temperature of the water its volume can be calculated. The methods for making such calculations are to be found in any large text-book on quantitative analysis and, therefore, will not be repeated here. In this connection see also the Bulletin of the Bureau of Standards cited above.

At the outset, however, an important point in the calibration of such pipettes should be noted: the usual rapid rate of outflow of the ordinary burette must be restricted or the results will be in error. This is because in calibrating the burette, successive, small portions (pipetteful) are drawn off with an interval of time between the readings while in an actual titration 30 to 40 cc. may be drawn off at once. The former method gives more water because, being the slower, there will be more drainage.[1] The difference due to variable drainage may amount to as much as 0.1 cc. in the lower part of the scale in burettes as ordinarily received from the manufacturers. If, however, the rate of outflow be sufficiently restricted (see footnote below) this difference in drainage between emptying the greater part of the burette in a series of small portions or all in one portion, becomes negligible. In earlier articles this point has received no mention, though the method of Morse and Blalock eliminates the error. These authors, however, do not discuss or even allude to this advantage of their plan. The same situation exists in the case of calibrating a burette by weighing. If successive small portions are drawn off in tandem the results obtained for the lower part of the burette will differ from those obtained by starting at zero, unless the rate of outflow is small. The Bureau of Standards, though recognizing the small size of the error occasioned by the tandem method of calibrating burettes with restricted outlets nevertheless follows the more accurate plan of starting at zero each time when drawing off the portion of water to be weighed.

Similarly, the author prefers the Morse-Blalock method for getting the capacity of the calibrating pipette. It has the merit of eliminating any possible tandem-error and at the same time is, if anything, a trifle shorter than other methods. As will be seen below, it does not give the true capacity of the pipette but rather the capacity corrected for any difference in drainage between emptying the burette in successive, small portions taken out in tandem, as compared with drawing out the same amount of water in one portion; for example, 0 to 5 cc., 5 to 10 cc., etc., to 45 to 50 cc. as compared with 0 to 50 cc. in one portion.

Morse and Blalock's procedure is to determine the capacity of the pipette in an indirect way, by dividing the volume of water delivered directly from zero to a mark near the bottom of the burette scale, by the

[1] Osborn and Veazey, *Bulletin B. of S.*, **4** (1908), 589.

[1] Schloesser, *Z. anal. Chem.*, **46** (1907), 392.

number of pipettefuls that can be drawn off to that mark. For example, with a pipette like the one shown here, the capacity of which is about 5 cc., it is evident that with a 50 cc. burette, 10 pipettefuls can be obtained if the capacity is less than 5 cc., or 9 pipettefuls if the capacity is a little more than 5 cc. Assuming the latter, let the reading of the burette be 45.23 cc. when the ninth pipetteful has been reached. To get the corrected capacity of the pipette, the burette is again filled to zero and the water allowed to flow out into a small flask to 45.23 cc. on the scale. This water is weighed, its temperature taken and its volume calculated. One-ninth of this is then the volume of the pipette to be used in calibrating burettes. It is not the true capacity of the pipette because the amount of water obtained by allowing the burette to empty itself at its normal rate from 0 to 45.23 is slightly less than the amount that would be gotten by drawing it out in nine portions with a considerable interval of time between each portion.

METHOD OF MARKING THE PIPETTE

The author of course hopes that no one will continue to put a mark on the lower stem of such calibrating pipettes, but there still remains the marking of the upper stem. This can be done as follows:

(1) A single mark arbitrarily placed is put around the upper stem. The exact capacity of the pipette from the stopcock to this mark is then determined by the method of Morse and Blalock. Such an instrument will measure successive portions of the same volume as they are drawn from the burette and the successive burette readings will correspond to the multiples of the capacity of the pipette. A variation of this plan consists in locating the mark on the upper stem so that it will correspond to some convenient whole number of cubic centimeters, such as 2 cc. or 5 cc. This is no advantage because, in any event, the burette readings will not fall on the marks of the burette representing such integral numbers or their multiples, and for plotting a correction curve the readings obtained by using an arbitrarily marked pipette would be of equal value with those obtained by the second method.

(2) A scale divided arbitrarily into small units approximating 0.01 cc. or so that each division corresponds exactly to 0.01 cc. may be combined with a major capacity mark which may be located in either of the ways described in (1) above. In using a pipette equipped with a scale, successive portions of the same nominal value, such as from 0 to 5 cc. on the burette, 5 to 10 cc. or whatever value the capacity of the pipette may be, are drawn out and their exact volume determined by measurement in the pipette.

"This appears to be an advantage, which is, however, more apparent than real, and will hardly pay for the extra labor required for the construction and location of such a scale unless a very large number of burettes are to be tested. In either case a correction curve can be made and the values corresponding to integral marks on the burette (1, 2, 3 cc., etc.) can be calculated upon the reasonable assumption that the bore of the burette does not change appreciably in a short length. Therefore, the error at any integral mark will be the same as at any reading in the immediate vicinity. Thus, if at 14.71 cc. the error is 0.05 cc., the same correction may be applied at 15 cc."

It might be interesting to compare the above method with the more laborious one employed in one of the previous articles on burette calibrating pipettes. The exact volume corresponding to the 50.00 cc. mark on a burette scale had been found to be 50.258 cc. and it was desired to find the volume corresponding to 49.52 cc. on the same scale. It was done by solving the proportion $50 : 50.258 :: 49.52 : x$, by which x is found to be 49.7755 cc. (The figures are given as they are found in the article in question.) If instead of making this calculation, it had been assumed that the error of the burette at 49.52 cc. was the same as at the near-by point, 50 cc.—namely, +0.258 cc.—the true value of the scale reading 49.52 could have been found by simply adding the correction 0.258. This gives 49.7780 cc. which differs from the other value, 49.7755 cc. so laboriously obtained, by only 0.0025 cc., an amount which under the circumstances could introduce no error.

In order to show the necessary details in manipulation and calculation there will now be given the complete procedure for determining the capacity of the calibrating pipette and for using the pipette in finding the errors of a burette.

DETERMINATION OF THE CAPACITY OF THE PIPETTE[1]

The pipette and a burette, connected as shown in the drawing, are filled with distilled water. Both instruments can be supported on one ring-stand by the use of two clamps. Air bubbles in the connecting parts can be avoided by having the enlargement at C full of water before the stopper is inserted. This causes an overflow through the hole, and if now the tip of the burette is also filled before it is put into the stopper, no air will be entrapped. The level of liquid in the burette is adjusted to zero and the pipette (which must be full) is allowed to empty itself through the tip at E. This point of filling and emptying before an actual measurement is made is necessary because the capacity of the pipette is affected by the amount of liquid on the interior. This amount must obviously be the same for the first pipetteful as for the subsequent ones. In the manipulation of the stopcocks it will be found convenient to leave the burette cock open and control the flow of water entirely with the two-way cock of the pipette.

[1] Before beginning an actual calibration, the rate of outflow of both the pipette and the burette should be adjusted once for all by properly constricting the outlet orifice. The stopcocks can then be opened to their full extent and the rate of flow will be correct without further regulation. Specifications from the Bureau of Standards require the outflow of a burette with a scale 50 cm. long—about that of a 50 cc. burette—to be not less than 90 seconds nor more than three minutes, and the free outflow time of a 5 cc. pipette to be not less than 15 seconds nor more than one minute. The most convenient way of adjusting the orifice to a given rate of delivery is to draw out the tip in a flame so that it is smaller than desired. One can then gradually enlarge it by filing or grinding across the end. By this procedure trial can be made from time to time without the necessity of waiting for hot glass to cool or for drying the wet glass before heating again, as would be the case if the usual method of allowing the tip to contract in a flame were employed. Finally, everything must be thoroughly cleaned with chromic-sulfuric acid mixture and rinsed with distilled water before beginning work.

With the level of water in the burette at zero and the pipette emptied, the next step is to allow water to flow from the burette into the pipette till the mark at B on the upper stem is reached. This portion is then allowed to flow out through the tip at E. In this way successive pipettefuls are drawn off and wasted through E till a point is reached on the burette beyond which another portion would bring the level of the water below the scale. This last burette reading must be carefully noted and, though it is the only one necessary for the calibration of the pipette, the intermediate ones should also be made and recorded because they may subsequently be used in determining the errors of the burette and because it is the simplest way of insuring the same conditions in the calibration as in the subsequent use of the pipette.

The next step is to find the volume corresponding to the last reading on the burette as obtained above. This is done by disconnecting the pipette, filling the burette with water, adjusting the meniscus to zero and then allowing the water to flow out at its normal rate into a tared flask till the point corresponding to the last pipetteful is reached. This portion of water is then weighed to the nearest milligram and from its weight and its temperature its true volume in cubic centimeters is calculated. The above experiments should of course be repeated several times till closely agreeing results are obtained, the averages of which are then used for the final calculations as follows:

Suppose that the capacity of the pipette is such that the tenth portion drawn from the burette by its use brings the level of liquid to 49.82 cc. on the burette scale and that the weighing of the water delivered directly from zero to this point gave its true volume as 49.88 cc. Since this volume corresponds to ten pipettefuls, it is evident that the capacity to be assigned to the pipette is 4.988 cc.

CALIBRATION OF A BURETTE

The calibration of a burette is carried out by connecting the pipette as described above and drawing off successive pipettefuls, noting the reading each time on the burette scale. Assuming a pipette with a capacity of 4.988 cc. and an average burette, readings would be obtained about as given in the first column of the table below. The second column gives the true

Table I

1 Burette readings	2 Correct volume	3 Corrections	4 Burette reading	5 Correct volume
5.05	4.99	—0.06	5.00	4.94
10.04	9.98	—0.06	10.00	9.94
15.04	14.96	—0.08	15.00	14.92
20.08	19.95	—0.13	20.00	19.87
25.06	24.94	—0.12	25.00	24.88
30.03	29.93	—0.10	30.00	29.90
35.06	34.92	—0.14	35.00	34.86
40.04	39.90	—0.14	40.00	39.86
45.05	44.89	—0.16	45.00	44.84
50+	Correction for 50.00 cc. is found by the method illustrated in Table II			

volume corresponding to the readings and is obtained by multiplying the capacity of the pipette by the serial number of the interval measured and rounding off the numbers to two decimals. Column 3 gives the corrections for the points in Column 1 and, since the corrections are the same for all points in the immediate vicinity of a given point, the numbers in Column 3 are also the corrections for the burette readings as given in Column 4. Column 5 gives the volumes corresponding to the "5 cc." points on the scale.

The above figures are from an actual burette and present a complication that may sometimes arise; namely, that when starting at zero the last pipetteful may bring the burette reading below the scale. This situation is, however, easily remedied by a simple trick of manipulation. Two or three sets of readings are wanted in any event in the interests of accuracy and when the first series shows that the last pipetteful brings the reading below the scale, the next series is started a little above the beginning of the second interval; in this case, for example, at 5.00 cc. on the burette scale. The burette readings are then as follows:

Table II

I Burette reading	II Correct volume
5.00	4.94
9.99	9.93
15.00	14.92
20.03	19.90
25.01	24.89
29.98	29.88
35.01	34.87
40.00	39.86
45.00	44.84
49.98	49.83

The correct volume corresponding to the burette reading of 5.00 cc. is taken from Table I

The true volumes corresponding to the readings are obtained by adding the appropriate multiple of the capacity of the pipette to the volume corresponding to the starting point which is taken from Table I and which must be checked by a separate experiment. This series of readings in Table II also gives the corrections for points in the immediate vicinity of those marks on the burette scale which are multiples of 5 and consequently may be applied at once to those marks. In other words, they are check readings on those of Table I, and in addition give the value of the correction for the 50 cc. mark.

If a correction curve is to be made, the above data are sufficient. In case it is desired to tabulate the corrections for each "cubic centimeter" mark on the scale of the burette the following procedure should be used: (1) The true volume of each 5 cc. interval of the burette is found by a series of subtractions based on the values in Table I, Column 5; (2) the value of 1 cc. in each interval is found by dividing the true volume of the interval by 5. Table III illustrates these two points.

Table III

Interval on burette scale	Volume of interval	Value of "1 cc." in interval
0 to 5	4.94	0.988
5 to 10 = (9.94 — 4.94) =	5.00	1.000
10 to 15 = (14.92 — 9.94) =	4.98	0.996
40 to 45 = (44.84 — 39.86) =	4.98	0.996
45 to 50 = (49.85 — 44.84) =	5.01	1.002

The final tabulation is made by adding these cubic centimeter values in Table III, the results being rounded off to two decimals. Table IV, below, covering part of the burette scale, shows this.

Table IV

Burette reading	True volume	Burette reading	True volume	Burette reading	True volume
1	0.99	8	7.94	44	43.84
2	1.98	9	8.94	45	44.84
3	2.96	10	9.94	46	45.84
4	3.95	11	10.94	47	46.84
5	4.94	12	11.93	48	47.85
6	5.94	..	.....	49	48.85
7	6.94	..	.....	50	49.85

If this plan is used, the tabulation should be made on a stiff piece of paper or board so that it can be hung up near the burette.

CONCLUSION

In this article there has been described a modification of a burette-calibrating pipette that eliminates the mark on the lower stem and provides for the use of a two-way cock as an automatic zero-adjusting device.

A discussion of the principles underlying the calibration and use of such pipettes is also given.

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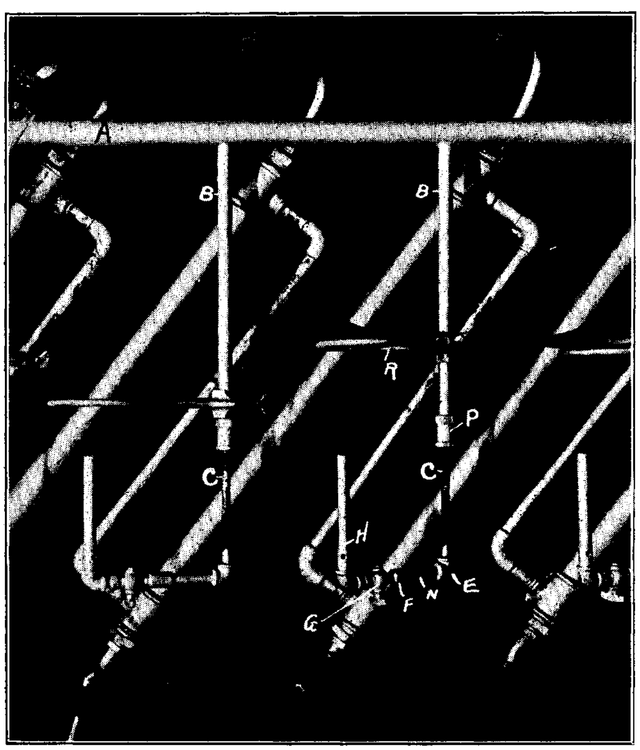
AN ADJUSTABLE BURNER SUPPORT FOR CONDENSATION APPARATUS

By H. E. BISHOP

Received April 19, 1915

The condensation apparatus described by H. E. Barnard and H. E. Bishop in the *Journal of the American Chemical Society*, **28** (1906), 999, was designed for use with flasks of uniform size only. The burner and flask supports were so arranged that in changing the adjustment of the still it was necessary to move them as a unit. To overcome this difficulty the burner and flask support to be described was designed.

The condensation tubes, water connection and their supports were not changed. The gas supply was changed from a position under the flask support to the top of the supports for the condensing tubes *A*.



The gas pipe was already tapped for $^1/_8$ in. air cocks to which the burners were attached. The air cocks were replaced by $^1/_8$ in. close nipples. An 11 in. length of $^9/_{16}$ in. (outside diam.) brass pipe, *B*, was tapped at one end to fit the $^1/_8$ in. close nipple and attached to the gas pipe. This pipe, hanging in a perpendicular position, forms the rod for the ring which supports the flask.

Into this tube was fitted a brass tube, *C*, which would slide easily. The lower end of this sliding tube was soldered into a $^1/_8$ in. brass elbow, *E*. A 2-in. $^1/_8$ in. nipple, *N*, was screwed into the other side of the elbow; then a $^1/_8$ in. coupling, *F*, which in turn took the air cock, was attached. Another elbow was attached to the air cock *G* which took the nipple for the tube of the Bunsen burner *H*.

The gas joint, which allows the burner to be adjusted up or down, is similar to the old gas drop-light which was on the market before the use of rubber tubing was so general. The lower end of the tube *B*, which forms the ring support and the outside member of the extension tube, was threaded to take an ordinary packing box, *P*, similar to those used at the top and bottom of the condensing tubes. Ordinary candle-wick packing, well oiled, was used. The addition of a ring, *R*, from the regular ring stand, completed the apparatus.

The great advantage of the apparatus is its wide range of adjustment for individual operations. Flasks from 5 in. to 14 in. high can be used simultaneously. The sliding gas tube overcomes the necessity for rubber connections and if more heat is desired, two burners may be turned under one ring. The cost of construction is small and the upkeep is *nil*.

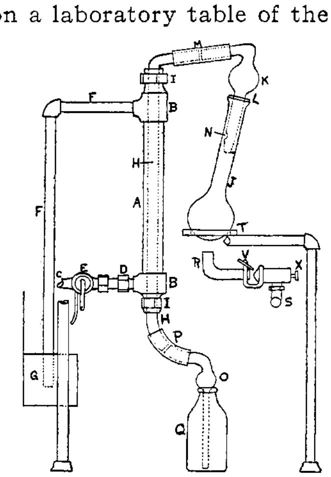
INDIANA STATE BOARD OF HEALTH
INDIANAPOLIS

A NEW AND IMPROVED FORM OF KJELDAHL DISTILLATION APPARATUS

By ARTHUR D. HOLMES

Received March 9, 1915

A description was given in THIS JOURNAL, **6** (1914), 1010, of a Kjeldahl apparatus which has given satisfactory service in this laboratory. This apparatus as described, when set up on a laboratory table of the usual height, has been found somewhat too high for convenience when used by a person of short stature. To avoid this difficulty, the apparatus may be modified as indicated in the accompanying sketch, which should be substituted for Fig. II of the original article. The height may be decreased 6 to 8 in. by replacing the upright type of burner with a horizontal offset burner, and shortening the condenser pipe accordingly. It is well to make sure, however, that the diameter of this pipe, and the rate of flow of the water in it, are sufficient to insure condensation in the tube *H*.



The modification not only lessens height, but also obviates the disagreeable results which often follow