ALCOHOLOMETRY FOR THE PHARMACIST.

BY A. B. LYONS.

Under existing laws in America alcohol determinations have assumed a new importance to the pharmacist. The U. S. Pharmacopoeia prescribes a method of making such determinations by taking the specific gravity of a distillate from the preparation under examination. Details of the routine process need not be entered into here. Suffice it to say that in any case it is imperative to make note of the exact temperature at which the specific gravity is taken. Two alternative procedures are possible. Either the distillate, the volume of which bears a simple relationship to that of the sample distilled, is brought to a fixed standard temperature (commonly either 15° C. or the equivalent of 60° F.) or else the specific gravity is taken at room temperature, and a correction applied for difference from said standard temperature. The latter plan is that more commonly adopted, and is that prescribed in the U. S. P. IX. The alcoholometric table supplied in the Pharmacopoeia, however, gives the necessary data, whichever of the two alternative procedures is adopted.

THE U. S. P. IX ALCOHOL TABLES.

Examination of these tables shows that they give with a minimum of brain-wear results of reasonable exactness, the possible error rarely affecting the first decimal by more than one unit, *viz.*, 0.10 percent, providing the preliminary distillation has been conducted with care and intelligence. Features of these tables which have been criticised are the following:

1. The specific gravities given are "apparent," not "true," *i. e.*, they do not take account of the buoyant effect of atmospheric pressure. The pycnometer if marked 25 Gm. must hold at 15.56° C. exactly 25,000 Gm. of distilled water under average atmospheric conditions, uncorrected weight, whereas, if weighed in a vacuum, it would be heavier by the weight of the displaced air, *viz.*, about 0.0269 Gm.

Many of the specific gravity tables constructed for practical use adopt the same principle. Those given in scientific works, unless otherwise specified, are calculated to a vacuum basis, and it is clear that only corrected figures are admissible as a foundation for exact mathematical conclusions. When we take into consideration, however, the insignificant actual amount of the corrections in question and remember that these involve three distinct factors, *viz.*, temperature, humidity and barometric pressure, we are justified in concluding that for practical purposes, correction to true specific gravity in an alcohol table for every-day use is a needless refinement. Percentages deduced from apparent specific gravities are in fact quite as exact as those from the corrected figures we have to accept as true specific gravities.

2. It may be held inconsistent that the U. S. P. alcohol tables do provide a correction for variations in barometric pressure. A moment's consideration, however, will reveal justification for this provision in the fact that while variations in atmospheric pressure dependent on meteorological conditions are insignificant in amount, it is otherwise with variations due to altitude. At a station 3000 meters above sea level, the barometric pressure is reduced fully thirty percent. The difference in indicated specific gravity in such a case is not wholly negligible, where great accuracy of work is sought. However, such altitudes except for avia-

tors are quite exceptional. It is safe to say that up to an elevation of 1000 meters, no attention need be given to the correction under consideration.

3. The U. S. P. tables carry specific gravities to the fifth decimal place. It is maintained by some that four places would suffice. That depends. If the pycnometer used holds but 10 Gm. of distilled water, the difference in weight of its contents at 15.56° C. for a difference of 1 percent in alcoholic strength in a total of 20 percent is only about 10 mg. Weighings would have to be exact to 0.1 mg., with equally accurate temperature readings to give even approximate significance to the second decimal in the deduced percentage.

The most convenient size for the pycnometer is that holding 25 Gm. of distilled water. This would make possible the recognition theoretically of differences of 3 units in the second decimal, provided the measurements of sample and distillate have been made with exactitude, and the distillate consists of nothing but alcohol and water. Dismissing these elements of uncertainty let us consider the advantage to be received from extending the number of decimal places in the table of specific gravities from four to five. Suppose that the four place table gives us at about 16 percent (volume) a specific gravity of 0.98000, while the five place table gives 0.97996. This will mean a discrepancy between the tables amounting to about 0.04 percent. It is easy to draw the conclusion that while little dependence is to be placed on the second decimal in alcohol percentages deduced from specific gravities, there is a distinct advantage in a fifth decimal in the specific gravity table. Since the interpolation of fractional percentages is hardly more difficult in one case than the other, the five decimal table is certainly to be preferred.

4. The U. S. P. tables assume a standard temperature of 15.56° C., conforming in this respect to established usage in English-speaking countries. All the tables used in America by custom house officials and others charged with carrying out government regulations, federal or state, employ this standard, which moreover differs only very slightly from that of 15° C. adopted generally in foreign countries not English speaking. Where specific gravities are taken by a pycnometer of the old type, with perforated stopper, a temperature so low as this is inconvenient. The air temperature in an average weighing room in America is almost always so high that moisture condenses on the pycnometer. Air currents also interfere with accuracy in making weighings under these conditions. To be sure, the Westphal balance may be used, taking care that the plummet of the balance is made of glass having the same coefficient of expansion by heat as that from which the pycnometer is made, but such a balance is not part of the equipment of the ordinary drug store.

Either, therefore, the pycnometer is to be filled with the distillate (previously brought accurately to correct volume) which has been allowed to come to the air temperature of the weighing room, and the percentage found corrected for temperature by the supplementary table, pp. 636 and 637, or else a pycnometer of the Squibb type must be used—to be "filled" at standard temperature and then brought to air temperature for weighing. The latter plan is to be preferred, yet the former has the advantage of rapidity of execution.

5. Non-essential features of the U. S. P. tables are the data with regard to percentages by weight and relation of weight to volume percentage and *vice versa.*

Such data are occasionally wanted, and so may well be included, although there is possibility that errors may result from carelessness in taking out figures from the wrong column.

THE NEW TABLE OF THE A. O. A. C.

There are cogent reasons for the adoption of a uniform temperature standard of 20° C. for all statements of specific gravity where the physical properties of the substance permit. The A. O. A. C. has recently published an elaborate alcoholometric table calculated on this basis. The figures of this five decimal table are said to have been computed by the Bureau of Standards, and I find them in close accord with those of the basic tables published by that Bureau. In criticism of the new table, the following points may be noticed.

1. The table multiplies figures needlessly, covering as it does nearly 14 twelve-column pages. If the observed specific gravity (density) is 0.97848, we find by reference to the table that the percent by volume of alcohol lies between 15.40 and 15.45. Interpolation gives us 15.40 plus (0.05 × 4 ÷ 6) which equals 15.43. Note that the 6 and 4 above result from subtraction, respectively, of 97846 and 97848 from 97852. Now suppose that the table gave specific gravities only for integral percentages, giving also, however, the factor for calculating fractional percentages: We have only to make one subtraction, *viz.*, 97897 − 97848 = 49 (units of fifth decimal). The table would supply the factor 0.901. For the fractional percentage, multiply 49 by 0.901 and add the product (49 × 0.901 = .44 (15)) to 15% giving the percentage as 15.44, a result practically identical with that deduced from the table. The interpolation is quite as easy in one case as in the other.

2. The table gives densities instead of specific gravities. This does not affect the use of the table, of course, but it is easier to verify the accuracy of a pycnometer if it is to contain at standard temperature an exact 25, 50 or 100 Gm. of distilled water, than if the quantity, *e. g.*, for a 25-Gm. pycnometer is to be 25,000 × 0.99823 = 24.9558 Gm.

3. The "specific gravities" (densities) given in the table are understood to be *in vacuo*, consequently all pycnometer weighings are to be reduced to a vacuum basis. This holds of course in the weighings to verify the calibration of a pycnometer. In the example given at the close of the foregoing paragraph the weight 24.9558 is to be calculated to apparent weight. The correction to vacuum weighing in this case would be, for a barometric pressure of 750 mm., humidity 50%, 25 mg. multiplied by 1.039 = 25.5 mg., subtractive, so that the apparent weight of the water filling the pycnometer at 20° C. should be 24.9558 − 0.0255 = 24.9303 Gm.

4. The one important criticism of the A. O. A. C. table, as I have already pointed out,* is that *its volume percentages do not agree with those of established usage.* The table is self-consistent indeed, in that the standard temperature of 20° C. is taken as that at which the weight volume relation is calculated. But we must bear in mind that *this ratio varies with the temperature, so that it is imperative that statements of volume percentages of alcohol shall assume an invariable standard temperature for this relation,* whatever the temperature be at which weighings are made. Otherwise there must result endless confusion in business transactions.

* Jour. A. Ph. A., 1921, p. 12.

Such standard has been fixed the civilized world over at 15° C. or the practically identical 60° F. (15.56° C.). The U. S. Bureau of Standards makes authoritative for the United States the latter of these alternatives, publishing full tables in which fractional decimals are carried to three places.

The general public cannot be expected to know that the volume percent of alcohol in a mixture will vary if the measurements are made at different temperatures, yet this is an obvious consequence of the difference in coefficient of expansion by heat of water and alcohol. Usage crystallized into legal enactment has given a fixed meaning to volume percentages of alcoholic beverages or mixtures. Only by international agreement should any change in that meaning be made in any alcohol table by which volume percentages are to be determined.

As it is, the A. O. A. C. is a house divided against itself, since, side by side with the new table, there is published by them an equally elaborate table (for determination of alcohol percentages by the refractometer) in which *we find throughout the old familiar weight-volume relationships*, although the observations are made at temperatures ranging from 17.50° C. to 25° C.

Why not then reckon alcohol percentages by weight exclusively? For two reasons: first, because in America quantities of any liquid are thought of and expressed in terms of volume, not of weight. Liquid medicines, for example, are prescribed and administered only in measured doses. Twenty percent (volume) means that a "teaspoonful" dose contains twelve minims of absolute alcohol, whether the medicine be a heavy syrup or merely a hydroalcoholic fluid of low specific gravity. If, on the other hand, the medicine contains 20 percent of alcohol by weight the actual quantity will depend on the specific gravity of the liquid. In the second place the weight percent of a distillate given by an alcohol table is only exceptionally the proportion of alcohol contained in the liquid yielding that distillate. The specific gravity (true) of that liquid must be ascertained, and the percent then calculated by the rule of three.

To be sure it would be possible to give to the expression "percent of alcohol by weight" conventionally a modified sense based not on the weight of the original sample but on a distillate therefrom having at standard temperature an equal volume. Merely to suggest such a possibility, however, is to make clear its impracticability.

CONCLUSIONS.

From the foregoing discussion the following conclusions may be drawn:

1. An alcohol table for every-day use by the practical pharmacist may well be an abbreviated form of the A. O. A. C. table, agreeing with that in assuming a standard temperature of 20° C. (perhaps preferably 25° C.) for taking specific gravities, but differing in the following particulars: (A) The standard temperature for weight-volume relations should be that in established use, *i. e.*, in America 15.56° C., until international agreement shall bring about adoption of a different standard. (B) The specific gravities should be on a basis of 20°/20° (or 25°/25°) not 20°/4°, preference to be given to 20° as the standard adopted generally by the Bureau of Standards. (C) Because of the unfamiliarity of many pharmacists with the reduction of apparent to true specific gravities, it seems best to give the former rather than the latter in any specific gravity table for determination of per-

centages by use of the pycnometer or Westphal balance. (D) The table should give specific gravities only for integral percentages, a column of factors being supplied for the easy calculation of fractional percentages. (E) The column for weight percentages corresponding with volume percentages may well be retained, and a corresponding column of factors for calculation of intermediate percentages could be added for completeness. A portion of such a table is given below, sufficient to illustrate the plan. The figures given may require slight modification, but they are substantially correct.

ALCOHOLOMETRIC TABLE I (IN PART).
Sp. Gr. app. 20°/20° C.
To be used at a Fixed Standard Temperature, *viz.*, 20° C.
Volume-Weight Ratio Taken at 15.56° C. (60° F.).

Percent alcohol vol.	Sp. gr. (app.) 20°/20°.	Factor for fractional percent.	Percent alcohol wt.	Factor for fractional percent.
0	1.00000	0.671	0.000	0.533
1	0.99851	0.676	0.795	0.539
2	0.99703	0.694	1.593	0.555
3	0.99559	0.704	2.392	0.565
4	0.99417	0.725	3.194	0.583
5	0.99279	0.746	3.998	0.600
6	0.99145	0.769	4.804	0.622
7	0.99015	0.794	5.612	0.643
8	0.98889	0.806	6.422	0.655
9	0.98765	0.826	7.234	0.671
10	0.98644	0.833	8.047	0.679

Example: A distillate is found to have a sp. gr. (apparent) at 20°/20° C. of 0.98700. To find volume percent take out from Column II the figure next above 0.98700, *viz.*, 0.98765. The difference (65) is to be multiplied by 0.826 from Column III (opposite 0.98765). The product, 65 × 0.826 = .537, is the required fractional percent (vol.) to be added to 9 (Column I).

To find percent by weight, use the same difference, but multiply by 0.671 (Column V). The product, 65 × 0.671 = .436, is the fractional percent by weight to be added to 7.234 (Column IV), giving the result 7.234 plus 0.436 = 7.670.

2. For many it will seem the easiest way to adjust the volume of distillate at the correct temperature and then to allow the fluid to come to the temperature of the weighing room. Make the necessary weighing at that temperature and then apply a temperature correction. For such the present U. S. P. table is to be recommended with some modifications. It will be seen that the tables on pages 633 to 635, inc., are really two distinct tables, that on the left half of the pages alone being that to be consulted in determining volume percentages. As already explained, the fourth column need not be taken into account unless the barometric pressure is lower than that normal at an altitude of 1000 meters.

It might be well to complete the table for temperature corrections by giving the figures for each integral percentage, only about one-half of these being given in the U. S. P. Table. With the table completed in this respect, interpolation for fractional degrees of temperature becomes a simple matter.

Example: Required the correction for 23.6° C. in a case where the uncorrected percent is 58. The correction for 23° is 2.66; for 24° it is 3.01. The difference is 0.35. For the fractional 0.6° multiply 0.35 × 0.6; the product 0.21 is simply to be added to 2.66 giving 2.87 as the required correction. In like manner an interpolation may be made for fractional percentages, but as a rule this is negligible.

ALCOHOLOMETRIC TABLE II (IN PART).

Giving Percent by Volume of Absolute Alcohol Corresponding with Different Apparent Specific Gravities at Different Temperatures.

Temperature.	24.99	24.98	24.97	24.96	24.95	24.94	24.93	24.92	24.91	24.90	24.89	24.88	24.87	24.86
15° C.	0.33	0.60	0.86	1.13	1.40	1.68	1.95	2.22	2.50	2.79	3.07	3.35	3.63	3.91
	.10	.10	.10	.10	.10	.10	.10	.10	.10	.11	.11	.11	.11	.11
15.56	0.27	0.54	0.80	1.07	1.34	1.62	1.89	2.16	2.44	2.72	3.00	3.28	3.56	3.84
16	0.23	0.50	0.76	1.03	1.30	1.58	1.85	2.12	2.40	2.68	2.95	3.23	3.51	3.79
17	0.13 .27	0.40 .26	0.66 .27	0.93 .27	1.20 .28	1.48 .27	1.75 .27	2.02 .27	2.29 .28	2.57 .27	2.84 .28	3.12 .28	3.40 .28	3.68 .28.
18	0.02	0.29	0.55	0.82	1.09	1.57	1.64	2.91	2.18	2.46	2.73	3.01	3.29	3.57
19	....	0.18	0.44	0.71	0.98	1.26	1.53	1.80	2.07	2.35	2.62	2.89	3.17	3.45
..	....	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.13
20	....	....	0.32	0.59	0.86	1.14	1.41	0.68	1.95	2.23	2.50	2.77	3.05	3.32
21	....	....	0.20	0.47	0.74	1.01	1.28	1.55	1.82	2.10	2.37	2.64	2.92	3.19
22	....	....	0.07 .27	0.34 .27	0.61 .27	0.88 .26	1.14 .27	1.41 .27	1.68 .28	1.96 .27	2.23 .27	2.50 .27	2.78 .27	3.05 .27
23	....	....	....	0.21	0.47	0.74	1.00	1.27	1.54	1.82	2.09	2.36	2.63	2.90
24	....	....	....	0.07	0.33	0.60	0.86	1.12	1.39	1.67	1.94	2.21	2.47	2.75
..	....	....	....	....	.14	.14	.14	.15	.15	.15	.15	.15	.15	.15
25	....	....	....	....	0.18	0.45	0.71	0.96	1.23	1.51	1.78	2.05	2.32	2.59
26	....	....	....	....	....	0.28	0.55	0.80	1.07	1.35	1.62	1.89	2.15	2.42
27	....	....	....	....	....	0.11 .26	0.38 .26	0.63 .27	0.90 .27	1.18 .27	1.45 .27	1.72 .26	1.98 .26	2.24 .27
28	....	....	....	....		....	0.21	0.46	0.73	1.00	1.27	1.54	1.80	2.07
29	....	....	....	....	....		0.03	0.28	0.55	0.82	1.09	1.36	1.62	1.89
..	....	....	....	....	....	....	.17	.18	.18	.18	.18	.18	.18	.18
30	....	....	....	....	....	....	....	0.10	0.38	0.64	0.91	1.07	1.43	1.70
31	....	....	....	....	....	....	....	....	0.20	0.46	0.72	0.98	1.24	1.51
32	....	....	....	....	....	....	....	....	0.01 .26	0.27 .26	0.53 .27	0.79 .26	1.05 .26	1.31 .26
33	....	....	....	....	....	....	....	....	....	0.07	0.33	0.59	0.85	1.11
34	....	....	....	....	....	....	....	....	....	....	0.12	0.38	0.64	0.90
..	....	....	....	....	....	....	....	....	....	.20	.21	.21	.21	.21

Upper horizontal line of figures is the apparent weight of volume equal to that of 25 Gm. of distilled water weighed in air at 15.56° C. (equals content of pycnometer which holds at 15.56° C. 25 Gm. of distilled water, apparent weight in air). Interpolation is facilitated by the figures indicating the average differences in percentage, respectively (vertically), corresponding with 1° C. in temperature, and (horizontally) for differences of 10 mg. in weight of the distillate.

The weight-volume relation is fixed at the standard temperature of 15.56° C. (60° F.) in accordance with customary usage.

In such a table a standard temperature for taking specific gravities may well be 20° C. The temperature corrections in such case would be additive below 20° C., subtractive above that temperature. It would be necessary to calculate independently these corrections, a somewhat laborious task, which I have once performed merely for my own satisfaction.

3. A convenient table for rapid determination of alcohol percentages in distillates assumes the use of a 25-Gm. pycnometer with perforated stopper, holding exactly 25 Gm., apparent weight in air, of distilled water at 15.56° C. The pycnometer is furnished of course with a counterpoise. From 50 cc of a preparation containing alcohol a distillate having the same volume is obtained with the usual precautions. Measurements of the sample and of the distillate must be made at 15.56° C. The distillate having been brought to the air temperature of the weighing room, the pycnometer is filled and rapidly but accurately weighed, with counterpoise in place. A portion of the proposed table, which should be self-explanatory, is given.

A table of this type need not extend further than to include percentages up to 25 at 34° C. The volume of the distillate is to be increased sufficiently to bring its strength within this limit. For a sample containing 20 to 40%, distil two volumes from one; between 40 and 70%, three volumes; above 70%, four volumes to one. The percentage taken out from the table is of course to be multiplied by 2, 3 or 4 as the case may be.

LABORATORY OF NELSON, BAKER & CO.,
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TANNIN IN WHISKY.

BY R. D. SCOTT.*

In connection with prohibition enforcement it is often of material importance as to whether a seizure of whisky was in defendant's possession, as frequently claimed, prior to 1919. Since counterfeit bottle labels and revenue stamps are not uncommon, an analysis of the liquor is usually necessary before a decision as to its age and composition may be made.

The customary determinations of esters, acidity, extract, etc., will generally yield sufficient information for this purpose, but in addition experience has shown that the amount of tannin present is a valuable index of the proportion of genuine whisky in the sample.

The difficulty, at present, of obtaining an extensive series of authentic whisky samples being obvious, the number of samples in which tannin was determined was not sufficient to permit of making any definite statement of the normal amount present in whisky of various ages and types. However, the 11 authentic samples of different brands of American Bottled in Bond Whisky examined were found to contain from 30.0 to 42.5 grams per 100 liters of tannin.

* State Department of Health, Columbus, Ohio.