Recently Richards and Shipley[23] obtained the value 1.973 for "heptane" compared with that of benzene, 2.286, at 20°. Apparently the authors have attempted to fix the value of this constant by the use of a product derived from petroleum having boiling points anywhere between 96.5° and 100°. They admit, "Probably the result represents an average value for several heptanes;" yet heptane of any desired degree of purity is available for the determination of physical constants and chemical characteristics. The value of the dielectric constant is now being redetermined on pure heptane in Professor Mathews' laboratory.

---

[1] R. E. Kremers, "A chemical study of Digger's pine oil and of the heptane therefrom." Unpublished thesis, Univ. of Wis., 1915.

[2] *Journ. Chem. Soc.*, 35 (1879), 296.

[3] *Amer. Chem. Journ.*, 20, 202.

[4] W. A. Gruse, unpublished results of the Forest Products Laboratory.

[5] Wm. Rabak, unpublished thesis, Univ. of Wis., 1915, note, p. 14.

[9] Smithsonian Physical Tables, 6th ed., 1914, p. 19.

[10] *Journ. Chem. Soc.*, 37 (1880), 141.

[11] *Ibid.*, 73 (1898), 905.

[12] *Ibid.*, 73 (1898), 917.

[13] Determination by W. A. Gruse; also K. E. Faville, Thesis, Univ. of Wis., 1916.

[14] Kaye and Laby, "Physical and Chemical Constants," p. 19.

[15] Wade and Merriman's Table, *Journ. Chem. Soc.*, 101 (1912), 2429.

[16] By Perkin, *Ibid.*, 45 (1884), 447.

[17] *Journ. f. prakt. Chemie*, 2d Ser., 64 (1901), 127.

[18] *Journ. Am. Chem. Soc.*, 23 (1901), 162.

[19] K. E. Faville, Thesis, Univ. of Wis., 1916.

[20] "Physiko-chemische Messungen," p. 260.

[21] *Proc. Royal Soc.*, 1894.

[22] *Phil. Trans. Roy. Soc.*, 185A (1894), 307.

[23] *Journ. Am. Chem. Soc.*, 41 (1919), 2007.

[24] *Journ. Phys. Chem.*, 22 (1918), 1; see also *Journ. Am. Chem. Soc.*, 36 (1914), 1787; and Richards and Mathews, *Ibid.*, 30 (1908), 1282.

PRACTICAL TESTING OF SPIRIT OF CAMPHOR.

BY A. B. LYONS.

The accurate determination of camphor in an alcoholic solution is not so simple a matter as it would at first appear. If the camphor is of the dextrogyrate variety, the polariscope will quickly solve the problem. But a polariscope does not usually form part of the equipment of a drug store. There is camphor, moreover, that does not affect the polarized ray.

The camphor is easily thrown out of solution by addition of strong saline solutions, and the precipitated camphor is readily taken up by such immiscible solvents as petroleum ether. The amount of camphor is shown by the increase in volume of the solvent. If the quantity of spirit taken for the test is 5 mils, this increase in volume will be, in the case of a standard U. S. P. spirit, 0.5 mil, a quantity not easily read off with an exactness of one part in forty. Every detail of the method as described by Penniman and Randall must be scrupulously adhered to if even this degree of exactness is to be secured, and the method involves the use of a Babcock milk testing outfit. In inexperienced hands, variations considerably greater than 0.25 percent (in a total of 10 percent) may be expected. If the experiment is made by aid of an ordinary cassia flask, without use of a centrifuge, still greater variations in results are inevitable. I must not be understood as condemning the test, which easily holds first place among the simple assay methods now practiced.

An empirical test of spirit of camphor which has found official recognition in some of the leading pharmacopoeias, notably the German, depends on the quantity of distilled water required to produce incipient precipitation in a given volume of the spirit. For 5 mils of the official (U. S. P.) spirit this quantity is something less than 5 mils. A difference of one-tenth in the quantity of camphor present makes a difference of about 0.3 mil in the volume of water required, so that a variation of 0.2 percent in the camphor content of the spirit is easily shown.

To secure such a degree of exactness, however, the test must be made under prescribed conditions which are to be rigidly adhered to. In the first place, the temperature at which the test is made must be carefully regulated. When water is added to the spirit, the temperature of the mixture rises several degrees. The test should be made at room temperature, which should be preferably near 25° C., at any rate between 20° and 25°.

Five mils of the spirit are measured into a 25-mil Erlenmeyer flask, and distilled water is added from a burette, drop by drop, with constant shaking until the precipitate redissolves somewhat slowly. The flask is then immersed in water kept at a constant temperature of 25° and allowed to remain so during 10 minutes. The addition of water is then continued, drop by drop, until a distinct turbidity is produced which persists a full minute, the flask remaining immersed in the water-bath. The volume of water added is then read off, and the corresponding quantity of camphor is taken out from a table constructed experimentally.

It is essential that the alcoholic strength of the spirit be known. In practice this is brought to a uniform basis by adding to the spirit of camphor to be tested an excess of dried potassium carbonate, which is allowed to act several hours, even though it shows no sign of incipient liquefaction. If the spirit has been made with alcohol of approximately 73 percent strength, as prescribed in the German Pharmacopoeia, it will require addition of the potassium carbonate in successive portions until it ceases to abstract water from the spirit, a considerable quantity of the salt remaining in solid form after several hours of contact with the spirit.

If the spirit proves to be practically free from water (other than the 5 percent, or thereabout, not abstracted by potassium carbonate), the 5 mils to be used for the test are measured out without making allowance for diminution of volume Otherwise the whole of the dehydrated spirit is to be drawn off, with due precautions against loss by evaporation, and the residual potassium carbonate is to be washed with several small portions of alcohol which has been dehydrated by potassium carbonate, these being added to the decanted spirit until this is brought to the original volume of the spirit taken. The result of a determination made in this manner should be trustworthy and sufficiently exact—provided, of course, that the spirit contains no foreign fluid such as acetone.

An alternative plan would be to apply the test to the spirit without preliminary dehydration and determine the percent of alcohol present by the usual method, after throwing out the camphor by the addition of a saline solution. Place in a

50-mil Erlenmeyer flask exactly 10 mils of the sample, add 40 mils of a 20 percent solution of sodium chloride (common salt) in distilled water, filter the solution through a pledget of absorbent cotton into a suitable still and wash the residual camphor with three successive portions (5 mils) of 20% salt solution. Distil slowly to obtain 25 mils [measured, as was the 10-mil sample, at 15.56° C. (60° F.)]. From the specific gravity of the distillate, deduce by reference to U. S. P. alcoholometric table the percent of alcohol present. Multiply this by 2.5 to find the percent of alcohol in the spirit. Multiply this again by 1.111 to find approximately the percent of alcohol in the spirit used to dissolve the camphor, on the assumption that the sample contains 10 percent of camphor. The possible error so introduced is practically negligible.

An approximate estimate of alcoholic strength may be made without distillation by mixing 10 mils of the sample with 41.5 mils of distilled water, shaking well, filtering and taking the specific gravity of the filtrate, which will not differ materially from that of a distillate 5 : 1. The corresponding alcoholic strength found by an alcoholometric table, multiplied by 5.556, will be very nearly the percentage strength of the spirit in which the camphor was dissolved.

The quantity of water required to cause turbidity in a spirit of camphor prepared from alcohol of a strength below 95 percent can be determined only by experiment. The following results were obtained in preliminary tests, which were, however, not made at a carefully regulated temperature, on spirits prepared from alcohol of the strengths specified. Five mils of the spirit were used in each test.

Percent camphor.	Alcohol "absolute." Water.	Alcohol 95%. Water.	Alcohol 90%. Water.	Alcohol 85%. Water.	Alcohol 80%. Water.	Alcohol 75%. Water.	Alcohol 70%. Water.
10	5.25 mils	4.70 mils	4.05 mils	3.45 mils	2.90 mils	2.38 mils	1.45 mils
8	5.25 mils	5.35 mils	4.50 mils	4.05 mils	3.45 mils	2.90 mils	1.80 mils
6	5.25 mils	6.25 mils	5.50 mils	4.85 mils	4.25 mils	3.50 mils	2.40 mils
4	5.25 mils	7.75 mils	6.80 mils	6.25 mils	5.45 mils	4.80 mils	3.50 mils

These approximate figures make clear the fact that we have to deal with two variables, whose effects are not only not mutually compensating but are positively synergistic. While it would be possible to construct an empirical table by which, the alcohol content of a sample of spirit being known, the quantity of camphor present could be deduced from the amount of distilled water required to cause incipient precipitation, yet even so, exact quantitative results would be difficult to reach, and the plan is therefore not to be recommended.

There remains an alternative method which seems to promise good results. Instead of adding water to the spirit of camphor until the solution is slightly supersaturated, we may add the spirit, suitably diluted, to a fixed quantity of water, until this is slightly supersaturated with camphor, as shown by a slight permanent turbidity. We should expect more uniform results from this procedure, first, because there would be little rise of temperature, owing to the very small quantity of alcohol present, and, second, because the proportion of camphor dissolved would vary only slightly, owing to the comparative uniformity in the alcoholic strength of the solvent.

It will be found most convenient to dilute the spirit with 80 percent alcohol so that it shall contain about 2 percent of camphor (not less). (Prepare the 80 percent alcohol by mixing 85.5 mils (at 15.56° C.) with water sufficient to make at the same temperature 100 mils.) Ten mils of water will require addition of about 1.65 mils of the dilute spirit to produce permanent turbidity, but the spirit must be added quite slowly, a few drops at a time towards the last, with constant shaking. If for distilled water we substitute a 5 percent solution of sodium chloride, the quantity of spirit required will be about 0.8 mil. In this case addition of the spirit must be even more gradual.

A better plan is to place in a small flask 7 mils of distilled water, and add to this slowly one mil of the diluted spirit. Shake the mixture, if turbid, during 1 minute. If it remain turbid, repeat the experiment, placing in the flask 8 mils of water and adding as before one mil of the diluted spirit. If the sample under examination contains 10 percent of camphor, a clear solution will result, at least after shaking. Make a third experiment, using 7.5 mils of water, when we shall expect that after shaking during 1 minute the solution will show no more than a faint opalescence. The three experiments may well be made simultaneously, and at the same time a fourth in which 8.5 mils of water are used. If the first three flasks show persistent turbidity, while the fourth clears up on shaking, we conclude that the original sample contains about 11 percent of camphor; if the fourth fails to clear up on shaking, the quantity of camphor is still greater. In case none of the flasks shows permanent turbidity, the quantity of camphor is below 10 percent.

All the foregoing experiments are to be made at a temperature near 20° C. (*i. e.*, between 18° and 23° C.). It is assumed that the original sample has been made with official alcohol (95%). If it has been made with a weaker spirit, a new dilution must be made which will contain approximately 81 percent of alcohol. Results of tests of this solution will be fairly exact.

Approximate determination of the percent of alcohol present in the original sample may be made by taking its specific gravity at any convenient temperature, subtracting the "correction" given below, and taking out from an alcohol table the corresponding alcohol percentage

Sp. gr.	Correction.
0.8910	—0.0110
0.8815	—0.0115
0.8720	—0.0120
0.8625	—0.0125
0.8530	—0.0130
0.8435	—0.0135
0.8340	—0.0140
0.8245	—0.0145
0.8150	—0.0150

Example.—The specific gravity of the sample at 20° C. (15.56°/15.56°) is 0.8750. Deduct the correction, 0.0120; the remainder, 0.8630, is approximately the specific gravity at 20° C. of alcohol of the same percentage as the sample, *i. e.* (by U. S. P. tables), 80.23 — 1.31 = 78.92%. To make a dilution of 81 percent strength, mix 2 mils of this spirit (= 15.78%) with 95% alcohol, equivalent to 81.00 — 15.78 = 65.22% absolute alcohol, or 68.65%, *i. e.*, 6.865 mils, of 95% alcohol, with water q. s. to make 10 mils at 20° C.

If nothing is known of the strength, either in camphor or in alcohol, of a sample, a cut-and-try procedure may be advantageously adopted. Make the normal test as just described. If turbidity is not produced, make a second dilution, 1 volume of the spirit to 3 of 80 percent alcohol. Failure to get a turbid solution will indicate great deficiency in camphor. According to the result of the test, make a new mixture, aiming to have present about 81 percent of alcohol. When a mixture is found to give turbidity when added to 7 mils of water, and a clear solution with 8 mils, it is clear that such mixture contains close to 2 per cent of camphor, from which the percent of camphor in the original spirit is easily deduced.

If in place of distilled water we employ in this form of the test a 5 percent solution of sodium chloride, precipitation of the camphor will be more prompt, but the precipitate which forms before the saturation point is reached is not readily redissolved. The difficulty, however, is overcome if the following routine procedure is adopted: Prepare a diluted solution as already described, containing presumably a 2 percent of camphor. Place in each of three small flasks, respectively, 11, 11.5 and 12 mils of distilled water. Add to each 1 mil of the diluted spirit, which should not cause permanent turbidity of the mixture in any of the flasks. Add now to each flask 2 mils of a clear saturated solution (about 26 percent) of sodium chloride. In case the diluted spirit contains 2 percent of camphor and about 81 percent of alcohol, the mixture in the first flask will be distinctly turbid after a minute's active shaking, that in the third will be clear, while that in the second will be cleared up almost completely by shaking.

If the sample examined contains more or less than the official percentage, the quantity can be arrived at by the cut-and-try method already described. Since the result of the test is materially influenced by variations in the quantity of alcohol present, it is perhaps best to dehydrate the spirit, if necessary, in the outset with anhydrous potassium carbonate, restoring the original volume by addition of 95 percent alcohol, then if the spirit prove to contain more than the standard quantity of camphor, reduce it by the cut-and-try method by adding 95 percent spirit before diluting, using, however, for the dilution 80 percent alcohol.

Obviously the precipitation tests are based on the assumption that alcohol of any given percentage strength will dissolve at any standard temperature always the same quantity of camphor. Thus it appears from the quantity of water required to cause incipient turbidity in spirits containing different quantities of camphor that 52 percent alcohol (volume) will dissolve more than 8 percent (weight-volume) of camphor, 50 percent spirit about 6.78 percent, 47 percent spirit less than 5 percent, 40 percent spirit only 2.14 percent. On the other hand, 10 percent alcohol dissolves only about 0.25 percent of camphor, 5 percent spirit about 0.125 percent.

It remains to consider the practicability of determining with exactness the percent of camphor in a hydro-alcoholic solution by its specific gravity. I take occasion here to retract the statement made by me in "Practical Standardization of Organic Drugs" (p. 299), that "the simplest and perhaps the best way of testing spirit of camphor is by determining its specific gravity." There are two reasons why this test is unsatisfactory; the first is that here again we have to do with two variables, each accentuating the influence of the other. The specific gravity is increased by any water which may be present as well as by the camphor we wish to determine. The second reason is that camphor in dissolving in alcohol increases its volume by more than its bulk in the solid state.

I accepted without verification the statement which I found in a book widely accepted as authoritative, *viz.*, that camphor dissolves in alcohol without change of volume; and on the strength of this statement I gave a table of the specific gravity (approximate) of solutions of camphor in official alcohol. The specific gravities given in this table are too high, and the error is the more serious from the fact that commercial alcohol in these days is apt to be above the official strength.

As a matter of fact, the specific gravity of spirit of camphor, U. S. P., is more near 0.832 than 0.8345, the 10 percent of camphor increasing the specific gravity of the alcohol by about 0.015 instead of 0.018, as would be the case if it dissolved without change of volume. Errors like this are hard to kill. This public statement should help to prevent perpetuation of the erroneous figure.

There is one way, certainly, in which we may gain information regarding the quantity of camphor in a sample of spirit, and that is by taking advantage of the fact that a saturated solution of camphor in diluted alcohol at any given temperature will have an invariable composition and therefore a constant specific gravity, while it is a simple matter to prepare from a sample of the spirit such a saturated solution by addition of water to incipient precipitation, at a fixed temperature. Here certainly is opportunity for constructing a useful empirical table.

A CRITICISM OF PART II IN THE U. S. P. IX.

BY HARRY L. THOMPSON.

In the pages devoted to Part II there is a great deal of unnecessary repetition, which increases the bulk of Part II. Pages 501 and 502 are necessary because they give an Index of the Contents of Part II.

On page 503 is the Table of Atomic Weights of the Elements. Why not add many of the important physical data often used in pharmaceutical assaying? On pages 504 to 519 are Elements and Pharmaceutical Chemicals. Why not enlarge the list to contain all chemicals known whether pharmacopoeial or not, or leave the list out entirely? The compends of physics and chemistry do a better job of it. Why not introduce logarithmic equivalents after the atomic and molecular weights or chemical equivalents? No chemist in the interest of speed and accuracy bothers with long mathematical calculations without using the short, quick processes of higher mathematics. Note the repetition of the elements and their atomic weights in heavy type.

On page 520, the Table of Multiples of Some Atomic and Molecular Weights might just as well be excluded entirely. Rarely four, five or more times of any element or radical is used in any chemical substance. I consider it a waste of printer's ink; and that it would be better to see it omitted entirely in the next U. S. P.

Why not adopt 20° C. as the standard? This conforms with the U. S. Government Bureau of Standards, and would bring about more uniformity. All accurately graduated volumetric apparatus is calibrated at 20° C. according to the U. S. Bureau of Standards. Why, then, does the U. S. P. persist in using 25° C. As a delegate to the pharmacopoeial convention I was opposed to the adoption of 25° C. Nearly every bit of graduated metric glassware used in manufacturing and