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ASSAY OF SPIRIT OF CAMPHOR.*

BY SAMUEL W. GOLDSTEIN AND WILLIAM F. REINDOLLAR.[1]

The assay of Spirit of Camphor official in the United States Pharmacopœia XI has been found very unsatisfactory in this Laboratory. The first supplement to the United States Pharmacopœia XI provides for the use of a 5-cc. sample, and it has been suggested that a further reduction of the amount of sample to 2 cc. is advisable (1). The official method involves treatment of the sample with solution of dinitrophenylhydrazine, refluxing on a water-bath for four hours, diluting and setting aside for twenty-four hours, collecting, drying and weighing the precipitate, and multiplying the resulting weight by a factor. We have found that the above reaction is not stoichiometric, the reagent used is exceedingly unstable, the procedure requires at least twenty-nine hours, and the results are unreliable.

The method recommended by Randall (2) is based upon precipitation of the camphor by an acidified aqueous calcium chloride solution in a Babcock bottle, dissolving the camphor in 1 cc. of benzin and, after centrifuging, noting the increase in volume, which when multiplied by a factor gives the per cent w/v of camphor in the spirit. This method, in the hands of one of us, gave unsatisfactory results, owing principally to the volatility of the benzin; hence a modified procedure has been developed.

EXPERIMENTAL.

Two samples of Spirit of Camphor were prepared by dissolving 9.7905 Gm. of natural camphor (A) and 9.8359 Gm. of synthetic camphor (B) in enough alcohol to make 100 cc.

Results obtained following the U. S. P. XI procedure are given in Table I.

TABLE I.—U. S. P. XI PROCEDURE.

Sample.	Amt. Used in Cc.	Gm. Camphor per 100 Cc.	Results Calcd. to 10% Spirit.
A	5	5.84	5.92
B	5	7.20	7.32
B	5	5.58	5.67
B	2	9.30	9.46
B	2	9.30	9.46
B	2	9.50	9.65
B	2	10.05	10.21
B	2	9.00	9.15
B	2	9.15	9.30
B	2	9.20	9.45

* Scientific Section, A. PH. A., New York meeting, 1937.

[1] From the laboratories of the Bureau of Chemistry of the State of Maryland Department of Health.

The use of 2-cc. samples gave much better results, but even with the smaller charge the figures show errors between +2.1 per cent and −8.5 per cent.

The factors involved in the following experiments were exactly the same as those brought out by the present authors in an earlier paper (3) on Spirit of Peppermint. The only factor which differs in the case of Spirit of Camphor is the volume relationship between the kerosene and the dissolved substance. In the case of oil of peppermint and kerosene the total volume observed is, for practical purposes, exactly additive; whereas in the case of camphor and kerosene the final volume is greater than the sum of the individual volumes. Therefore, the factor 4 which may be used in the assay of Spirit of Peppermint cannot be used for Spirit of Camphor. Since, however, a factor is required it was determined for Gm. of camphor per 100 cc. of spirit.

A weighed sample of camphor, 2.8375 Gm. was dissolved in 5 cc. of purified kerosene in a calibrated graduated 10-cc. cylinder. The final volume was 8.01 cc., or an increase of 3.01 cc. as a result of the added camphor. Five Babcock divisions are equivalent to 1 cc., hence 0.5 Gm. of camphor (the amount in a 5-cc. sample of Spirit) is equivalent to 2.67 Babcock divisions. The factor required to express the above result in Gm. per 100 cc. of Spirit is $\frac{10.00}{2.67}$ or 3.75.

The following method is recommended for the assay of Spirit of Camphor. *Apparatus.*—Calibrated 8 per cent Babcock bottles; a pipette calibrated to deliver 1 cc. of kerosene; an accurate 5-cc. pipette. *Reagents.*—A concentrated solution of calcium chloride, in 4 per cent hydrochloric acid, having a specific gravity of 1.36 (approximately 818 Gm. $CaCl_2$ to each 1000 cc. of 4 per cent HCl solution); purified kerosene U. S. P. XI. *Procedure.*—Transfer exactly 5 cc. of the Spirit to a calibrated Babcock bottle, graduated to 8 per cent, add acidified calcium chloride solution (specific gravity 1.36) until the bottle is filled to the shoulder, stopper the bottle with a cork previously wetted with calcium chloride solution and mix the contents vigorously. Add exactly 1 cc. of purified kerosene from a pipette calibrated to deliver that amount, stopper and agitate the mixture for about one minute. Add acidified calcium chloride solution to bring the liquid up to the highest mark in the neck of the bottle, stopper and centrifuge for five minutes at about 1500 revolutions per minute. Observe the number of divisions occupied by the oily layer, reading the lower curvature of the menisci, subtract five divisions for the kerosene added and multiply the remaining number by 3.75. The product is the number of grams of camphor in 100 cc. of the Spirit.

The following results were obtained using 5-cc. samples of Spirits A and B employing the procedure described. Three different lots of purified kerosenes (1, 2 and 3) and one commercial kerosene (4) were used.

TABLE II.—RESULTS BY RECOMMENDED ASSAY.

Sample.	Kerosene.	Gm./100 Cc.	Results Calcd. to 10% Spirit.
A	1	9.75	9.96
A	1	9.78	9.99
A	1	9.75	9.96
B	1	9.94	10.11
B	1	9.90	10.07
B	1	9.83	9.99
A	2	9.75	9.96
A	2	9.71	9.92
A	2	9.78	9.99
A	2	9.67	9.88
A	2	9.72	9.92
B	2	9.75	9.92
B	2	9.67	9.84

B	2	9.75	9.92
B	3	9.90	10.07
B	3	9.94	10.11
B	3	9.94	10.11
B	4	9.83	9.99
B	4	9.90	10.07
B	4	9.78	9.94

These figures show that the results obtained by the recommended assay lie within the range −1.6 per cent and +1.1 per cent, and that this accuracy is maintained with kerosenes obtained from different sources.

SUMMARY.

The present assay given in the United States Pharmacopœia XI for Spirit of Camphor is both inaccurate and time consuming.

A modified assay based on the procedure of Randall has been devised. This assay yields results that lie within ±2 per cent of the theoretical value and which when obtained in duplicate are in good agreement.

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THE HOBBY OF A DRUGGIST.

Joseph V. Tallman, a pioneer of Pendleton, Oregon, and collector of arrowheads for forty-eight years or more, has a collection of 20,000 arrowheads. He has donated eight beautiful specimens, through Secretary E. F. Kelly, for the Museum of the AMERICAN PHARMACEUTICAL ASSOCIATION. The collection is said to be one of the largest, if not the largest, in this country and there are rich shades of stone, cornelians, agates, etc. Many of these arrowheads come from Yellowstone Park. A long description by L. C. Dixon is published in the *Portland Journal* of January 3, 1937.

Mr. Tallman has written the following beautiful tribute to arrowheads:

"Sharp and true, the handiwork of the ancient artisans—buffeted by endless time and harassed by the elements—lie before us glistening in barbaric splendor, relic of a powerful empire—a mighty race.

"Together with the bones of the master craftsmen who wrought these mementoes of stone is buried the secret of his craft, an art lost to even his own descendants—a mystery unsolved by modern science.

"Challenging the human imagination, we observe the arrowhead—delicate, yet strong as steel—beautiful, yet formidable. We cannot, in due appreciation, contemplate these ancient works without paying tribute to the hand and heart which wrought them."
