APPARATUS FOR THE DETERMINATION OF VOLATILE OIL.*

J. F. CLEVENGER.[1]

The principle of steam distillation is the basis of the methods commonly used in obtaining the volatile oil from plant products. This is carried out either by passing steam through a suitable vessel containing the plant material and condensing the steam or by boiling the material with water in a suitable vessel, distilling and collecting the distillate. The volatile oil is carried over with the steam and condenses with it. Being only slightly soluble in water, it subsequently separates from the aqueous portion of the distillate in layers. Boiling methods have been applied by Duvel, (4) Thörner, (5) and Bidwell and Sterling, (6) in the determination of moisture in various materials.

A method for the determination of "volatile ether-soluble extractive" in drug products is described in the United States Pharmacopœia (1), the National Formulary (2), and the Methods of Analysis of the Association of Official Agricultural Chemists (3). The "volatile ether-soluble extractive" is commonly considered the equivalent of the volatile oil. In this method the drug is extracted with anhydrous ether, the solution is evaporated, and the residue is dried at room temperature and weighed. The residue is then heated to 110° C. until the weight becomes constant and weighed. The difference in weight represents the "volatile ether-soluble extractive." The method is more or less empirical and is subject to several criticisms. (*a*) The loss in weight does not always represent the volatile oil that usually is the desirable or active constituent, but it may include volatile materials resulting from the decomposition of unknown substances; (*b*) the prolonged heating of the residue at 110° C., which is necessary to remove the volatile matter completely from the ether-soluble extractive, increases the possibility of decomposition with subsequent erroneous results;[2] (*c*) the volatile constituents of the product in question are not available for subsequent examination, which is desirable in many instances.

An apparatus for the determination of volatile oil has been devised which provides for a direct reading of the quantity of volatile oil obtained and makes it available for subsequent examination, such as for the determination of the specific gravity, optical rotation, index of refraction, and possibly minimum boiling point. It permits in most cases a direct quantitative determination of the volatile oil of most plant products without preliminary extraction with ether or other solvents.

APPARATUS.

The apparatus (Figs. 1 and 2) consists essentially of three parts: (*a*) A round-bottomed flask, in which are placed the material containing the volatile oil and a given quantity of water; (*b*) a separator, in which the oil is automatically separated from the distillate in a graduated tube, thereby permitting a direct reading of the quantity of the oil; and (*c*) a convenient condenser. The size of the flask

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[2] The boiling temperatures of most of the fractions of the volatile oils are much above 110° C.

may vary from 100 cc. to approximately 2 liters, depending upon the nature of the material and the percentage of volatile oil present. The quantity of the material taken should be such as to obtain, if possible, from 1 to 3 cc. of volatile oil. The flask should not be heated by a direct flame on account of the danger of charring the material containing the volatile oil, thereby giving erroneous results. An oil-bath heated electrically or by a suitable gas flame has been found satisfactory for this purpose.

APPARATUS FOR THE DETERMINATION OF VOLATILE OIL.

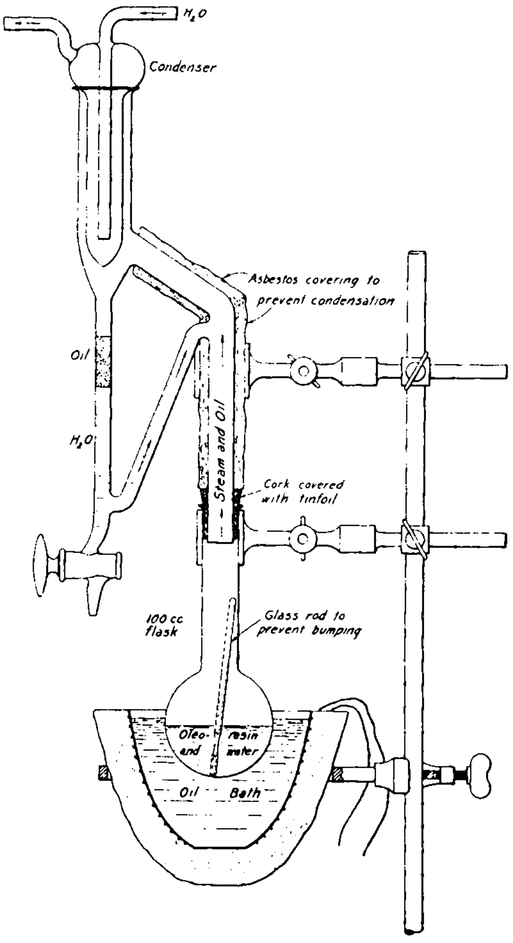

Fig. 1.

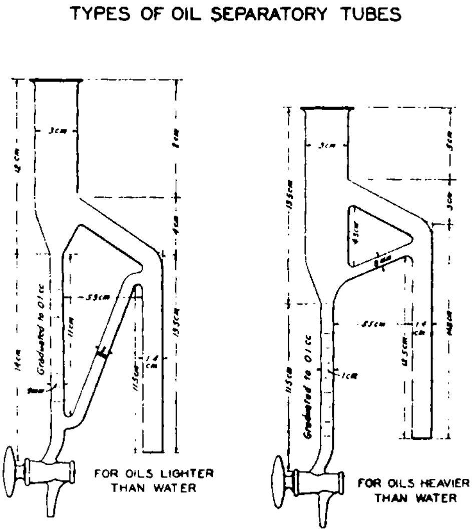
TYPES OF OIL SEPARATORY TUBES

Fig. 2.

METHODS FOR THE DETERMINATION OF VOLATILE OIL.

(*a*) *For Plant Products Containing Little or No Starch or Mucilage.*—If the material consists of roots or thick products, place a suitable quantity of the coarsely comminuted material in a flask of suitable size and add water until the flask is half full. Leaf-like material may be placed directly in the flask without first being comminuted or ground. Set up the apparatus as indicated in Fig. 1. Boil the contents for approximately two hours, or until all of the volatile oil has been driven off. The steam carrying the volatile oil condenses and falls into the graduated tube of the separator. The water is separated from the oil by gravity and automatically flows back into the distillation flask. It has been found that a small amount of paraffin added to the flask prevents excessive foaming which occurs especially in case of powdered products. (Care must be taken that the distillation be conducted at a rate sufficiently slow to prevent the escape of vapors around the condenser, thus insuring against loss of volatile oil.)

(*b*) *For Crude Material Containing Considerable Starch or Mucilage.*—Exhaust a weighed amount of material with a suitable solvent (alcohol or ether) in an automatic extractor. Transfer the extract to a suitable flask and evaporate the solvent, using a current of air, on a slowly simmering steam-bath until the odor of the solvent is no longer detected. Proceed as outlined in (*a*).

(*c*) *For Fluidextracts Containing Volatile Oil.*—Transfer a given quantity of extract to a suitable flask and evaporate as outlined in (*b*) and, after evaporation, proceed as outlined in (*a*).

A number of volatile oils having a specific gravity slightly greater than that of water, for example clove oil, will slowly settle in water. Such oils cannot be determined directly by the use of the separator for oils lighter than water (Fig. 2). Attempts have been made to render the same apparatus serviceable for oils heavier than water by adding a given quantity of a volatile solvent lighter than water and immiscible with it directly to the separatory tube before beginning the determination and making appropriate corrections for the added solvent. The volatile solvent which has been added to the separator before beginning the experiment must be removed from the volatile oil before the constants can be determined directly on the oil. The results obtained from experiments by this procedure were not considered satisfactory by the writer.

In order to overcome the difficulty encountered and to obtain a volatile oil unmodified by other solvents, an apparatus has been devised for oils heavier than water (Fig. 2). The graduated tube of the separator extends below the return flow tube, thus facilitating the separation and permitting a direct reading of the quantity of the volatile oil. Some difficulty is frequently experienced in obtaining a complete and satisfactory separation of the volatile oil, owing primarily to the surface tension of the two liquids. This may be overcome for the most part by occasionally agitating the liquids in the separator with a suitable wire. Any error due to the necessary use of this wire is believed to be negligible and within the limits of experimental error.

DETERMINATION OF CONSTANTS.

The volatile oil obtained may be finally transferred to a test-tube (10 x 75 mm.) and allowed to stand until perfectly clear (over night is usually sufficient) or it may be dried at once with a suitable dehydrating agent, such as anhydrous sodium sulphate, and filtered. The index of refraction may be determined by the usual method. In spite of the small amounts of volatile oil usually obtained (0.75 to 1.5 cc.), the determination of the optical rotation may be made in a 50-mm. micropolarizing tube and the specific gravity may be determined in a Sprengel specific gravity bottle of approximately 1-cc. capacity. The minimum boiling point may be determined by the method described by Smith and Menzies (7). In this method the volatile oil is introduced into a small glass bulb, approximately 5 mm. in diameter, from which a bent capillary tube, approximately 6 cm. long, extends. The volatile oil is introduced into the bulb by immersing the end of the capillary tube in the oil in question and applying a small flame to the bulb for a short time. This causes the air in the bulb to expand and escape from the end of the capillary tube. Upon cooling the bulb, the volatile oil enters. The bulb thus approximately half filled with oil is attached to a thermometer and immersed in a molten paraffin-bath. The paraffin-bath is gently heated until bubbles of the volatile oil freely flow from the end of the capillary tube. The heat is then removed and the bath is allowed to cool until the level of the paraffin in the capillary tube becomes level with the volatile oil in the bulb. This temperature is noted and regarded as the minimum boiling point for the volatile oil.

COMPARISON OF THE UNITED STATES PHARMACOPŒIA METHOD WITH THE PROPOSED METHOD.

In order to compare the United States Pharmacopœia method for the determination of the volatile ether-soluble extractive (usually considered the equivalent of the volatile oil) with the proposed method for the determination of volatile oils, experiments were carried out with several different materials. The results obtained are given in Table I.

TABLE I.—VOLATILE ETHER-SOLUBLE EXTRACTIVE BY U. S. P. METHOD AND THE VOLATILE OIL BY NEW METHOD.

Substance.	Volatile ether ext. by U. S. P. method. Per cent by wt.	Volatile oil by new method. Per cent by wt.
[1]Clove (buds)	18.1	16.3
[1]Oregano, Monterey (leaves)	3.1	2.8
[1]Ginger (oleoresin)	25.5	23.9
[2]Ginger, Jamaica (rhizomes)	1.2	1.1
[2]Ginger, Jamaica (rhizomes)	1.4	1.4
[2]Ginger, African (rhizomes)	2.9	2.2
[2]Ginger, African (rhizomes)	3.0	2.4
[3]Ginger, Cochin (fluidextract)	1.7	1.5
[3]Ginger, African (fluidextract)	3.0	2.4

[1] Volatile oil determined by method (a).
[2] Volatile oil determined by method (b).
[3] Volatile oil determined by method (c).

The yields of volatile matter obtained by the official method were in general somewhat higher than those obtained by the new method. It is believed that the results by the new method more nearly represent the correct percentage of the volatile oil available in the product. There is a possibility that these results may be a little low on account of the slight solubility of the oil in water.

PHYSICAL CONSTANTS OF VOLATILE OILS GIVEN IN THE U. S. PHARMACOPŒIA AND PHYSICAL CONSTANTS OF SIMILAR OILS OBTAINED BY THE NEW METHODS.

As the boiling method is not the method usually employed for obtaining volatile oils, the physical constants of these oils may differ from the physical constants of similar oils recognized as standard in the U. S. Pharmacopœia. Experiments were conducted with several materials in order to compare the physical constants given in the U. S. Pharmacopœia for a number of volatile oils with the constants determined on similar oils freshly obtained with the apparatus described above. The results obtained are given in Table II.

TABLE II.—PHYSICAL CONSTANTS OF VOLATILE OILS GIVEN IN THE U. S. P. AND PHYSICAL CONSTANTS OF SIMILAR OILS OBTAINED BY THE NEW METHOD.

	Physical constants (U. S. P.).			Physical constants (determined).		
Material.	Specific gravity.	Optical rotation.	Refractive index.	Spec. grav. $\frac{25^\circ \text{ C.}}{25^\circ \text{ C.}}$	Opt. rot.*	Ref. ind.*
Nutmeg (seed)	0.859–0.924	+12°–+30°	1.4780–1.4895	0.874	+30°	1.480
Caraway (fruits)	0.900–0.910	+70°–+80°	1.4840–1.4880	0.904	+73°	1.485
Eucalyptus (leaves)	0.905–0.925	± 10	1.4600–1.4690	0.912	+6°	1.464
Fennel (fruits)	0.953–0.973	+12°–+24°	1.5280–1.5380	0.963	+18	1.529
Clove (buds)	1.038–1.060	Does not exceed −1°–10′	1.5300–1.5350	1.053	−0.6°	1.533
Orange (peel)	0.842–0.846	+94°–+99°	1.4723–1.4737	0.844	+95°	1.471**

* Room temperature, approximately 24° C.

** Within U. S. P. variation recognized as occurring in distilled oil.

These results show that the constants obtained on these volatile oils are within the limits given in the U. S. Pharmacopœia for similar volatile oils.

ACKNOWLEDGMENT.

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THE BOYCOTT OF SPANISH ERGOT.

BY H. H. RUSBY.

In the *Second Annual Report of the Pharmacological Laboratories of the Pharmaceutical Society of Great Britain*, page 10, occurs the following statement regarding their assays of extracts of ergot, "prepared by the method of the United States Pharmacopœia."

"An important practical conclusion was reached that, whereas most samples of Spanish or Portuguese ergot contain a fair proportion of the specific alkaloid, samples of Russian and Polish ergot are uniformly deficient."