wheat produced upon that soil and its bread-making value. Credit is due Mr. L. O. Bernhagen for assistance rendered in the analytical work.

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## THE PRECIPITATION METHOD FOR THE ESTIMATION OF OILS IN FLAVORING EXTRACTS AND PHARMACEUTICAL PREPARATIONS.

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The polariscopic method for the estimation of essential oils in commercial extracts is of but limited application, the oils of lemon and orange being the only ones that can be accurately determined in this manner. For the estimation of such oils as peppermint, clove, wintergreen, and many others, two procedures are open: (*a*) the application of methods for the estimation of the most important constituents of these oils, such as menthol, eugenol, or methyl salicylate, and (*b*) the method by precipitation as suggested by Mitchell[1] and now adopted with modifications as official by the A. O. A. C.

In most instances the first procedure, as applied to extracts, is obviously capable of affording but little better than a general idea as regards strength or quality, while results by the second process involve the application of a large and variable correction. Thus, in the case of lemon oil Mitchell[2] found that results near to the truth were obtainable only in the presence of a relatively large proportion of oil—a 6 per cent. extract, for instance, showing 4.80 per cent. recoverable, while a 2.50 per cent. extract afforded by this procedure less than one-half of the oil actually present.

With a less proportion of oil the error becomes still greater, and when we consider in addition that this error apparently varies not only with the quantity of oil, but with the kind, it is evident that for the examination of many of the miscellaneous extracts and essences now on the market—many of them containing as they do but one or two per cent. of oil—the method as at present carried out is of but very limited value. This fact will be appreciated by any who has attempted to examine some of the cheaper grades of peppermint essence.

By the modified method here proposed the writer has obtained most excellent results. The procedure has the advantage that no correction whatever for oil retained in solution is necessary, and moreover, with the single exception of almond extract, it affords equally accurate results in the case of alcoholic solutions of almost any one of the large

[1] THIS JOURNAL, 21, 1132 (1899).

[2] *Loc. cit.*

class of essential oils. The advantages of simplicity and rapidity of execution may also be claimed, it being possible to carry through a series of several determinations in ten minutes.

*Procedure.*—To 10 cc. of the extract, pipetted into an ordinary Babcock milk bottle, are added in the following order, 25 cc. of cold water, 1 cc. hydrochloric acid of 1.2 specific gravity and 0.5 cc. chloroform. The mouth of the bottle is then closed by the thumb and vigorously shaken for not less than one minute. By this means all of the oil is dissolved by the chloroform, while the latter, in saturating the water, apparently serves to displace any appreciable trace of oil otherwise retainable by the alcohol-water mixture. The bottle is now whirled in the centrifuge for one and one-half to two minutes and the resulting clear supernatant liquid is removed to within 3 or 4 cc. by the insertion of a glass tube of small bore connected with an aspirator. To the residue 1 cc. of ether is added and the contents of the bottle well agitated. Holding the latter at a slight angle it is plunged to the neck in a boiling waterbath, and, giving a gentle rotary motion, is maintained at this temperature for exactly one minute. This step is best carried out by removing one of the small rings from a water- or steambath and holding the bottle in the live steam. The ether serves the purpose of steadily and rapidly sweeping out every trace of chloroform—a result that would be otherwise attainable only with considerable difficulty and loss of oil. The latter by this procedure has been found to be inappreciable. Finally the bottle is cooled and filled with water at room temperature so as to bring the oil into the graduated stem of the bottle, and after centrifuging for one-half minute the reading is taken to the highest point of the meniscus; the reading multiplied by 2 gives the per cent. of oil.

If it be desired, a special milk bottle with stem of smaller bore, or a skim milk bottle provided with a straight introductory tube, may be employed. It has been found, however, that with the ordinary Babcock bottle there is no difficulty in securing check results to one-tenth per cent.

*Modification for the Heavier Oils.*—In the case of oil of wintergreen it was found to be impossible to secure a compact readable column of the oil by means of salt solution. This procedure also proved to be not satisfactorily applicable for almond extract. For the estimation of these oils use was at first made of a specially devised form of the so-called Hortvet tube, in which the bore of the stem is so reduced that the graduated portion contains 2 cc. instead of 5 cc., the subdivisions having therefore the same values as in the case of the Babcock bottle. Using this form of tube, in the case of almond extract the most satisfactory results were obtained by employing double the quantities of chloroform and ether specified. Working in this manner it was found pos-

sible to recover practically 100 per cent. of the oil from a 1 per cent. extract, but with stronger extracts 80 to 90 per cent. only proved recoverable.

In most cases, however, the use of the ordinary Babcock bottle with a suitable heavy liquid will be found to be preferable. For this purpose, except with the oils of cinnamon and cassia, the use of salt solution is out of the question. Trials were made of the applicability of diluted sulphuric acid, diluted glycerol and of sugar solution. The two latter were found to serve well for the lighter oils, but with wintergreen a gravity of not less than 1.2 is requisite and this involves a too high degree of viscosity. On the other hand, diluted sulphuric acid (1–2) was found to answer admirably. While it might be objected that the acid would tend to decompose some of the oils—notably those of clove and cinnamon—and thus afford low results, yet it was found that if agitation is avoided and the temperature of the acid mixture does not exceed 25°, no readable error is involved.

As a result of a large number of trials of this method, it was found that (except in the case of almond extract) not only could practically the theoretical amount of oil be recovered from 1, 3, 5 and 10 per cent. strengths of alcoholic solutions, but that also in the case of lemon and orange extracts results thus obtained very generally agreed to $^1/_{10}$ per cent. with those obtained polarimetrically, if the factor designated by Mitchell and Leach (3.4) was used.

It is well recognized that results by the polarimetric method of examining lemon and orange extracts are not to be implicitly relied upon as indicating in all cases the true proportion of oil present. The use of small quantities of cane sugar in the preparation of these extracts is apparently somewhat more common than has been generally supposed. Without doubt, so-called "washed" or "distilled" oil is being used to some extent in the making of extracts, and furthermore the addition of high polarizing orange turpenes for the purpose of increasing the rotatory power is a perfectly practicable form of adulteration.

The precipitation method, therefore—aside from merely providing material for a refractometric examination—affords a direct and valuable check on the polarimetric results. For instance, if the results by precipitation are materially lower than those obtained polarimetrically, there is ground for the suspicion that other than a "straight" oil has been used; if on the contrary, they are higher and the oil is present in moderately large quantity, such would be proof-positive either of adulteration with a foreign oil, or else of the use of an oil that had undergone marked deterioration, while if the polarimetric reading was but slight, or zero, any precipitated oil might be assumed to represent citral or one of the other lemon oil substitutes.

The results presented below were obtained on solutions of definite strength prepared with 90 per cent. alcohol. Results obtained with commercial extracts are also submitted.

| Extract. | Strength. Per cent. | Oil recovered. Per cent. |
|---|---|---|
| Lemon | 5.0 | 5.0 |
| " | 1.0 | 1.0 |
| Peppermint | 1.0 | 1.0 |
| " | 3.0 | 3.0 |
| " | 5.0 | 5.0 |
| Clove | 1.0 | 1.0 |
| " | 10.0 | 10.2 |
| Cassia | 1.0 | 1.0 |
| Wintergreen | 1.0 | 1.1 |
| " | 2.0 | 2.0 |
| " | 5.0 | 5.1 |
| Bitter almonds | 1.0 | 1.0 |
| " " | 3.0 | 2.5 |
| Citral (pure, optically inactive) | 3.0 | 3.0 |
| " | 0.5 | 0.5 |

COMMERCIAL EXTRACTS.

| Variety. | Oil by precipitation. | Oil by polarizatior |
|---|---|---|
| Lemon | 4.8 | 4.80 |
| " | 4.6 | 4.63 |
| " | 4.0 | 4.10 |
| " | 5.0 | 5.00 |
| " | 4.40 | 4.50 |
| " | 4.8 | 4.70 |
| Peppermint | 3.8 | .... |
| " | 5.6 | .... |
| " | 12.4 | .... |
| Cinnamon | 3.0 | .... |
| Checkerberry | 4.0 | .... |
| " | 12.5 | .... |
| Rose | 0.6 | .... |

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## A COMPARISON OF TWO TESTS OF RED LEAD.

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The tests generally used for the determination of the amount of free litharge, PbO, in red lead are the lead acetate test and the lead peroxide test. The latter is made in two ways, by the gravimetric and volumetric methods.

We will first consider the lead acetate test. This test depends upon the solubility of lead oxide in a solution of lead acetate. A weighed quantity of red lead is taken, and to it is added, in a beaker, a like quantity of lead acetate crystals dissolved in about 150 cc. of hot water. After