obtained from the wood by steam distillation and extraction seem to be of simpler nature than those obtained by destructive distillation. The terpenes obtained by destructive distillation have a wide variation of boiling-points, ranging from 149° to 208°. Even the properties of the compounds of the same boiling-points seemed to have been changed during the process of destructive distillation. The following is a comparison of the two terpenes.

	Norway terpene.		Fir terpene.	
	Steam Dist.	Destructive Dist.	Steam Dist.	Destructive Dist.
Specific gravity at 20°	0 8636	0.8666	0.8621	0.8662
Boiling-point....................	153–154°	158-160°	153.5–154°	157–160°
Index of refraction at 20°...	1.47127	1.4716	1.47299	1.47246
Optical activity............ $(\alpha)_D$	$= +$ 17.39	—7.56°	—47.2	—29.4°

These terpenes are now being studied.

UNIVERSITY OF MINNESOTA.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A METHOD FOR THE DETERMINATION OF CITRAL IN LEMON OILS AND EXTRACTS.

BY EDWARD MACKAY CHACE.

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THE detection of the adulteration of lemon oils and extracts is a problem that has long been disturbing those chemists who are engaged in food and drug analyses. Methods for the detection of the crude forms of adulterations have been devised and are in the main satisfactory. Unfortunately, as the lemon oil industry has developed, certain by-products have come into existence and in the effort to cheapen the cost, these products have been used to produce a grade of impure oil.

With the introduction of these oils the detection of factitious oils and extracts has become a more difficult matter. When the adulteration consisted in the addition of foreign substances such as turpentine or of the substitution of other oils for lemon oil, determinations of the physical constants of the sample and of the first fractions of its distillate were generally sufficient. Now, however, when it consists in varying the proportion of the constituents themselves, physical constants alone are not sufficient.

Lemon oil is composed of 90 per cent. *d*-limonene, 4 to 6 per cent. citral, the remainder being other aldehydes and oxygenated bodies.

It will be readily seen that the physical constants of citral would have to be greatly different from those of lemon oil in order that its partial removal could be detected. As a matter of fact, in their optical activity the two are markedly different, citral being inactive while lemon oil has a rotation of +60° at 20°. Methods, however, depending upon the polarization of the oil before and after the removal of the citral have not been brought to a satisfactory state of perfection, probably on account of the difficulty of freeing the oil from citral. The citral sulphite compound has a tendency to split up in the presence of the alkali formed in the reaction.

As for chemical methods no satisfactory method has yet been devised for the determination of any of the constituents. Many attempts have been made to perfect methods for estimating citral but all have serious faults affecting their accuracy. Little or no work has been done toward amplification or improvement of the methods on lemon extracts since the work of Mitchell[1] although attention has been called to the need of a method for citral.

The method which is described in the following pages was an attempt toward the determination of citral in lemon oil, but the error made in comparing the solution and standard becomes so great when multiplied to correct for the dilution that it somewhat impairs the usefulness of the method for oils. On extracts the conditions are different and nothing is wanting in the way of accuracy. Medicus in 1895[2] published an article on the determination of aldehydes in distilled liquors, this method depending upon the recoloration of a solution of fuchsin in sulphurous acid. Tolman testing this method while working on whiskies in this bureau discovered that it was essential that the color should be developed at a low temperature.

In modifying the method to admit of its use on lemon oils this fact was verified. It was at first thought that the reagent would have to be made up in alcohol on account of the insolubility of lemon oil. No satisfactory way of preparing an alcoholic reagent was discovered, however. The reagent finally used is similar to that of Medicus but containing a much larger quantity of sulphurous acid. The method as modified is as follows: Reagents, aldehyde, free alcohol 95 per cent. by volume. The alcohol was

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[1] This Journal, 21, 1132 (1899).

[2] Forch. Ber. Lebensm. 1895, 299.

allowed to stand over alkali for several days, distilled, and the distillate boiled for several hours under a reflux condenser with 25 grams per liter of metaphenylenediamine hydrochloride and finally distilled. After this treatment it contains only minute traces of aldehydes.[1] Fuchsin solution: Dissolve 0.5 gram of fuchsin in 100 cc. of water and add a solution of sulphurous acid containing 16 grams of sulphur dioxide. Allow to stand until decolorized and make up to one liter. This solution deteriorates on standing and should therefore be made up every two or three days.

Standard citral solution: Dissolve 1 gram of chemically pure citral and make up to one liter with 50 per cent. by volume alcohol. The citral used was obtained from Schimmel & Company, guaranteed chemically pure. Its physical constants corresponded to those of pure citral. Two samples purchased at different times were identical. Manipulation: While in use all reagents were kept in a water-bath cooled to 15°, and all comparison tubes were left in the bath for ten minutes before the comparison was made. A bath such as was described by Given[2] was used.

For lemon oil 2 grams of the sample were weighed and transferred to a 100 cc. flask with alcohol, cooled to 15°, and made up to the mark. For lemon extracts a larger amount was necessary, usually 20 to 30 grams. Aliquot portions of this solution, about 4 cc. measured at the temperature of the bath, were placed in comparison tubes, 20 cc. of the aldehyde-free alcohol added, then 20 cc. of the fuchsin solution and finally made up to 50 cc. with the alcohol. Comparison tubes were prepared in the same way taking 4 cc. of the standard solution. All the tubes, after mixing, were allowed to remain in the bath for ten minutes, when they were removed and the comparisons made either by direct matching or by the use of a colorimeter. When a colorimeter was used which read percentages of color as compared with the standard, a correction had to be made, owing to the fact that the color developed was not proportional to the amount present. This correction varies somewhat with the conditions under which the samples are worked. In order to avoid it, the first sample weighed out was used as a trial estimation, a second sample being used for the correct determination. The amount weighed for this sample was sufficient to give the solution approximately the same strength

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[1] For another method see Dunlap: This Journal, 28, 395.

[2] This Journal, 12, 1519 (1905).

as the standard, *i. e.*, 1 mg. citral per cubic centimeter, using the trial determination as a basis for the calculation. The readings on the second sample were usually so close as not to require a correction. Two or three comparisons were made on this solution and the average taken. The color developed by the lemon oil is not exactly the same shade as that developed by citral. This fact may be due to the presence of citronellal, as the color is not altered by the addition of limonene to the standard.

To test the accuracy of the method the following determinations were made. A sample of limonene containing some citral was used as a base and several samples made by adding known quantities of citral. The method was also tried on solutions of citral and on lemon oil. Four determinations were made on the limonene as follows: A, 2.27 per cent.; B, 2.31 per cent.; C, 2.41 per cent.; D, 2.36 per cent.; average, 2.34 per cent. citral. Sample A was composed of 97 grams of the limonene and 3 grams of citral having in all 5.28 grams of citral per 100 grams. Two determinations were made. both giving 5.29 per cent. citral. Sample B contained 5.46 grams of citral in 94.54 grams of citral-free limonene making it contain 5.46 per cent. Four determinations resulted as follows: 5.74, 5.82, 4.90, 4.87 (the poor results here can only be accounted for by the fact that the fuchsin sulphurous acid solution was too old for accurate use). Sample C contained 20.85 grams of a terpene containing 0.25 per cent. of citral or 0.0521 gram, to which were added 1.0075 gram citral, making the oil contain 4.85 per cent. Five determinations gave a minimum of 4.90 per cent., maximum of 5.21 per cent., average 5.05 per cent. Sample D, 97.83 grams limonene containing 0.225 gram citral and 4.63 grams of added citral, the whole containing 7.71 per cent. citral. Three determinations gave 7.61, 7.57 and 7.62 respectively. Sample E was made up of terpenes containing 0.1150 gram of citral and 0.0770 gram of citral, having 3.78 per cent. of the latter. Three determinations resulted as follows: 3.61, 3.84, 3.47, averaging 3.62.

Lemon extracts were made up as follows:

	Gram citral per 100 cc.	Found.
A	0.1065	0.1092
B	0.1060	0.1110
C	0.0968	0.1071
D	0.30	0.282
E	0.12	0.129
F	0.25	0.23

A great many other determinations were made on known samples and as stated above. Satisfactory results were always obtained in the case of lemon extracts, while the results on oils were not so good. The maximum error on oils was usually less than 0.5 per cent. while the average was in the majority of cases within 0.2 per cent.

The essential point to be observed in using the method is to keep the temperature of the reagents and the comparison tubes down to at least 15°, and give the standard and sample exactly the same treatment throughout.

[Contribution from the Food Division of the Bureau of Chemistry, U. S. Dept. of Agriculture. Sent by H. W. Wiley.]

ESTIMATION OF SUGARS BY MEANS OF THE REFRACTOMETER.

By L. M. Tolman and W. B. Smith.

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In a great many materials such as syrups, molasses, and similar substances which are for all practical purposes solutions of sugar and water, the estimation of sugar has long been made by determining the specific gravity with a hydrometer or pycnometer and from the specific gravity calculating the percentage of sugars from a table or by some formula.

This figure, if the solution is a mixture of a pure sugar and water, can be very accurately determined but in syrups and molasses which are impure mixtures, it represents more nearly a determination of the total substances in solution or the total solids. The determination of total solids is a very important one in a great many food products as a check on the other determination and it is for work of this kind that the specific gravity is of value. The accuracy of the specific gravity method in a mixed sugar solution such as we ordinarily have to deal with, depends on the fact that the different sugars have very nearly the same specific gravity for the same concentration. The specific gravity method is also especially useful with substances which are decomposed by drying at a high temperature, such as solutions containing large amounts of invert sugar, where results by drying are too low.