may be made the basis for the calculation of a factor which can be applied for the calculation of the heating effect of other samples from the same seam.

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LEMON FLAVORING EXTRACT AND ITS SUBSTITUTES.

BY A. S. MITCHELL.

Received September 18, 1899.

AS many valuable papers have lately appeared upon the subject of vanilla flavoring extract, while little has been done upon lemon extract and its substitutes, I have ventured to here outline the results of the investigation of these goods as found upon the market, and made in the course of work for the Wisconsin Dairy and Food Commission.

Lemon extracts, following the U. S. P. formula for "Spiritus Limonis" should contain at least five per cent of oil of lemon dissolved in deodorized alcohol and should be colored only with the coloring from lemon peel.

A preliminary examination of the extracts supplied by grocers showed them to contain alcohol in amounts varying from fourteen to ninety-four per cent. by weight and oil of lemon from none to eight per cent.

The extracts low in alcohol had in many cases a fine aroma derived from agitation with new oil of lemon in some cases but more frequently produced by citral and the so-called "soluble oil of lemon" or from lemon-grass or citronella aldehyde and frequently with the addition of tincture of nutmeg, mace, or capsicum. The cheaper grades contained so little oil in solution that the addition of water frequently failed to produce turbidity.

As no standard methods were in use for the examination of lemon flavoring extracts, it was thought desirable to make an examination of the oils used. Optical methods proved most satisfactory for this purpose. The following table gives the behavior of pure oil of lemon and of the various oils and substances entering into the composition of adulterated and sophisticated lemon extracts.

	Rotation in alcohol.			
	Five per cent.	One per cent.	Rotation of oil.	Refraction at 30° C. showing dispersion.
Oil of Lemon (F. B.)	16.4	3.3	64.0	67–71
Oil of Lemon (D. B.)	16.2	3.2	63.2	68–72
Oil of Lemon (S.)	...	..	...	68–72
Oil of Lemon (H.)	16.5	3.3	64.3	67–71
Oil of Limes (E. & A.)	9.2	1.8	36.0	83–87
Limonene (E. & A.)	9.2	1.8	36.0	87–95
"Soluble Oil of Lemon" (F. B.)	1.7	0.3	7.0	82–98
"Citral 80 per cent." com	1.5	0.3	5.9	80–86
Oil of Lemon grass (D. B.)	—1.2	—0.2	—4.7	80–90
Oil of Lemon grass (F. D.)	—1.1	—0.2	—4.3	83–95
Oil of Lemon grass (F. B. double rect.)	—1.6	—0.3	—6.3	82–90
Oil of Citronella (D. B.)	—2.8	—0.6	—10.9	78–83
Citronella aldehyde (F. B.)	1.7	0.3	6.6	36–38
Oil of Turpentine	..	..	..	59–61

The rotation was determined in the Schmidt and Haensch polariscope upon the solution in a 200 mm. tube, direct and using the cane-sugar scale. The figures given in the column headed "rotation of oil" are calculated to circular degrees for comparison with standards.

The refraction is given in degrees of the Zeiss butyrorefractometer, which instrument is to be had in most food laboratories. It will be noticed that many of the oils exhibit wide dispersive powers, which property proves a valuable aid in their detection in the precipitated oil obtained in small quantities from the extracts in the process to be described.

From these figures it will be seen that oil of lemon will produce a dextrorotation of about 3.4° for each per cent. of oil in alcoholic solution under the above conditions.

Soluble oil of lemon or commercial citral can only be used in amounts of 0.33 per cent. or less owing to the pronounced flavor. Upon this basis the largest quantity of these oils that could be used in an extract would produce an effect equivalent to one-tenth per cent oil of lemon (0.1° to 0.2°).

Oils of citronella, lemon-grass and citronella aldehyde are used in much smaller amounts, so that while their tendency is to counteract the optical effects of oil of lemon, their actual effect

is wholly insignificant. All are used in amounts less than one-tenth per cent.

Oil of limes is slightly more expensive than lemon oil and equally insoluble in weak alcohol. There is therefore no incentive to its use. The same may be said of limonene, but if either of these were used they would be indicated by the greater refraction of the recovered oil.

In the absence of sugar, then, the oil of lemon may readily be estimated by polarizing the extract in a 200 mm. tube and dividing the result in degrees by 3.4. A ready check may be made, and a portion of the oil may be had for examination with the refractometer, by the following process.

A flask similar to a Babcock skim-milk bottle is obtained. This bottle should have a capacity of approximately eighty cc. and have two necks. The larger tube (used for filling) should enter at the side and pass almost to the bottom of the flask. The smaller tube (used for measuring the precipitated oil) should have an internal diameter of about three mm. and a length of about fourteen cm. Such a tube will contain one cc. between its extreme graduations. This should be graduated in ten equal parts and each tenth subdivided into fifths. Each of the smallest divisions will indicate two-tenths per cent. when ten cc. of extract are used.

For the purposes of examination ten cc. of the extract are pipetted into the flask above described. About ten drops of concentrated hydrochloric acid are added (sulphuric acid must not be used) together with thirty cc. of warm water. The flask is then placed in water at a temperature of 70° C. with occasional shaking until the oil separates, which will usually take about thirty minutes. The flask is then filled with warm water by means of the side tube and may then be whirled in the centrifuge and the oil brought into the graduated neck. Fair results may be had with the ordinary Babcock bottle but the precipitation is not as complete as when more water is used and the measurement is not sufficiently exact with the small amount of extract taken.

Recovery of the oil by the above process is most complete with extracts containing five per cent. or more of oil. As a rule a six per cent. extract will yield 4.80 per cent. by precipitation, a five per cent extract 3.80 per cent., and a two and a half per

cent extract about 1.20 per cent. The results obtained by precipitation should then be corrected accordingly, after which the results should agree within two-tenths per cent. of those obtained by polarization, unless foreign optically active substances are present.

"Soluble oil of lemon" is recommended by makers to be used in amounts of about 0.33 per cent. only, but if it were used in large amount it would largely be precipitated by this method. Three per cent. may be recovered from a five per cent. solution in stronger alcohol.

The claim is frequently made that limonene, which is undesirable, is all that is excluded when an extract is made with weak alcohol and subsequently clarified with magnesia. This statement is misleading. With the limonene sample obtained from Eimer and Amend three and four-tenths per cent. was recovered from a five per cent. solution by the above method, showing that in weak alcohol (about twelve per cent.) limonene is even more soluble than pure oil of lemon.

In recovering oil from extracts containing less than two and a half per cent. oil and which are always weak in alcohol, twenty cc. of extract may be taken.

A portion of the oil precipitated may then be removed with a two cc. pipette and examined with the refractometer. If pure oil has been used the refraction will be nearly normal as given in the table.

Oil of limes, limonene or citronella oil would be indicated by a higher refraction as would also soluble oil of lemon. Citronella aldehyde and oil of lemon-grass would tend to lower the refraction but neither could be used in an extract in quantities sufficient to greatly alter it.

For the accurate determination of the alcohol, twenty-five cc. are pipetted into a 100 to 110 cc. sugar flask, and about two cc. each of a concentrated solution of aluminum chloride and disodium hydrogen phosphate are added and the flask is filled to 110 cc. with water and well mixed. The mixture is poured upon a dry filter and 100 cc. of the filtrate received for distillation. Twenty-five cc. of water are added to the 100 cc. fraction and the whole distilled to 100 cc. The alcohol is then estimated from the specific gravity of the distillate.

In most cases, however, it is sufficient to prove the absence of sugar, glycerine or solid extract by evaporating ten grams on the water-bath. These substances being absent and the specific gravity of oil of lemon (0.858) and stronger alcohol (0.820) being approximately the same, when an extract does not contain over six per cent. of oil, the alcohol may be approximated within one per cent. directly from the specific gravity of the extract.

Methyl alcohol may be looked for by adding ten cc. of a fresh one per cent. solution of sodium nitroprusside in water to an equal volume of extract and then making the mixture strongly alkaline with ammonia. A red color will appear within a few moments when wood alcohol is present. Oil of lemon does not interfere. Unfortunately this test is valueless for the detection of the more highly purified grades of methyl alcohol, such as "Columbian spirits" and "synthetic alcohol." These can only be detected by the more complicated tests as described in Allen's "Commercial Organic Analysis."

The coloring of lemon extracts is seldom from lemon peel but is generally an aniline. Curcuma is seldom used owing to its liability to fade. Indications of the coloring used are frequently yielded upon the addition of hydrochloric acid during the precipitation of the oil. Sulphonated azo dyes (tropæolins) which are frequently met with react pink or red upon the addition of the acid, and dinitrocresol is indicated by the bleaching of the solution.

The coloring-matters are best obtained by evaporating the alcohol and dyeing skeins of wool with the aqueous solution of the dye. The coloring-matter may then be identified as indicated in Allen's "Commercial Organic Analysis" and in Weyl's 'Sanitary Relations of the Coal-tar Colors.'

The following table gives the results of examination of a few characteristic extracts.

1. ..... : Alcohol, 21.0 per cent. by weight; rotation 0.2°, oil of lemon less than one-tenth per cent.; coloring-matter, naphthol-yellow.

2. "Special Extract of Lemon:" Alcohol, 20.6 per cent.; rotation 4.6°, cane-sugar 1.31 per cent.; rotation due to oil 0.6°, equivalent to two-tenths per cent. oil of lemon; colored.

3. "Triple Extract of Lemon:" Alcohol, 94.3 per cent.; ro-

tation 23.1°, equal to six and seven-tenths per cent. oil; color, lemon peel only.

4. "Ten Cent Lemon:" Alcohol, 71.7 per cent.; rotation 21.5°, equal to six and three-tenths per cent. oil; precipitation with correction showed five and six-tenths per cent. oil; difference due to presence of cane-sugar; color, tropæolin.

5. "Monarch Lemon Extract:" Alcohol, 94.66 per cent.; rotation 25.7°, equal to seven and a half per cent. oil; precipitation gave seven and three-tenths per cent. oil of lemon, having a refraction of 65°–69°.

6. "Bon-ton Extract of Lemon:" Alcohol, 22.85 per cent.; rotation 0.1° (trace of oil); coloring-matter, dinitrocresol.

7. "Extract of Lemon:" Alcohol, 89.9 per cent.; rotation 20.8°, equal to six and one-tenth per cent. oil; precipitation yielded six and two-tenths per cent. oil of lemon, of refraction 63°–68°.

8. "Double Strength Lemon Extract:" Alcohol, 54.4 per cent.; rotation 1.8°, equal to one-half per cent oil; color, dinitrocresol.

9. "Lemon Extract from druggist:" Alcohol, 92.0 per cent.; rotation 15.9°, equal to four and nine-tenths per cent. oil; precipitation showed five per cent. oil, of refraction 64°–68°.

Only such extracts as fail to precipitate with water occasionally show a slight laevorotation.

ON THE DETERMINATION OF VOLATILE COMBUSTIBLE MATTER IN COKE AND ANTHRACITE COAL.

By Richard K. Meade and James C. Attix.

Received July 28, 1899.

SOME years ago a discussion arose between the consumer and the manufacturer of a coke as to its value. The user objected to the high ash and in support of his claim gave the analysis of his chemist, in which the ash was reported at eighteen per cent. The maker replied that the analysis was worthless as the chemist who made the analysis was probably incompetent, since he had reported nearly three per cent. of volatile combustible matter and that in a seventy-two hour coke the volatile combustible matter could not be nearly so high. The question was referred to a well-known analytical chemist. His analysis, while agreeing with that of the consumer's chemists in the percentage of ash, gave the volatile combustible matter as six-