

practical to calculate the lactose originally present in the milk that has soured from the apparent lactose and the acidity. However, there is little or no loss of lactose if the acidity of the sample is not above 0.2 per cent, and milk that contains a larger amount of acid is not generally considered fresh.

TABLE II—EFFECT UPON THE MOLECULAR CONCENTRATION CONSTANT OF THE ACIDITY AND OF USE OF FORMALDEHYDE AS A PRESERVATIVE

Sample No.	DESCRIPTION OF SAMPLE	Held before Analysis	Per cent Lactic Acid	Per cent Lactose	Mol. Conc. Constant
35	Market "Fresh" Milk.....	0	0.14	4.85	73.2
	Kept on ice.....	3 days	0.15	4.84	73.0
	3 days on ice then at 15° C.	1 day	0.18	4.78	72.5
		2 days	0.42	4.45	68.8
36	Market "Fresh" milk.....	0	0.15	4.78	72.6
	Kept at 15° C.....	2 days	0.16	4.77	72.7
	Warmed to 25° C., then on ice	1 day	0.34	4.54	70.2
37	Market "Fresh" Milk.....	0	0.18	4.30	64.6
	Kept on ice.....	1 day	0.21	4.30	64.6
		2 days	0.24	4.25	64.0
		3 days	0.27	4.23	63.8
38	Market "Fresh" milk.....	0	0.16	4.68	72.8
	Kept on ice.....	1 day	0.18	4.71	73.1
		2 days	0.19	4.65	72.5
		3 days	0.22	4.63	72.3
39	Market "Fresh" milk.....	0	0.15	4.86	75.2
	Kept on ice.....	3 days	0.17	4.83	74.8
		6 days	0.20	4.79	74.4
40	0.2 per cent formaldehyde added to sample No. 39 while fresh.....	0	4.83	75.0
	Kept on ice.....	3 days	4.84	75.0
		7 days	4.83	74.8
		9 days	4.85	75.1
41	Market "Fresh" milk.....	0	0.15	4.88	71.3
	Added formaldehyde, 1 part to 2500; on ice.....	5 days	4.81	70.6
		8 days	4.81	70.6
42	Market "Fresh" milk.....	0	0.15	4.85	71.4
	0.1 per cent formaldehyde added, then kept at room temp. (22° C.).....	1 day	4.85	71.4
	Kept at room temperature..	3 days	4.87	71.7
		5 days	4.85	71.4
		9 days	4.85	71.1
		12 days	4.84	71.5

If a sample of milk cannot be analyzed while it is fresh, it should be preserved with formaldehyde. The results of Nos. 40, 41 and 42 of Table II show that the amount of formaldehyde necessary to preserve a sample of milk at room temperature for 12 days will not affect the determination of the molecular concentration constant.

The freezing point of the samples of milk in Table I was determined by J. T. Keister.¹ The effect produced by a given amount of added water is about the same in each case, but since the freezing point has a smaller variation than the molecular concentration constant, the former method is more accurate for the detection of a small amount of added water. However, the molecular concentration constant is determined by a simple chemical analysis, and, since a sample can be preserved for some time and the constant still be determined, the method should be a valuable aid in the detection of watered milk.

SUMMARY

I—The thirty-one samples analyzed showed values for the molecular concentration constant between 71.1 and 82.6.

II—The development of acidity has the same effect upon the constant as the addition of water; however, the use of formaldehyde as a preservative is permissible.

III—On the three samples to which 8 per cent of water was added in each case this method showed the presence of added water.

¹ THIS JOURNAL, 9 (1917), 862.

IV—If a sample of milk can be examined while fresh the freezing-point method is more accurate, but, if it is desired to preserve the sample, the determination of the molecular concentration constant is better for the detection of added water in milk.

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A METHOD FOR THE DETERMINATION OF THE VOLATILE OIL CONTENT OF CITRUS FRUITS

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In the course of the investigation of the by-products of citrus fruit it was found necessary to devise a method for determining the total volatile oil contained in the peel.

Several attempts were made to extract this oil from the ground peel by means of various organic solvents, such as alcohol, ether, benzol, gasoline, chloroform, and carbon tetrachloride. It was found that invariably a large amount of water became mixed with the solvent, even when benzol, carbon tetrachloride and similar solvents were used. No practical method was found to drive off this water without loss of oil.

In order to avoid this difficulty the ground peel was dehydrated with anhydrous copper sulfate or sodium sulfate and the mixture extracted as before. Trouble was experienced, however, on account of the large amount of dehydrating material required, which caused packing or caking in the thimble and prevented complete extraction. Even when extraordinary care was exercised in carrying out this method it was found impossible to remove the last traces of solvent without loss of oil. Results were always low, as can be seen by comparing the figures obtained by the steam distillation of peel and by extraction with absolute ether of another sample of the same peel previously dehydrated by mixing with anhydrous copper sulfate.

TABLE I—COMPARISON OF STEAM DISTILLATION METHOD AND EXTRACTION METHODS OF DETERMINING LEMON OIL

Determinations made on Peel, Calculated to Entire Fruit	
METHOD	Per cent Oil in Fruit
Steam Distillation.....	0.81
Extraction, Ether.....	0.31
Extraction, Ether.....	0.25

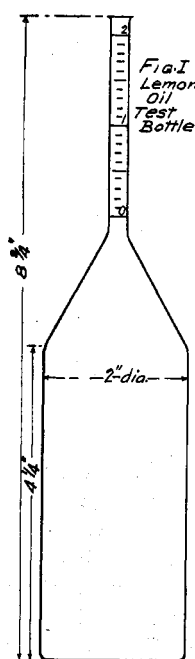
The extraction method not being very satisfactory, steam distillation was tried. After a number of experiments the following procedure has been evolved and has been used for a large number of determinations:

METHOD FOR THE DETERMINATION OF VOLATILE OIL IN CITRUS FRUIT OR FRUIT PEEL

PREPARATION OF SAMPLE—Pass the entire sample of whole fruit three times through a fine cutting food grinder and mix thoroughly.

DETERMINATION—Immediately after grinding, weigh 200 g. of the sample into a 1½ liter flask and mix with 700 cc. of water. Attach the flask to a 15 in. straight condenser by means of a Kjeldahl bulb. Connect with a steam generator, place a small flame under flask and distil the sample rapidly in a current

of steam until the oil ceases to come over. About 200 cc. of distillate are usually sufficient.



The distillate is received in a special oil flask through a long stem funnel, the latter being used to avoid clogging in the neck of the flask with subsequent loss by overflow. The special flask is shown in Fig. I. It is made similar to a Babcock milk test bottle: the body has a capacity of 200 cc. and the neck 2 cc., the latter being graduated in $\frac{1}{10}$ cc.

As soon as the distillation is complete, bring the oil into the graduated neck of the flask by the addition of water and whirl in a centrifuge until all of the oil has collected in a clear layer. Note the volume of the oil, reading the extreme of the meniscus at the top as well as at the bottom of the column. Calculate the weight of the oil from its volume and specific gravity by the following formula:

$$V \times 0.849 \times 0.996,$$

where V is volume of the oil obtained, 0.849 the average specific gravity of California lemon oils, and 0.996 the factor correcting for determinations made at $25^\circ/25^\circ$ C. in air. In exact work the specific gravity of the oil should be predetermined for the particular kind of fruit used and an average of a number of determinations on distilled oil taken. The volume reading should be made at the same temperature as that at which the specific gravity determinations are made.

For oil distilled from California lemons the specific gravity factor at $25^\circ/25^\circ$ C. determined in air with brass weights is 0.849.

If preferred the oil may be weighed directly by drawing it into a tared weighing pipette, such as was described by Mertes,¹ and weighed directly. This method is not as accurate as the first method given, owing to the difficulty in transferring all of the oil to the pipette without admixture of water.

By the steam distillation method, calculating weight of oil from its volume and specific gravity, a number of determinations may be run simultaneously and results are satisfactory. Duplicate determinations should not vary more than 0.1 cc. on a volume of 1.5 cc. and the weights of the oil should check within 0.05 per cent.

TABLE II—COMPARATIVE RESULTS OF OIL DETERMINATIONS ON THE SAME FRUIT, ONE DETERMINATION BEING MADE ON ENTIRE GROUND FRUIT, THE OTHER ON THE GROUND PEEL

The Percentage of Oil in Both Cases Is Calculated to the Entire Fruit		OIL IN FRUIT		OIL IN PEEL		CALC. FROM PEEL	
BY DIST. OF WHOLE FRUIT	PER	PER	IN PEEL	PER	IN PEEL	PER	IN PEEL
No.	Per cent	Lbs. per Ton	Per cent	Per cent	Per cent	Lbs. per Ton	Lbs. per Ton
1057....	0.67	13.4	32.7	1.02	0.33	6.6	6.6
1058....	0.74	14.8	29.2	1.13	0.33	6.6	6.6
1060....	0.67	13.4	27.3	0.89	0.24	4.8	4.8
1061....	0.68	13.6	29.5	1.78	0.52	10.4	10.4

While it is possible to distil the ground peel alone instead of the whole fruit, and calculate back to the

¹ THIS JOURNAL, 7 (1915), 236.

entire fruit from the percentage of peel, the results obtained are usually low. This is shown by Table II.

Low results on the ground peel are attributed to loss of oil in the peeling and grinding operations, when considerable free oil is exposed to the air and there is every chance for volatilization.

In the earlier work all determinations were made by weighing the oil in the special pipette. It was found difficult, however, to remove all of the oil from the bottle without taking a small amount of water with it, and this occasioned considerable error. It was thought likely that the specific gravity of the distilled oil would vary within such narrow limits that by reading the volume of the oil and applying a factor, more accurate results would be obtained than by weighing the oil direct.

With a view to determining this factor for California distilled lemon oil the specific gravities of a number of samples of oil were taken. The determinations were made at $25^\circ/25^\circ$ C. using brass weights in air, as the oil when removed from the centrifuge was usually within two or three degrees of that temperature. Samples of lemons of the different varieties grown in California and also from different localities were used to determine whether or not the specific gravity of the oil in any case varied greatly from the average. The results are shown in Table III:

TABLE III—SPECIFIC GRAVITIES OF DISTILLED LEMON OILS AT $25^\circ/25^\circ$ C.

VARIETY	No.	Date Rec'd	WHERE GROWN	Sp. Gr.
Eureka.....	639	12/ 6/15	Santa Paula	0.8489
	646	12/13/15	Whittier	0.8494
	678	12/29/15	San Fernando	0.8449
	696	1/18/16	Arlington Heights	0.8476
	713	1/26/16	Whittier	0.8502
	717	1/31/16	San Fernando	0.8502
	726	2/ 5/16	Carpinteria	0.8504
	955	6/16/16	Whittier	0.8495
	957	6/16/16	Claremont	0.8462
	998	7/ 6/16	Carpinteria	0.8494
Average.....				0.8487
Lisbon.....	637	12/ 1/15	Chula Vista	0.8506
	662	12/21/15	Chula Vista	0.8511
	692	1/12/16	Corona	0.8482
	695	1/15/16	Corona	0.8506
	706	1/24/16	Whittier	0.8468
	806	3/11/16	Arlington Heights	0.8454
	826	3/24/16	Escondido	0.8501
	833	3/25/16	Whittier	0.8479
	851	4/ 6/16	Chula Vista	0.8506
	880	4/24/16	Whittier	0.8475
	915	5/18/16	San Dimas	0.8434
	920	5/22/16	Bonita	0.8503
Average.....				0.8484
Villa Franca.....	675	12/27/15	Bonita	0.8508
	883	4/24/16	Bonita	0.8489
	921	5/22/16	Bonita	0.8485
Average.....				0.8494
GENERAL AVERAGE.....				0.8487

It will be seen from Table III that the average of all the determinations is 0.8487. This table shows the averages for Eureka and Lisbons to be practically the same, and that for the Villa Francas to be a little higher. In the latter case, however, all the samples are from the same tree and may not represent the average for the variety.

Table IV gives a comparison of the oil yield obtained by direct weighing and by calculating, using the factor 0.846. $0.849 \times 0.996 = 0.846$.

The largest volume of oil obtained in the determinations is 1.81 cc., and the lowest 0.96 cc. Taking this, largest volume (1.81 cc.) and calculating the weight

TABLE IV—COMPARISON OF LEMON OIL DETERMINATIONS BY DIRECT WEIGHING OF DISTILLED OIL AND BY CALCULATION OF WEIGHT OF OIL FROM VOLUME AND SPECIFIC GRAVITY AT 25°/25° C.

No.	PER CENT OIL Direct Weight	Cc. Oil from 200 g.	WEIGHT OF OIL Cc. × 0.846	LBS. OIL PER TON Direct Weight	By Calculation
637.....	0.69	1.73	1.464	13.8	14.6
639.....	0.43	1.06	0.897	8.6	9.0
646.....	0.48	1.22	1.032	9.6	10.3
662.....	0.66	1.64	1.387	13.2	13.9
675.....	0.70	1.70	1.438	14.0	14.4
678.....	0.60	1.48	1.252	12.0	12.5
692.....	0.71	1.73	1.464	14.2	14.6
695.....	0.75	1.81	1.531	15.0	15.3
696.....	0.54	1.36	1.151	10.8	11.5
706.....	0.55	1.44	1.218	11.0	12.2
713.....	0.42	1.09	0.922	8.4	9.2
717.....	0.57	1.40	1.184	11.4	11.8
726.....	0.45	1.11	0.939	9.0	9.4
806.....	0.58	1.46	1.235	11.6	12.4
826.....	0.49	1.23	1.041	9.8	10.4
833.....	0.37	0.96	0.812	7.4	8.1
851.....	0.43	1.12	0.948	8.6	9.5
880.....	0.38	1.00	0.846	7.6	8.5
883.....	0.58	1.42	1.201	11.6	12.0
915.....	0.46	1.19	1.007	9.2	10.1
920.....	0.49	1.21	1.024	9.8	10.2
921.....	0.62	1.54	1.303	12.4	13.0
955.....	0.47	1.22	1.032	9.4	10.3
957.....	0.45	1.15	0.973	9.0	9.7
998.....	0.40	0.99	0.838	8.0	8.4

of oil from the specific gravity, using the largest, smallest and average values for specific gravity, we have:

$$\begin{aligned} 1.81 \times 0.8511 \times 0.996 &= 15.34 \text{ lbs. per ton} \\ 1.81 \times 0.8434 \times 0.996 &= 15.20 \text{ lbs. per ton} \\ 1.81 \times 0.8490 \times 0.996 &= 15.31 \text{ lbs. per ton} \end{aligned}$$

The greatest difference is only 0.14 lb. per ton, which is well within the limits of experimental error. For determinations involving smaller volumes of oil the possible error involved through use of the factor is of course reduced. The yield of oil, pounds per ton, obtained by use of the factor is in every case a trifle higher than that obtained by direct weighing.

It is the intention to continue the work and determine the specific gravities of the distilled oils of other California citrus fruit in order to arrive at a factor similar to that applied to lemon oils. That an idea may be had of the oil content of the fruit the data already obtained is given.

TABLE V—PERCENTAGES OF OIL IN VALENCIA ORANGES, TANGERINES AND GRAPEFRUIT BY DISTILLATION METHOD

No.	Cc. Oil dist. from 200 g.	Per cent Oil Direct Weight	Sp. Gr. of Oil 25°/25° C.
Valencia Oranges(a).....			
999	1.80	0.71	0.8411
1001	1.77	0.70	0.8410
1002	2.49	0.99	0.8411
1004	3.23	1.29	0.8424
Tangerines.....			
835	1.35	0.52	0.8425
.....	1.70	0.67	0.8388
.....	1.78	0.69	0.8418
Grapefruit.....			
1361	0.79	0.30	0.8420

(a) In a recent article by Hood [THIS JOURNAL, 8 (1916), 709] data are given on the oil content of Florida Valencias. Amounts were found not exceeding 0.53 per cent. This fruit was peeled and the determinations made on the peel. In our experience, as above stated, this practice invariably yields low results.

SUMMARY

I—The steam distillation method is the most practical one thus far developed for the determination of the volatile oil content of citrus fruit.

II—A special calibrated receiving flask has been designed to meet the needs of this determination.

III—For rapid and reasonably accurate work the weight of the oil distilled from lemons may be calculated by multiplying the volume of the distilled oil at 25° C. by 0.846.

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THE DETERMINATION OF AVAILABLE OXYGEN IN PYROLUSITE

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Pyrolusite is the principal manganese ore. The ore has value for the available oxygen and the manganese contained therein. Hence the determination of these two elements in the ore evaluate it for the industries. Various methods for the determination of manganese have been studied by many chemists, but the methods in use for the determination of available oxygen have received but little attention.¹

Results for the percentage of manganese dioxide obtained by various responsible chemists have given differences of as much as five per cent on a carefully prepared sample, while differences of a per cent or two are quite common.² This paper contains the results of a detailed study as to the causes of such discrepancies and recommends two accurate methods for the analysis of oxidized manganese ores.

Three methods have been in general use for the determination of available oxygen in pyrolusite: the oxalic acid method,³ the ferrous sulfate method⁴ and the chlorine evolution method.⁵ Of these methods the oxalic acid method is perhaps the most universally applied for this determination. Bunsen's method is seldom used due to the inconvenience of distilling the chlorine, which process becomes very time-consuming when a large number of ores are to be analyzed.

THE OXALIC ACID METHOD

The oxalic acid method consists in dissolving a weighed portion of pyrolusite in a known quantity of oxalic acid in the presence of dilute sulfuric acid, heating the solution to facilitate reaction. The excess of oxalic acid is then titrated with standard permanganate and the per cent of manganese dioxide or available oxygen computed.⁶

Any discrepancy existent in the analysis of an ore should be evident when samples of the ore are analyzed under such conditions that the factors involved in the determination are alternately kept constant and made variable. Thus one can maintain a constant weight of sample, constant volume, constant amount of oxalic acid, constant temperature and make variable the sulfuric acid concentration. Two such series of results⁷ are given in Table I. An approximately $N/4$ oxalic acid solution was prepared and standardized from time to time against standard permanganate of approximately $N/10$ strength. The

¹ See Bibliography of the Analytical Chemistry of Manganese, Talbot and Brown, Smithsonian Institution, Washington, D. C., 1902.

² See also Certificate of Analyses, Standard Sample Number 25, U. S. Bureau of Standards.

³ Hempel, "Neue Methoden zur Prüfung des Braunsteins usw.," C. F. Winter, Heidelberg, 1843.

⁴ Originated by Levöl, *J. pharm. chim.*, [3] 1 (1842), 210; modified by Weldon and Lunge, *Dingler's Polytech. J.*, **235**, 300; **236**, 231, 236; *Chem. News*, **41** (1880), 129, 141.

⁵ Bunsen, *Ann. chim.*, **86** (1853), 283.

⁶ Fresenius and Will (*Ann. chim.*, **47**, 87; **49**, 137; *Dingler's Polytech. J.*, **90** (1843), 219) measure the CO_2 produced.

⁷ Samples 101, 102, 103, 104, 105, 106 were air-dried samples, received from The C. F. Burgess Laboratories. The samples had no tendency to give up or take on moisture when being weighed for analysis. These samples were ground to pass 200 mesh silk bolting cloth and kept in glass-stoppered weighing bottles.