The Refractometric Method for The Determination of Oil in Coconut and Sesame Oil Cake*

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OIL mill operators need a rapid and accurate control method for oil determinations. The ether extraction method, which is generally used, falls short of this requirement since it requires several hours to complete a test. Coleman and Fellows (1) have described a refractometric method with mono-chloronaphthalene as the solvent in bulletins 71 and 1471 of the U. S. Department of Agriculture. They devised the method for the determination of oil in flax-seed and linseed oil cake. We have used this method in our laboratory for five years for checking the cake from a coconut and a sesame oil mill and have found the method to be rapid, accurate and economical in materials used. The method is so easy to do that checks may be made on the stock in process and on cake from each individual expeller at frequent intervals.

The following is a brief history of the contributions toward the development of this method:

In 1912, Richter (2) calculated the oil content from the refractive index by extracting the oil bearing material with a mixture of ether and alcohol. Evaporation of the volatile solvents affected the accuracy of his results.

In 1920, David Wesson (3) overcame this objection in his work on cottonseed cake and meats by using halowax—a very satisfactory solvent because of its high boiling point, high index of refraction, uniform quality and reasonable price.

Leithe (4) used an immersion refractometer and a gasoline fraction bp. 90°-100° as the solvent with a resultant accuracy of 0.3-0.5 per cent for the macro method and 0.5-0.8 per cent for the micro method.

Leithe and Muller (5) used a special Schering-Kahlbaum petroleum ether for the refractometric analysis of soya beans with results averaging 0.4 per cent lower than the gravimetric method. Variations of refractive index of soya oils of German origin were negligible, with slightly larger variations in oils of other origin.

Hoyt (6) states that the change of refractive index of solvents in which the same amounts of fat or oil are dissolved is not at all proportional to the refractive indices of the solvents, but is rather some function of chemical structure and the accuracy of the method may be increased by a suitable choice of solvents.

Illarionoff and Demkovsky (7) state that the refractive index of oil-solvent mixtures changes with the composition along a straight line only when mixing is not accompanied by changes of volume. If the change in volume is positive, the index of refraction is less than the calculated value; if the change in volume is negative, the reverse is true. Of all the solvents investigated, chlorbenzene, because of its low volatility, was found most suitable.

A. Ermakoff (8) used alpha-mono-bromonaphthalene claiming an advantage for this solvent over alpha-mono-chloronaphthalene due to its higher boiling point and higher index of refraction.

Geddes and Lehberg (9) found that the accuracy of the refractometric analysis of flaxseed may be increased by drying the sample before extraction. The addition of anhydrous sodium sulphate during the extraction obviated the necessity of preliminary drying. Further improvement was claimed by the use of 50 per cent volume of halowax and alpha-mono-bromonaphthalene.

Leithe (10) found that parallel determinations by the refractometric method using alpha-mono-bromonaphthalene gave results which checked to $\pm$ 0.1 to $\pm$ 0.2 units of the fat percentage. Gravimetric values were found to be generally 0.1 to 0.3 per cent higher. He states that this difference is not due to the lack of solubility of the true fats, but to the difficult 14 soluble constituents in the crude fat, such as lecithin.

The method of Coleman and Fellows with some modifications is used in our laboratory. Of first importance is the grinding of the sample since it must be fine enough to permit the solvent to dissolve all the oil. The grinding is not such a task since the sample used is small. A two-gram sample of the finely ground meal is weighed into a 3-in. mortar and dried. Unless coconut meal is dried, it grinds with halowax to a pasty mass which is difficult to filter and gives low results. We dry the coconut meal at 212° F. for a minimum of 20 minutes and then allow it to cool to 120° F. before adding the halowax. Coconut meal, partially dried in this manner, will grind to a fluid condition with the solvent. It is not necessary to dry sesame meal, but it should be heated to 120° F. before adding the halowax to insure perfect extraction of the oil. Anhydrous salts may be added to remove moisture, but they have not proved as efficient as oven drying. Four c.c. of halowax is added from a 25 c.c. burette of small diameter. A small amount of sea sand is added and the sample ground thoroughly. The mass is poured on a thin, porous 9 cm. filter paper and a few drops of the filtrate placed on the prisms of an Abbe' type refractometer. It is important to keep a constant temperature on the prisms. We find 25° C. a convenient temperature. The refractive index of halowax decreases .00045 for each 1° C. increase in temperature. The oil content of the sample may be calculated from the refractive index by dividing the decrease in refractive index due to the oil by the known decrease for 1 per cent oil. However, we prefer to use a graph with the per cent oil in solution plotted as abscissi and the refractive index readings as ordinates. The per cent oil in the sample is written along the line to permit an easy interpolation of values.

An accurate refractometer, reading in the proper range, is essential for oil analysis. The Abbe' type

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instrument used for this work has a range from 1.3000 to 1.7000, which is not suitable since we use less than 10 per cent of this scale. An instrument reading accurately to five places is preferable. The dipping type instruments are more accurate tha nthe Abbe', but the ones we have investigated require two prisms to cover the range. The use of two prisms which must be changed is impractical and adds an unnecessary expense.

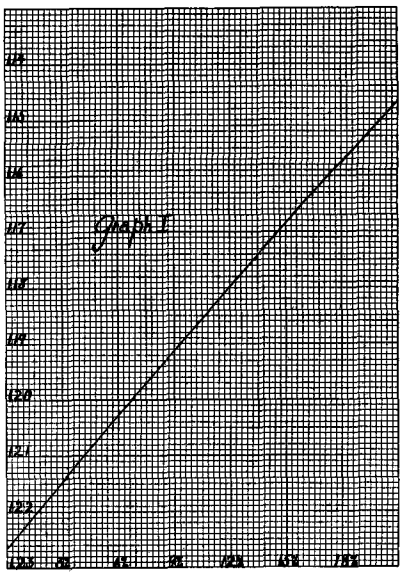
We were interested in knowing what changes in volume occur when coconut oil and halowax are mixed. In case there is an appreciable contraction or expansion, the change in reading for each 1 per cent oil would not be constant over the entire range.

We prepared a series of seventeen standard solutions of coconut oil in halowax representing oil contents of samples from 1-75 per cent which covers the range from coconut meal to copra. Seventy gram standards were prepared to insure accuracy in weighing. An average sample of crude coconut oil with 5.6 per cent f.f.a. was used. The specific gravity $\frac{25°}{4°}$ was determined on each sample, using a 50 c.c. pycnometer. The refractive indices were also read on each of the standard, using an Abbe' type instrument. This instrument reads directly to three decimal places leaving the fourth place to be estimated. We read to the fourth place by magnifying the scale with the moncular tube of a microscope. This enabled us to read in the fourth place with very good agreement. The results of this work are recorded in Table I. Graph I

TABLE I.
Coconut Oil in Halowax.

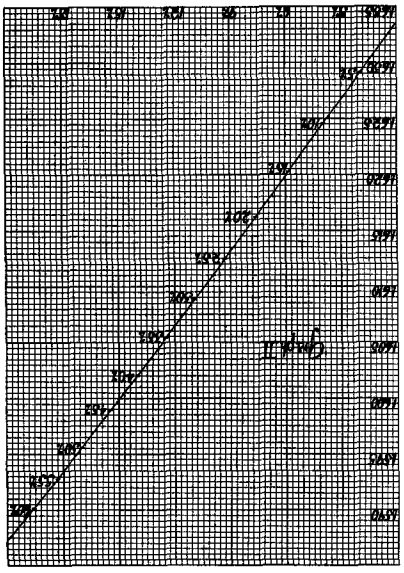
% Oil in Sample	% Oil in Sol'n. (by Weight)	25° Sp. G. 4°	Refractive Index at 25° C.
Halowax		1.2263	1.6335
1	.4060	1.2255	1.6327
2.0078	.8120	1.2240	1.6318
5.082	2.030	1.2183	1.6291
10.379	4.060	1.2104	1.6244
15.905	6.090	1.2027	1.6198
21.675	8.12	1.1946	1.6151
27.706	10.15	1.1869	1.6104
34.016	12.18	1.1791	1.6061
35.0	12.488	1.1782	1.6054
40.0	14.022	1.1725	1.6020
45.0	15.503	1.1670	1.5989
50.0	16.934	1.1618	1.5957
55.0	18.317	1.1570	1.5928
60.0	19.655	1.1523	1.5901
65.0	20.950	1.1476	1.5875
70.0	22.204	1.1429	1.5847
75.0	23.418	1.1389	1.5823
CoconutOil		0.9180	1.4535

shows the specific gravities plotted against the per cent oil in the solution. This relationship proves to



GRAPH I.

be practically a straight line function, permitting the use of a simple formula for calculating the oil content of coconut oil products with less than 2 per cent error. Graph II shows the refractive in-



GRAPH II.

dices plotted against the per cent oil in solution. This graph, drawn on a larger scale, is very convenient for conversions to oil content for routine analysis. It is interesting to note that this is practically a straight line. By placing a straight edge on the curve, the line appears slightly concave to the abscissi.

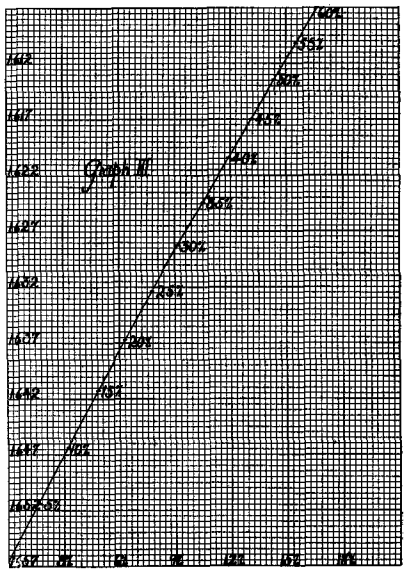
Since increased accuracy is claimed for alpha-mono-bromonaphthalene due to its higher index of refraction (1.6564 at 25° C. compared to halowax (1.6335 at 25° C.), a series of seventeen standard solutions of crude coconut oil in this solvent were prepared and the refractive indices read. This data is shown in Table 2 and plotted in

TABLE 2.
Coconut Oil in Alpha-Mono-Bromonaphthalene.

% Oil in Sample	% Oil in Sol'n. (by Weight)	Refractive Index at 25° C.
Alpha-Mono-Bromonaphthalene		1.6564
1	.3341	1.6554
5	1.6485	1.6513
10	3.2436	1.6461
15	4.7874	1.6412
20	7.5397	1.6177
25	7.7327	1.6324
30	9.1380	1.6283
35	10.5010	1.6243
41.06	12.0992	1.6199
45	13.1081	1.6170
50	14.3554	1.6135
55	15.5671	1.6102
60	16.7457	1.6069
65	17.8915	1.6038
70	19.0062	1.6009
75	20.0910	1.5982
Coconut Oil		1.4535

$\frac{25°}{4°}$ Sp. G. Alpha-Mono-Bromonaphthalene = 1.4915.

Graph III. The increase in range



GRAPH III.

of the alpha-mono-bromonaphthalene over halowax is slightly less than .0001 in refractive index reading for 1 per cent oil content, which is about the accuracy of the readings. Due to its higher specific gravity there is a greater chance of error in measuring alpha-mono-bromonaphthalene than halowax. Following are the weights of 4 c.c. of the two solvents:

4 c.c. halowax.....4.9052 gms.
4 c.c. alpha-mono-bromonaphthalene .....5.9660 gms.

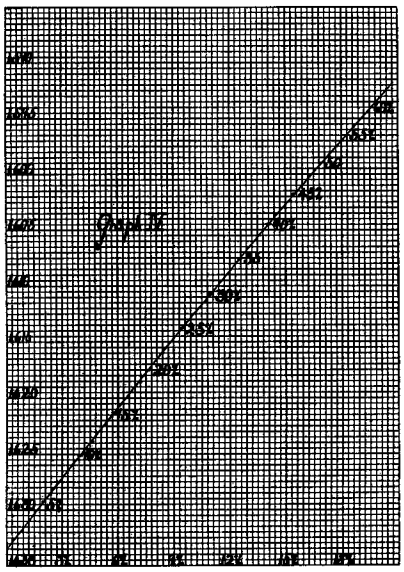
A series of thirteen standard solutions of crude sesame oil in halowax were prepared and the refrac-

tive indices read. This covers the range from sesame cake to sesame seed. The results are shown in Table 3. The percentages of oil

TABLE 3.
Sesame Oil in Halowax.

% Oil in Sample	% Oil in Sol'n. (by Weight)	Refractive Index at 25° C.
Halowax		1.6335
1	.40607	1.6326
5	1.9979	1.6291
10	3.9177	1.6251
15	5.7634	1.6213
20	7.5397	1.6179
25	9.2503	1.6142
30	10.8937	1.6109
35	12.4883	1.6077
40	14.0223	1.6047
45	15.5033	1.6018
50	16.9342	1.5991
55	18.3175	1.5965
60	19.6553	1.5939
Sesame Oil		1.4709

in solution are plotted against the refractive indices in Graph IV,



GRAPH IV.

which also proves to be practically a straight line. We use this graph for regular routine conversions from refractive index to per cent oil in the sample.

To determine the influence of the free fatty acid content of the oil in the sample on the refractive index reading, we prepared fatty acids from the coconut and sesame oil used for the previous tables and read the refractive indices. The results are shown in Table 4. Since the oil in fresh cake does not vary materially in free fatty acid content and the per cent oil in the halowax solution from an ordinary cake is low, no corrections are required on regular mill cake. The influence of the free fatty acid content must be considered in samples of high

TABLE 4.
Influence of the Free Fatty Acid Content on the Refractive Index.

	Coconut Oil	Sesame Oil
Acid No. of Crude Oil ...	11.14	1.19
Acid No. of Fatty Acids.	258.7	200.5
Refractive Index of Crude Oil at 25°.....	1.4535	1.4709
Refractive Index of Fatty Acids at 25°.....	1.4415	1.4619
Decrease	.0120	.0090

One per cent increase in the free fatty acids (as lauric) of coconut oil gives a calculated depression of .00013 refractive index.

One per cent increase in the free fatty acids of sesame oil (as oleic) gives a calculated depression of .00009 refractive index.

oil content when the contained oil differs by a definite limit from the free fatty acid content of the oil used for the standards.

We have found the refractometric method to be valuable for the analysis of finished cake, first cut expeller cake and cake from the bleaching presses. We have obtained low results on high oil content samples like copra and sesame seed. No special work has been done on adapting the method for copra and seed, because we have not needed a rapid method for these products. Probably the whole difficulty lies in the sampling and grinding. The ether method extracts sufficient oil for special tests on the oil.

A comparison of the refractometric and ether extraction methods on coconut and sesame mill products is shown in Table 5. All samples were ground to pass a 30 mesh screen. The petroleum ether extractions were allowed to run for 24 hours and all duplicates checked within .05 per cent. The refractometric analysis on sesame meals checked with the ether slightly better than the copra, which bears out our previous experience on these two meals. The alpha-mono-bromonaphthalene shows only slightly greater accuracy than halowax. On all samples, the checks with the ether extractions were sufficiently close for control work.

It is best to make a graph for each oil, using the same instrument which is to be used for the routine analysis. A reading must be made on each new lot of solvent and a correction made if necessary. It must be remembered that the readings are all relative, being based upon small changes in the refractive index due to dissolved oil. The instrument should be checked at regular intervals with the test glass supplied by the manufacturer in order that all readings may be based on the same standard.

Although our experience has been confined principally to coconut and sesame meals, we have also used this method on hempseed, peanut, and kapok seed meals with equally satisfactory results. There is no reason why this method can not be adapted to cottonseed meals or other oil bearing materials. Being able to determine the oil content of the mill run or an individual expeller in 8 minutes instead of 8 hours should be of paramount importance to any crushing plant.

TABLE 5
Comparison of the Refractometric with the Petroleum Ether Method.

COCONUT MEAL

Sample	Ether	Halowax	Error	Sample	Ether	Mono-bromo-Naphthalene	Error
1.....	7.01%	7.2%	+.19%	1.....	7.01%	7.0%	—.01%
2.....	7.86	8.0	+.14	2.....	7.86	8.0	+.14
3.....	8.94	9.1	+.16	3.....	8.94	9.1	+.16
4.....	9.66	9.9	+.24	4.....	9.66	9.5	—.16
5.....	6.93	7.1	+.17	5.....	6.93	6.8	—.13
6.....	7.48	7.6	+.12	6.....	7.48	7.3	—.18
7.....	20.02	20.0	—.02	7.....	20.02	20.0	—.02
8.....	16.76	16.7	—.06	8.....	16.76	16.7	—.16
9.....	18.20	18.0	—.20	9.....	18.20	18.1	—.10
10.....	18.40	18.5	+.10	10.....	18.40	18.2	—.20
		Av. Error	.14			Av. Error	.12

SESAME MEAL

Sample	Ether	Halowax	Error
1.....	7.54%	7.4%	—.14%
2.....	7.11	7.0	—.11
3.....	5.53	5.3	—.23
4.....	8.32	8.2	—.12
5.....	7.20	7.1	—.10
6.....	6.97	6.9	—.07
7.....	28.07	28.0	—.07
8.....	20.51	20.5	—.01
9.....	25.16	25.3	+.14
10.....	18.46	18.5	+.04
		Av.	.103

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