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Summary

The methyl esters of a specimen of menhaden oil have been fractionated in an efficient still. The C_{12}, C_{14}, C_{16}, and C_{18} main fractions have been studied, mainly by low temperature crystallization procedures. The oil has been shown to contain traces of lauric and dodecenoic acids. The C_{14} acids are made up of 2.2% tetradecenoic acid and 97.8% of myristic; based on the whole ester composition of Table I, these values amount to 0.1 and 6.8%, respectively. The C_{16} acids are palmitic, 50.9%; hexadecenoic, 46.6%; and hexadecatrienoic (including a small amount of tetrenoic acid) 2.5%, or based on the whole esters, 15.5, 14.1 and 0.8%, respectively. A very rough calculation of the composition of the C_{18} fraction gives the following results, values based on the whole esters being included in parenthesis: stearic, 11.5 (3.1); octadecenoic, 58.6 (15.7); octadecadienoic, 13.4 (3.6); octadecatrienoic, 7.2 (1.9); and octadecatetrenoic, 9.3% (2.5%). In the course of this investigation the following acids and their methyl esters were isolated from the oil by crystallization procedures; myristic, tetradecenoic (80%), palmitic, hexadecenoic, stearic, and oleic. Evidence was presented that the octadecenoic acids of this oil were a mixture of oleic acid with isomeric acids of this series, a finding which is in agreement with a recent report from this laboratory (11), describing the multiple nature of the octadecenoic acids of a number of animal fats.

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Determination of Moisture in Peanut Kernels

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THE official methods of analysis of the American Oil Chemists' Society (1) for peanut kernels specify two oven-loss methods for the determination of moisture. Original moisture on the sample as received is determined by the loss in weight on heating a 50-gm. sample of kernels, after grinding in a Universal food grinder using a 12-tooth blade, for one hour at 130° C. in a forced draft oven. Second moisture is determined on the sample used for the determination of oil and ammonia. This sample is prepared by heating the kernels for 20 minutes at 130° C. to dry them partially and then grinding with a Universal food grinder using a peanut butter blade. The loss in weight of a 5-gm. sample of this material heated for 2 hours at 101° C. in either a forced draft or a convection oven gives second moisture. It is doubtful that these two oven procedures for first and second moisture reduce the sample to the same degree of dehydration. It is presumed in these procedures that there is no change in moisture content during the original grinding and other handling of the samples prior to weighing the analytical samples. If the moisture content of the peanuts is high, loss in original moisture might occur, or if the content is low, moisture could be gained from the atmosphere. That this is actually the case has been demonstrated by grinding weighed samples of whole peanuts in the shell through the Universal food grinder using the 12-tooth blade. Care was used to avoid loss of material and the ground material was weighed. This procedure gave losses, assumed to be moisture, of 1.52 and 1.39% for two different samples. The ground samples contained 8.21 and 8.38% moisture, respectively, as determined by heating at 130° C. for one hour in a forced draft oven. Original moisture should therefore be determined on the whole rather than on ground kernels.

The determination of the moisture content of biological material by oven loss in weight methods is a purely empirical procedure, governed by the following variables: 1. temperature, 2. pressure, 3. time, and 4. size and surface of the sample. Hence, in determining moisture by oven loss in weight methods, it is necessary to learn what combinations of these variables may be used to give satisfactory and reproducible results without being influenced by oxidation, decomposition, volatilization of non-moisture constituents, or a combination of these factors. These considerations indicate it is highly improbable that control and inspection methods may be developed to give the true moisture contents. Consequently, suitable oven

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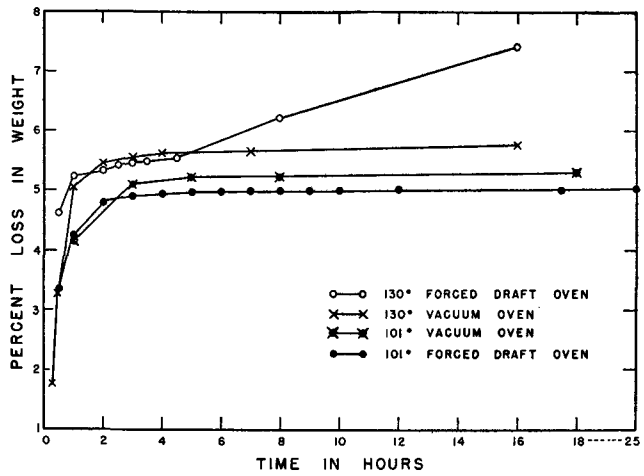

FIG. 1. Loss in weight on drying 19-tooth ground Spanish peanut kernels under different oven conditions.

conditions should be determined for each individual commodity or each class of commodities.

The purpose of the present work was to re-examine the oven methods of determining moisture in peanut kernels and to find the time, temperature, and pressure conditions needed to obtain the same moisture values when using either whole or ground kernels and when using either 50-gm. or 5-gm. samples of ground material. Other methods, such as the use of the Karl Fischer reagent, were not included in this study.

The combination of factors chosen must give comparable results in different laboratories with high precision. It is essential that the first and second moisture values used in the calculation of oil and ammonia to an "as received" basis be based on procedures that dry the samples to the same degree of dehydration.

Pickett (3) has shown that at oven temperatures of less than 140° C. there is practically no alteration of the sugars and very little denaturation of the protein of the peanut. The temperatures and pressures selected for study fulfill these necessary theoretical requirements and are those already in common use.

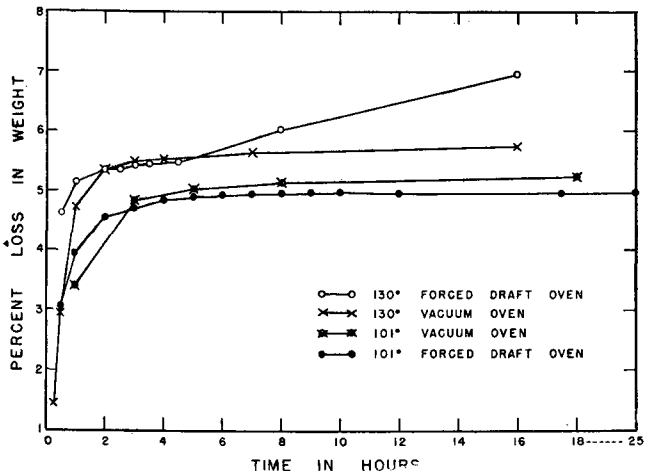

FIG. 2. Loss in weight on drying 12-tooth ground Spanish peanut kernels under different oven conditions.

Experimental and Discussion

Shelled Spanish peanuts (32.4 gm. per 100 kernels) and Virginia peanuts (136.5 gm. per 100 kernels) were used as sample material. The kernels were conditioned by allowing them to attain a moisture content at equilibrium with that of the air of the laboratory. The conditioned Spanish peanuts were divided into three portions. The first two were ground in the Universal food grinder, one lot with the 19-tooth blade and the other with the 12-tooth blade. The third portion and the entire lot of Virginia peanuts were used whole. The samples were stored in sealed containers. The 19-tooth ground, the 12-tooth ground, and the whole kernel samples of Spanish peanuts were expected to have the same moisture content but not necessarily that of the Virginia peanuts. Time moisture loss data were obtained for these samples of whole and ground peanut kernels using forced draft and vacuum ovens each held at both 101° C. and 130° C. (Figures 1 to 4 inclusive). The points shown are averages of duplicate analyses which usually agreed within 0.02%. The vacuum oven was evacuated to a pressure of less than 5 mm. of mercury. For original moisture tests 50-gm. samples were used in all cases. The 5-gm. samples used for second moisture on the

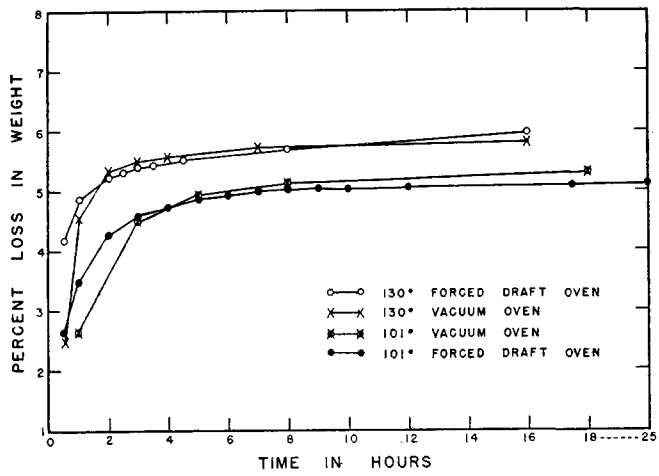

FIG. 3. Loss in weight on drying whole Spanish peanut kernels under different oven conditions.

ground samples were compared with 50-gm. samples (Table 3, Figure 5). Metal dishes, 9 cm. in diameter and 3 cm. deep, and having tight fitting covers, were used as containers for the 50-gm. samples. The official A.O.C.S. moisture dishes were used as containers for the 5-gm. samples.

The forced draft oven used in obtaining the original data of Figures 1 to 4 inclusive, was equipped with a torsion balance sensitive to 5 mg. and a mechanism by use of which the samples could be weighed at the specified time intervals without opening the oven and removing them.

In order to compensate for the cooling effect of placing samples in the vacuum oven the oven was heated above the required temperature prior to introducing the samples. The amount to overheat, so that the desired temperature was reached promptly on closing and evacuating the oven, was determined by preliminary trials. This procedure permitted accurate timing of the heating period. After placing independent duplicate samples in the oven the thermostats were reset to maintain 101° or 130° C. The pressure in the vacuum chamber was equalized with that of the atmosphere at the end of the drying period by admitting air through a calcium chloride filled drying train.

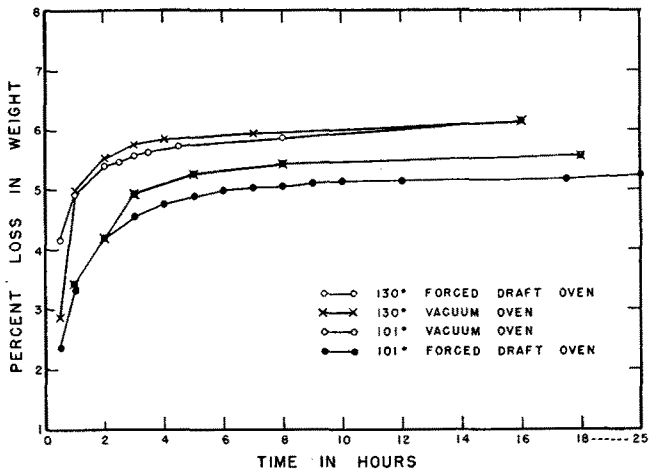

FIG. 4. Loss in weight on drying whole Virginia peanut kernels under different oven conditions.

A continued small loss in weight was found on prolonged heating of samples in the vacuum oven at 130° C. In order to get some idea of what non-moisture constituents may be lost under these conditions an all glass distilling system was assembled with the distilling flask containing 50 gm. of ground Spanish peanuts in a constant temperature oven and the receiver just outside the oven. The distilling system was evacuated and maintained at 130° C. for 5 hours. No moisture condensed in the receiver, but 30 mg. of fatty material were recovered from it. Five hours' additional heating at 150° C. yielded 67 mg. of this fatty material. While these amounts of non-moisture distillate are relatively small, they are an indication of losses in the vacuum oven at higher temperatures.

To check the influence of the moisture content of peanuts on the values found on analysis moisture was determined by a number of selected oven procedures before and after addition of known amounts of moisture to samples of the conditioned lots of ground and whole peanuts previously used. In each case moisture was determined in duplicate on the conditioned samples (Table 1), and two additional weighed samples were placed in high humidity chambers for three days to increase the moisture content by absorption. These samples were then reweighed and dried under the oven conditions indicated in Table 1. Excellent agreement was found between the total moisture determined and the sum of the moisture in the conditioned samples and that added. It appears that within the range of moisture levels examined the amount of moisture does not influence the dry weight values obtained by the specified oven procedures.

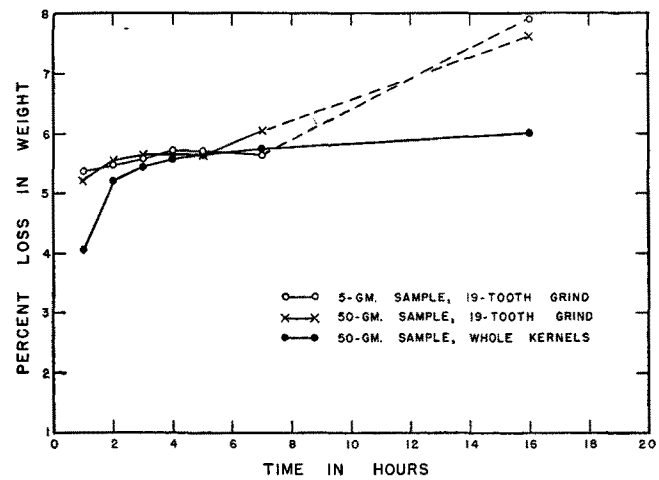

FIG. 5. Loss in weight on drying Spanish peanut kernels in forced draft oven at 130° C.

Some characteristics determined on oils extracted from Spanish peanuts, after drying for the determination of moisture by several oven procedures, indicate that during the drying there is little alteration of the oil. Higher oven temperatures raised the peroxide number slightly, and there appears to be a trend toward the development of higher peroxide values in the oil in the whole than those in the ground samples dried at 130° C. Values are shown in Table 2.

Figures 1, 2, 3, and 4 show that higher temperatures not only increase the initial rate of loss but also increase the total loss on heating. When reduced pressures were used, the initial rate of loss was slightly lower than that observed for the same temperature at atmospheric pressure. This is due undoubtedly to the slower rate of heat transfer in the

TABLE 1

Recovery of Moisture Added to Specified Peanut Samples by Specified Procedures, Values Expressed on Basis of Conditioned Samples

Peanut sample (50 gm.)	Moisture in conditioned sample[1]	Moisture added[2]	Total moisture calculated[3]	Total moisture found
	%	%	%	%
At 101° C. for 16 hours in forced draft oven				
19-tooth ground Spanish	5.07	7.07	12.14	12.11
		6.59	11.66	11.64
12-tooth ground Spanish	5.05	4.87	9.92	9.86
		6.78	11.83	11.81
Whole Spanish kernels....	5.03	4.65	9.68	9.48
		3.68	8.71	8.53
Whole Virginia kernels....	5.19	2.77	7.96	7.92
		2.94	8.13	8.06
At 130° C. for 2.5 hours in forced draft oven				
19-tooth ground Spanish	5.40	5.56	10.96	10.93
		7.23	12.63	12.61
12-tooth ground Spanish	5.34	6.50	11.84	11.83
		5.25	10.59	10.57
At 130° C. for 5 hours in forced draft oven				
Whole Spanish kernels....	5.46	3.73	9.19	9.13
		4.14	9.60	9.55
Whole Virginia kernels....	5.74	2.60	8.34	8.27
		3.03	8.77	8.72
At 101° C. for 8 hours in vacuum oven				
19-tooth ground Spanish	5.29	7.57	12.86	12.84
		7.28	12.57	12.57
12-tooth ground Spanish	5.22	6.53	11.75	11.79
		5.79	11.01	10.96
Whole Spanish kernels....	5.09	4.01	9.10	8.93
		4.09	9.18	9.03
Whole Virginia kernels....	5.43	3.07	8.50	8.52
		4.21	9.64	9.64
At 130° C. for 5 hours in vacuum oven				
19-tooth ground Spanish	5.69	7.91	13.60	13.54
		8.72	14.41	14.52
12-tooth ground Spanish	5.75	9.92	15.67	15.69
		8.47	14.22	14.11
Whole Spanish kernels....	5.56	5.15	10.71	10.75
		4.14	9.70	9.81
Whole Virginia kernels....	5.90	5.82	11.72	11.80
		5.44	11.34	11.56

[1] Obtained by procedure specified.
[2] Moisture added by exposure of weighed sample in moist chamber.
[3] Calculated by addition of values found in first two columns.

TABLE 2

Some Characteristics of Oils Extracted from Spanish Peanuts Dried Under Specified Conditions

Peanut Sample	Temperature of drying	Time of drying	Refractive index 25° C.	Iodine number Wijs	Peroxide number[1]
	°C.	Hours			
Check	.....	0	1.46886	94.1	0.3
Forced draft oven					
Ground[2]	101	16	1.46850	93.7	0.6
Whole kernels	101	16	1.46864	93.6	0.7
Ground[2]	130	2.5	1.46889	94.6	1.0
Whole kernels	130	5	1.46902	92.9	3.3
Vacuum oven					
Ground[2]	101	8	1.46857	94.8	0.7
Whole kernels	101	8	1.46873	94.0	0.8
Ground[2]	130	5	1.46882	94.0	1.2
Whole kernels	130	5	1.46884	93.8	1.4

[1] Millimoles of peroxide per kg. of oil.
[2] Ground in Universal food grinder using 19-tooth blade.

vacuum oven. However, the loss in weight in the vacuum oven soon exceeds that in the forced draft oven and continues at the higher value with prolonged heating except at 130° C. in the forced draft oven when oxidative decomposition increases the loss in weight after an induction period.

Samples of Spanish, Virginia, and Runner peanuts were conditioned and ground as before. Losses in weight on heating 5- and 50-gm. samples of 19-tooth ground and 50-gm. samples of whole kernels in a forced draft oven are compared in Table 3. The agreement at 130° for 5 hours is excellent in all cases except that of the 5-gm. sample of Runner. This sample of Runner peanuts was somewhat deteriorated, with organoleptic rancidity being very apparent. It seems probable that this high value was due to oxidative decomposition with the induction period ending before the samples had been heated for 5 hours.

TABLE 3

Comparison of Percent Moisture Loss on Heating of 5- and 50-gram Samples of Peanuts by Specified Oven Drying Procedures

Time	19-tooth ground		Whole kernels
	5-gm. sample	50-gm. sample	50-gm. sample
Hours	%	%	%
Spanish peanuts at 130° C. in forced draft oven			
1	5.37	5.24	4.06
2	5.48	5.52	5.20
3	5.58	5.63	5.44
4	5.72	5.68	5.57
5	5.70	5.65	5.68
7	5.66	6.06	5.78
16	7.96	7.62	6.01
Spanish peanuts at 101° C. in forced draft oven			
16	5.19	5.24	
Spanish peanuts at 101° C. in vacuum oven			
16	5.76	5.71	
Virginia peanuts at 130° C. in forced draft oven			
5	5.90	5.88	5.89
Runner peanuts at 130° C. in forced draft oven			
5	6.67	6.56	6.50

In the determination of original moisture by the methods used it is observed that the approach to constant weight occurs in whole kernels almost as rapidly as in the ground samples. As in the case of soybeans (2) at 101° C. in the forced draft oven, moisture apparently cannot be removed completely even with prolonged heating. The effect of vacuum drying at 101° C. was to increase the moisture value approximately 0.25% over those obtained at atmospheric pressure at the same temperature. Approximately 0.50% higher loss was obtained at 130° than at 101° C. in the forced draft oven. A rapid rate of loss was observed for the ground samples after approximately 5 hours' heating at 130° C. in the forced draft oven. This increased loss is presumed to be due to oxidative decomposition.

As was expected, fineness of grinding has some influence in increasing the initial rate of loss of moisture on heating. This effect was less marked at higher temperatures and lower pressures. It is assumed to be associated with rate of penetration of heat and diffusion of moisture depending on particle size. Pickett (3) has shown that appreciable time is required for heat to penetrate into whole peanut kernels. This time increases with increased moisture content.

Summary and Conclusions

Losses in weight of whole and ground peanut kernels have been studied in vacuum and forced draft ovens maintained at both 130° and 101° C. Under vacuum at higher temperatures appreciable non-moisture material is lost. There is little change in the characteristics of the oil in the peanut after heating for the times indicated for the determination of moisture. The amount of moisture in peanuts has very little or no influence on the length of time required to attain a constant dehydration level at the times and temperatures of heating studied. Though fineness of grinding increases the initial rate of loss, this effect is less marked at higher temperatures. Kernel size seems to have little or no influence on rate of loss after several hours' heating at higher temperatures.

Losses in weight of 5- and 50-gm. samples of 19-tooth ground and 50-gm. whole kernel peanuts in fresh condition after 5 hours at 130° C. in a forced draft oven show excellent agreement (Table 3). This indicates that original moisture should be determined on whole kernels and second moisture on 19-tooth or similarly ground kernels by heating for 5 hours in a forced draft oven at 130° C. However, some of the values (Figures 1, 2, 3, and 4) indicate that heating for 3 hours at 130° C. in a forced draft oven might be adequate for the second moisture determination. The shorter heating time on the ground sample would also reduce the possibility of oxidative decomposition of the small samples used for second moisture. These procedures provide conditions of drying which reduce both the first and second moistures to a basis of equal dehydration of the sample material. Errors due to changes in moisture content of peanut kernels during grinding for original moisture are avoided. A basis is provided for planning collaborative investigations on the procedures for the determination of moisture in peanut kernels for inspection and control purposes in the trade and processing industries.

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